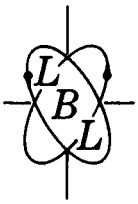

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Parts 2 & 2A

Instrumentation for Environmental Monitoring

WATER

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DISCLAIMER

CONTENTS

*In preparation

*In preparation

ABSTRACT

A comprehensive survey of instrumentation for environmental monitoring is being carried out by the Lawrence Berkeley Laboratory originally under a grant from the National Science Foundation and now by the Division of Biological and Environmental Research of the Department of Energy. Instruments being investigated are those useful for measurements in Air Quality, Water Quality, Radiation, and Biomedicine related to environmental research and monitoring. Consideration is given to instruments and techniques presently in use and to those developed for other purposes but having possible applications to this work. The results of the survey are given as (a) descriptions of the physical and operating characteristics of available instruments, (b) critical comparisons among instrumentation methods, and (c) recommendations of promising methodology and development of new instrumentation. Information is also given regarding the pollutants to be monitored: their characteristics and forms, their sources and pathways, their effects on the ecosystem, and the means of controlling them through process and regulatory controls.

The survey material will be compiled in seven loose-leaf binders which can be periodically updated.

Volume	Parts	Category
1	1 and 1A	Air Monitoring, Gases
1	2	Air Monitoring, Particulates
2 and 2A		Water Monitoring
3		Radiation Monitoring
4		Biomedical Monitoring

INDEXING METHOD

The sections of the survey are indexed by a series of mnemonic descriptors. The caption in the upper right-hand corner of each page provides the necessary filing information. The first three-character descriptor indicates the category of monitoring:

Category	Mnemonic descriptor
Air Monitoring	AIR
Water Monitoring	H20
Radiation Monitoring	RAD
Biomedical Monitoring	BIO

The second descriptor indicates the type of parameter under discussion. For example, oxygen monitoring instruments are identified by "H20-DO." A list of descriptors is given in the contents.

The third descriptor is used to identify the specialized topic, type of sampling or use, for example, "H20-PES, Laboratory" signified laboratory instruments suitable for monitoring pesticides.

The manufacturer or developing laboratory is indicated as the fourth descriptor. Additional instrument notes in this category, parameter, and use by this manufacturer, are indicated by numerals after the manufacturer's name.

The last descriptor is the date the note was first issued. Revised notes bear a new date. Descriptions of equipment bearing a new model number will be issued as additional notes.

PROLOGUE

"I often say that when you can measure what you are speaking about and express it in numbers you know something about it, but when you cannot measure it, when you cannot express it in numbers, your knowledge is of a meager and unsatisfactory kind...it may be the beginning of knowledge, but you have scarcely, in your thoughts, advanced to the stage of science whatever the matter may be."

Lord Kelvin, 1883

The wilderness and the parched land shall be glad; and the desert shall rejoice, and blossom as the rose. It shall blossom abundantly, and rejoice, even with joy and singing;....And the parched land shall become a pool, and the thirsty ground springs of water;....

Isaiah 35: 1,2,7

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PREFACE

It is essential to the nation's program of environmental improvement that accurate and efficient measurements be made of the parameters affecting the environment in which we live and work. In many important areas the present state of the art of instrumentation for environmental monitoring is inadequate. There are many reasons for this inadequacy; more relevant, however, is the question: Where are we now and where do we go from here? The Lawrence Berkeley Laboratory, under grants from the National Science Foundation and the Division of the Department of Energy, is conducting a survey of instrumentation suitable for the measurement of the quality of our environment. The results of the survey appear in four volumes which discuss monitoring of air, water, and radiation, and treat biomedical problems due to environmental causes.

Air Monitoring, Volume 1, primarily considers the chemical parameters known to contribute (or suspected of contributing) to environmental degradation. Physical parameters, usually recorded to establish standard conditions of measurement, are also included.

Water Monitoring, Volume 2, deals with instrumentation suitable for fresh water and estuarine water; coastal and off-shore oceanic waters have been excluded from the survey. Chemical and biological contaminants have been included as well as physical parameters.

Radiation Monitoring, Volume 3, considers both ionizing radiation and non-ionizing radiation. A description of the type of radiation present at various sources of radiation is followed by sections containing a discussion and the specifications for the instrumentation used to monitor its radiation. The non-ionizing sections describe instrumentation used to monitor microwave, laser, and ultraviolet radiation in the environment.

Biomedical Instrumentation, Volume 4, deals with those parameters which affect human, animal and plant life presently considered to arise from environmental problems. Hospital instrumentation is not included. Biomedical problems arising from contamination of the air or water are discussed here, e.g., in the mercury section an overview describes the sources, metabolism, food chain and genetic effects, followed by a description of the methods for detecting mercury in biological samples.

A number of environmental contaminants are well identified, others are at present only suspect, still others are potentially insulting to the ecological balance, and the effects of some substances are unknown. Upon the advice of recognized authorities, the effort expended in compiling this survey has been distributed in proportion to the severity of the problem. If problems are well identified and existing instrumentation is considered satisfactory, presently available instruments are emphasized. f current methods of detection are inadequate -because, for example, of insensitivity, the ime consumed in making the measurement or the mbiguity resulting from interfering parameters --present methodology is surveyed and new ethods of detection and analysis are explored. Recommendations are made for development and exploitation of techniques that are employed in other disciplines and appear to be applicable in the environmental field.

Each volume contains (a) an overview of the basic problems, (b) comparisons among the basic methods of sensing and detection, and (c) instrument notes that summarize the characteristics and evaluate the presently available instruments and techniques. Steps that should be taken to alleviate the problems are recommended if appropriate.

Contact has been made with the staffs of federal, state, university, regional and local laboratories as well as with manufacturers interested in instrumentation for environmental monitoring. Due to the nation-wide concern in this field, it is obvious that not all the experienced professionals in any given specialty could be contacted; however, as the survey continues, an endeavor will be made to utilize all the experience and expertise that comes to the attention of the group.

This survey deals predominantly with instrumentation which is available commercially from U. S. sources. The information is derived from manufacturers' catalogs and specifications, the periodic literature, and scientific and engineering reports. Instrumentation from outside the U. S. has been included whenever it has been found to be widely used or merits attention by our readers because of some particular characteristic.

The survey has been compiled from the aforementioned information sources. The limited scope of this program, however, has not allowed the in-house evaluation of operating instruments at this laboratory.

It is realized that no survey can be exhaustive and complete. If any existing or potentially useful instrument or technique has been omitted, it is urged that information about it be communicated to the Environmental Instrumentation Survey Group at once.

It is important to state that the explicit function of this survey is to aid in, but not to be the sole information relied upon in, the choice of instrumentation. Manufacturers' information and the periodic literature in particular must be considered by any potential user.

The technical information in this survey has been compiled from the best available sources and is believed to be correct. The mention of commercial products, their source or their use in connection with material reported herein is not to be construed as either an actual or implied endorsement of such products. The opinions expressed herein represent the opinions of the LBL Environmental Instrumentation Group and do not necessarily express the opinion of the National Science Foundation, the Department of Energy or the University of California.

Mary S. Quinby Hunt
Environmental Instrumentation Survey Group

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INTRODUCTION TO WATER MONITORING INSTRUMENTATION

WATER MONITORING INSTRUMENTATION

I. GENERAL CONSIDERATIONS

Water ranks along with air among our most valuable natural resources. The Earth has been endowed with an ideal purification system through the evaporation-precipitation cycle; unfortunately, however, due to population pressures, economic tradeoffs and human carelessness, water often reaches the ultimate user in a form far less pure than raindrops or melted snow. As McKee and Wolf point out in terms as appropriate today as fifteen years ago: (Ref. 1)

> "The domestic water-supply industry is caught between two strong trends in water quality. On the one hand, domestic and industrial customers are demanding improved quality and greater uniformity in the water delivered at the tap... On the other hand, the sources of raw water have been deteriorating under the inexorable impacts of modern civilization and may be expected to get worse in future years. The waterworks industry, therefore, must produce a better and more uniform product while drawing upon a poorer and less predictable source of supply. Fortunately, there are many recent improvements in technology that are capable of bridging the widening gap in quality between raw and finished waters. One of the greatest needs today in water-supply technology is reliable quantitative information relative to the potential harmful effects of trace substances in raw and treated water."

The purpose of this Survey is to describe the instrumentation which is presently available to provide the quantitative monitoring information on water today. Techniques and experimental equipment which may be developed into instrumentation are also discussed. In addition, recommendations for improved or new instrumentation are included.

Each section of this volume on a particular pollutant or parameter will contain an introduction discussing relevant background information. This will be followed by a detailed critique of analytical instrumentation and techniques. Information pertinent to the individual instruments is given in the Instrument Notes. Readers should consult the Instrumentation techniques section for general remarks as well as the Instrument Note for that instrument.

A. Categories of Water

Water has been studied in a variety of ways. In general, studies concerned with water quality subdivide the subject into several categories depending upon the approach taken by the studies. Standard Methods for the Examination of Water and Wastewater (Ref. 2) divides water into two main categories: 1) Natural and treated waters in the absence of gross pollution and 2) Polluted and wastewaters including bottom sediments and sludges. The 1976 Annual Book of ASTM Standards, Part 23, Water; Atmospheric Analysis (Ref. 3) considers Industrial Water and Industrial Wastewater. The Report of the Committee on Water Quality Criteria (Ref. 4) and the subsequent NAS/NAE report, Water Quality Criteria (Ref. 5) further divide waters into five general areas of use: 1) Recreation and Aesthetics, 2) Public Water Supplies, 3) Fish, other Aquatic Life and Wildlife, 4) Agriculture and 5) Industry.

Instrumentation discussed in this Survey will be considered as that suitable for monitoring three categories of water:

1) Fresh Water includes raw or treated water either for domestic, industrial or agricultural use. Gross pollution is not expected to be observed in this category of water.

2) Waste Water includes domestic and industrial wastewater, effluent from waste treatment plants and other polluted waters, as well as bottom sediments and sludges.

3) Saline Water includes brackish waters normally found in estuaries. Brackish waters contain from 1,000 ppm to about 10,000-15,000 ppm total dissolved salts, chiefly those of sodium, calcium, magnesium, sulfate, chloride and bicarbonate. Nitrates, fluorides and potassium are found in smaller amounts (Ref. 5). Saline water contains 10,000 to 33,0000 mg/l of dissolved salts.

• Statistics

Only about 0.6% of the 326 million cubic miles of total water found on the earth is on land; the remaining 99.4% is in the seas and polar ice caps (Ref. 6). Of the 2 million cubic miles of the water on land, about one million is found in the first half-mile of the earth's crust, and an almost equal amount in the next mile and a half. Only about 1% of surface waters is in all rivers, and less than 0.001% in the atmosphere.

In the U. S. there are more than 3 million miles of streams, 88,000 miles of tidal shoreline and millions of ponds, lakes and bayous. Total daily water use in the U. S. in 1970 was 385 billion gallons (Ref. 7) of which 121 billion (31%) were for steam electric utilities, 119 billion (31%) were for irrigation, 56 billion (15%) were for industrial, commercial and government agencies, 27 billion (7%) were for public water utilities and the remaining 16% for other uses. In 1900 the total water used was only 40 billion gallons; by 1980 the figure is expected to rise to 443 billion gallons.

For many years pure water was almost taken for granted; now, however, the impact of pollution is beginning to be felt. The total outlay for water pollution control in the U.S. in 1969 was 3 billion dollars; by 1974 the amount was expected to exceed 4 billion (Ref.7). The following section discusses the areas where problems arise.

B. Deleterious Effects

Water should not contain pollutants in such concentrations as to be a health hazard to the consumer. Pollutants in this sense may be either biological or chemical, with the latter sometimes the result of the former. The solubilization of elemental mercury by microbiological action to form the highly toxic methyl mercury is an example. The analytical or monitoring problem in this case, as in others such as for bacterial and algal toxins, is usually chemical in nature. In some instances, however, especially in assessing multicomponent industrial wastes, resort is made to bioassay where the effect of the waste on test organisms is determined.

The biological safety of water means its freedom from pathogenic organims, of which the common types are bacteria, viruses, protozoa, and multicelled parasites. In most instances pathogens enter the water by the fecal route. The direct determination of pathogens, especially viruses, is very difficult at present and impossible for effective control purposes. Resort is therefore made to indicator organisms, specifically the coliform group, present in the intestinal tracts of all warm-blooded animals. Their presence in a water is presumptive evidance of fecal contamination and hence the possible presence of pathogens (Ref. 6,8).

C. Water Standards, Criteria and Legislation

1. Historical

In early history men were more concerned about the health-giving properties of water than in purifying those sources that were polluted. The first municipal water-filtration plant was built in Paisley, Scotland about 1800. By 1852 the city of London had passed an ordinance requiring that all water be filtered. Early water-quality standards included such parameters as color, odor, taste and turbidity. However, as later experience has shown, the quality of water can be adequately determined only by observing its chemical and physical properties and biological content. The U. S. Government expressed its interest in water pollution in the Rivers and Harbors Act of 1899 and the Oil Pollution Act of 1924. Quoting from McKee and Wolf (Ref. 1) "The 1899 Act prohibits the depositing of waste materials, other than that flowing from streets and sewers in a liquid state, in or on the banks of navigable waters and their tributaries.... The 1924 Act prohibits the discharge of oil into the coastal navigable waters of the United States.

"The third major federal enactment regarding water pollution was a provision in the Public Health Service Act of 1912, which gave specific authority to the Public Health Service to conduct investigations of the pollution of streams and lakes by sewage and otheer causes...

"The first comprehensive-type legislation in the pollution control field was the Water Pollution Control Act of 1948...which authorized expanded activities by the Public Health Service... This law...added the principles of State-Federal cooperative program development..." (Ref. 1).

The particular concern of the federal government in the growing national pollution problem resulted in the Federal Water Pollution Control Act (P.L. 84-660, 84th Congress), which was approved by the President on July 9, 1956.

"The Federal Water Pollution Control Act amendments of 1961 considerably elevated the significance of the entire federal water-pollution-control program... It (was) now administered directly by the Secretary of the Department of Health, Education, and Welfare... The act stated in part, that the Secretary shall, in cooperation with other federal, state, and local agencies have related responsibilities, collect and disseminate basic data on chemical, physical, and biological water quality insofar as such data or other information relate to water pollution and the prevention and control thereof...." (Ref. 1) With this legislation the U. S. proposed that the primary responsibility for water pollution control rested with state governments.

The U. S. Public Health Service originally established Drinking Water Standards in 1914; these were revised repeatedly. In 1962 further revisions were made to "Standards to which drinking water and water supply systems used by (those) subject to federal

Table 1. Comparison of Various Drinking Water Standards

Bacteriological Characteristics	U. S. Public Health Service 1962, Ref. 9	AWWA Recommended Potable Quality Water Goals[a] 1968, Ref. 9	National Interim Primary Drinking Water Regulations 40 CFR 141, 7/1/77 and Proposed National Secondary Regulations 40 CFR 143, Proposed 3/31/77, 42 FR 17143
Coliform Bacteria	a. Dilution technique, five 10-ml portions 1. Not more than 10% of all portions examined each month shall show presence of coliform bacteria (coliform MPN $\leq$ one per 100 ml) 2. No two consecutive samples taken from the same location, and not more than 5% of all samples examined each month, shall show presence of coliform bacteria in three or more of the five portions	a. Dilution technique, five 10-ml portions No coliform organisms	a. Fermentation Tube 100 ml samples NOT BE PRESENT IN - > 60% portions/mo. - 5 portions in > 1 sample if < 5 samples/mo. - 5 portions in > 20% of sample if > 5 samples/mo.
	b. Dilution technique, five 100-ml portions 1. Not more than 60% of all portions examined each month shall show presence of coliform bacteria (coliform bacteria MPN $\leq$ 0.9 per 100 ml) 2. No two consecutive samples taken from the same location, and not more than 20% of all samples examined each month shall show presence of coliform bacteria in all five portions examined	b. Dilution technique, 100-ml portions No coliform organisms	b. Fermentation Tube 10 ml samples NOT BE PRESENT IN - > 10% of portions/mo. - 3 or more portions if < 20 samples/mo. - 3 or more portions in > 5% of the samples if > 20 samples/mo.

Table 1. (Continued)

Bacteriological Characteristics	U. S. Public Health Service 1962, Ref. 9	AWWA Recommended Potable Quality Water Goals[a] 1968, Ref. 9	National Interim Primary Drinking Water Regulations 40 CFR 141, 7/1/77 and Proposed National Secondary Regulations 40 CFR 143, Proposed 3/31/77, 42 FR 17143
	c. MF technique, using 50, 100, 200 or 500 ml 1. The arithmetic mean coliform bacterial count of all samples examined during any month shall not exceed one per 100 ml 2. The coliform count per sample shall not exceed three per 50 50 ml, four per 100 ml, seven per 200 ml, or 13 per 500 ml in two consecutive samples taken from the same location, nor in more than 5% of all samples examined during any month	c. MF technique No coliform organisms	c. Membrane filter techniques NOT TO EXCEED - 1/100 ml - arith. mean - 4/100 ml if less than 20 samples per mo. - 4/100 ml in > 5% if > 20 samples/mo.

Physical Characteristics (µg/ℓ)	U. S. Public Health Service 1962		AWWA Recommended Potable Quality Water Goals 1968	National Interim Primary Drinking Water Regulations 40 CFR 141, 7/1/77 and Proposed National Secondary Regulations 40 CFR 143, Proposed 3/31/77, 42 FR 17143
	Recommended limit[b]	Tolerance limit[c]		
Color, units	15	–	< 3	15 (proposed)
Corrosivity	–	–	–	non-corrosive (proposed)
Odor, threshold number	3 inoffensive	–	no odor	3 (proposed)
Residue, filterable (µg/ℓ)	500,000	–	< 200,000	–
non filterable (µg/ℓ)	–	–	virtually suspension free	–
Total	–	–	–	–
Taste	inoffensive	–	non objectionable	–
Turbidity, units	5		< 0.1	1 per mo., 2 for 5 days

Table 1. (Continued)

Chemical Constituents (µg/ℓ)	U. S. Public Health Service 1962 Recommended limit[b]	U. S. Public Health Service 1962 Tolerance limit[c]	AWWA Recommended Potable Quality Water Goals 1968	National Interim Primary Drinking Water Regulations 40 CFR 141, 7/1/88 and Proposed National Secondary Regulations 40 CFR 143, Proposed 3/31/77, 42 FR 17143
Substance				
Alkyl benzene sulfonate	500	—	< 200	—
Aluminum	—	—	—	—
Arsenic	10	50	< 50	50
Barium	—	1000	—	1000
Cadmium	—	10	—	10
Carbon Alcohol Extract	—	—	< 100	—
Carbon Chloroform Extract	—	—	< 40	—
Chloride	250,000	—	—	250,000 (proposed)
Chromium	—	50	—	50
Copper	1,000		< 200	1000 (proposed)
Cyanide	10	20		
Fluoride	0.8-1.7[d,e]	1.4-2.4[d]		1.4-2.4[f]
Foaming Agents	—	—	—	500 (proposed)
Hardness	—	—	80,000-100,000	—
Iron	300	—	< 50	300 (proposed)
Lead	—	50	—	50
Manganese	50	—	10	50 (proposed)
Mercury	—	—	—	2
Nitrate	45,000	—	—	10,000
pH	—	—	—	6.5-8.5 (proposed)
Phenolics	1	—	—	
Selenium	—	10	—	10
Silver	—	50	—	50
Sulfate	250,000	—	—	250,000 (proposed)
TDS		—		500,000 (proposed)
Zinc	5,000	—	< 1000	5000 (proposed)
Pesticides				
Endrin				0.2
Lindane				4
Methoxychlor				100
Toxaphene				5
2,4-D				100
2,4,5-TP				10

Table 1. (Continued)

Radioactivity pCi/ℓ	U. S. Public Health Service 1962 Recommended limits[g]	AWWA Recommended Potable Quality Water Goals 1968	National Interim Primary Drinking Water Regulations 40 CFR 141, 7/1/77 and Proposed National Secondary Regulations 40 CFR 143, Proposed 3/31/77, 42 FR 17143
Radium 226	3		combined 5 pCi/ℓ
Radium 228			
Gross α			15 pCi/ℓ (including Ra 226 but excluding U, Rn
Hydrogen sulfide			50 (proposed)
Strontium 90	10		8 pCi/yr (bone marrow)
Gross β	1000[h]	<100	
Man-made radionuclides			
β and photon			< 4 millirem/yr
2 or more radionuclides			< 4 millirem/yr
Tritium			20,000 pCi/yr (total body)

[a]Not a public health standard but desirable consumer goals.

[b]Recommended limit: Concentrations which should not be exceeded where more suitable water supplies are available.

[c]Tolerance limit: Concentrations above which shall constitute grounds for rejection of the supply.

[d]Dependent on annual average maximum daily air temperature over not less than a 5-yr period.

[e]Where fluoridation is practiced, minimum recommended limits are also specified.

[f]Depends upon temperature of water supply.

[g]Water supplies containing concentrations in excess of these limits will be approved if surveillance of total intake of radioactivity from all sources indicates that such intakes are within the limits recommended by the Federal Radiation Council for control action (see Chap. 13). In absence of strontium 90 and alpha emitters.

quarantine regulations must conform." These are shown in Table 1 (Ref. 9). The endorsement of these Standards by the American Water Works Association resulted in general acceptance for all public supplies in the U. S. (Ref. 6). In 1968 the American Water Works Association issued a report "Quality Goals for Potable Water", which defines "goals for non-toxic quality characteristics of the water delivered to the consumer." (Ref. 10). These goals are also found in Table 1.

As can be seen from Table 1, many of the pollutants and characteristics controlled in the 1977 Drinking Water Regulations, were also covered in the 1962 Regulations. An important exception is mercury. Until 1970, drinking water standards of the U. S. Public Health Service and the World Health Organization did not include limits for mercury. In the spring of 1970, the U. S. Public Health Service tentatively proposed a standard of 5 ppb for mercury in drinking water (Ref. 11).

2. Current Standards, Criteria and Legislation

In the past decade a large body of legislation concerning the quality of the nation's water supply has been enacted; Table 2 lists the major pieces of legislation.

The Federal Water Pollution Control Act (FWPCA) authorized both the states and the federal government to establish water quality standards for surface waters by 1967. With the passing of the amendments to this Act, P.L. 92-500, came an increase in the number and complexity of water control standards. Some of the legislation is not yet completely understood; many of the standards are still to be promulgated. In fact, water pollution law is in a considerable state of flux. The only way to remain up to date is to consult the Federal Register frequently and consult with the state and local agencies (as well as federal) concerned.

P.L. 92-500, in essence, sets out its goal as that "discharge of pollutants into navigable waters be eliminated by 1985". In order to achieve this goal, many programs were initiated. These include series of grants for research into water quality and methods for achieving it, a program for providing federal funds for construction of publicly owned treatment plants, the National Pollutant Discharge Elimination System (NPDES), and a massive program to develop standards and criteria to help achieve as an interim goal by 1983, "water quality...which shall assure protection of public water supplies, agricultural uses, and the protection and propagation of a balanced population of shellfish, fish and wildlife and allow recreational activities in or on the water... ." To follow the progress of these programs, to allow enforcement of them, and to establish the water quality of the U. S. water supplies, an extensive monitoring program was initiated to determine the quality of all "navigable waters, and waters in the contiguous zone," (P.L. 92-500) and to identify all sources, point and non-point, of pollution.

Following the enactment of the Federal Water Pollution Control Act Amendments, there was enacted a second major law concerning water quality: the Safe Drinking Water Act, P.L. 93-523, of 1974. P.L. 93-523 provides for primary regulations to protect public health, as well as secondary regulations regarding the taste, color, and appearance of drinking water. In addition, it provides for protection of underground water supplies. To meet these ends, it requested studies of health, economic, and technological problems of drinking water supplies and a survey to determine the quality and availability of rural water supplies (Ref. 12).

The latest amendments (P.L. 95-217) to the Federal Water Pollution Control Act serve as a mid-course correction of P.L. 92-500.

Table 2. Major water quality legislation

Public Law No. or Reference	Title	Date Enacted
P.L. 84-660	Federal Water Pollution Control Act	1961
P.L. 92-500	Federal Water Pollution Control Act Amendments	1972
P.L. 93-523	Safe Drinking Water Act	1974
P.L. 94-469	Toxic Substances Control Act	1976
P.L. 95-217	Federal Water Pollution Control Act Amendments	1977

They provide for a revision of deadlines in promulgation of effluent standards, new guidelines and limitations, establishment and addition to a list of 65 toxic chemicals, and the extension of deadlines for compliance (particularly for publicly-owned treatment works, (POTW's).

The amendments to the Federal Water Pollution Control Act (P.L. 95-217), The Toxic Substances Control Act of 1976, TSCA (P.L. 94-469), and the "Consent Decree" issued as a result of the litigation, Natural Resources Defense Council vs. Train* require the regulation of discharges of toxic substances into the nation's waters.† These are further discusssed in Section e, Toxic Chemicals Legislation.

The impact of these acts the Federal Water Pollution Control Act, its amendments (P.L. 92-500 and P.L. 95-217), the Safe Drinking Water Act, the Toxic Substances Control Act and the Consent Decree is far reaching. The results (among others) have been the development and publication of many criteria, and methods for analysis, standards for public water supplies, a national pollutant discharge elimination system and a wide body standards establishing effluent limitations and guidelines for existing sources, new source performance standards, and pretreatment standards for new and existing sources for point source categories. The toxic substances program is just beginning to show its potential and programs for non-point source monitoring are just underway.

a. Criteria Documents and Standard Methods of Analysis. Since the enactment of P.L. 92-500, two criteria documents have been released (Refs. 5 and 13). The first is a report by the National Academy of Sciences and National Academy of Engineers (hereafter NAS/NAE report) and the second was an update of these criteria by the EPA. Both refer to the study by McKee and Wolf (Ref. 1) and to some extent to Ref. 4.

The NAS/NAE report (Ref. 5) considers the quality characteristics of waters used for a variety of purposes (uses); public water supplies, agriculture and silviculture (for irrigation and livestock drinking), freshwater life and wildlife, marine life and wildlife, industrial and aesthetic and recreational purposes. It establishes criteria for each pollutant or parameter where possible. Sometimes the criterion is an absolute value; for example, for mercury (to protect freshwater aquatic life) in unfiltered water is 0.05 µg/ℓ (0.05 ppb). In other cases the value is relative - based on the number of sensitive species which remain alive after a specified length of time; for example, the recommendations for phenolics in freshwater is 0.05 times concentration which after 96 hours is lethal to 50% of a sensitive species present. Sometimes a range is specified - i.e. the pH recommended for public water supplies is from 5.0 to 9.0.

The EPA publication (Ref. 13) updates the NAS/NAE report. For some pollutants (aluminum, antimony, bromine, cobalt, fluoride, lithium, molybdenum, thallium, uranium and vanadium) the reader is referred to the NAS/NAE report. The EPA report considers each pollutant or water quality characteristic, establishing criteria when it considers them necessary specifying the water usage at that time.

Both these volumes (Refs. 5 and 13) and Ref. 1 are essential to the reader who is interested in the effects of a variety of pollutants and water quality parameters on the aqueous ecosystem. They also provide an excellent introduction to the literature.

Appendix A is a compilation of the currently applicable water quality criteria for waters of designated uses. The majority of the criteria are from the NAS/NAE report. Those which have been updated and are therefore from the latest EPA criteria document (Ref. 13) are marked with the superscript "b". The reader should not rely solely on the compilation provided here, but should refer to both criteria documents which give the basis for the criterion and its intent. He should also check the Federal Register to find out if new criteria documents have been published.

- Use of Water Quality Criteria to Form Water Quality Standards. As stated in 43 FR 29589, July 10, 1978, the current EPA approach to water quality standards is as follows. A water quality standard consists of a "use" designated for a body of water and a "criterion" which limits the amount of pollutant or value of a water quality characteristic which is "sufficient to support" the water's designated use. The use of a water should be "fishable and swimmable" except in very limited circumstances. Downgrading of water "use" discouraged and upgrading encouraged.

*The cases under consideration were: Natural Resources Defense Council, Inc. et al. vs. Russell E. Train; Environmental Defense Fund, et al., vs. Russell E. Train; Citizens for a Better Environment, vs. Russell E. Train, and Natural Resources Defense Council vs. James A. Agee, et al., No. 73-453, 75-172, 75-1698 and 75-1267, June 8, 1976.

†The actual decree which is referred to is NRDC vs Train; however the actions referred to now came under NRDC vs. Costle. The action is still under litigation. The NRDC filed a contempt motion for non-compliance. The EPA then responded with a motion for amendment and industry has filed to vacate. By the time this discussion is in print, the entire situation will probably have changed again.

Currently, the states, if their water quality plans have been accepted, may establish their own water quality standards, which are sufficient to maintain the waters' designated use. Until recently, the EPA has expected the states to use its promulgated criteria (as appear in Ref. 13) or to carefully justify the use of a less stringent criterion. If the justification is inadequate, then the EPA may step in and issue a standard. On the other hand, if a state has not regulated a pollutant or characteristic at all, the EPA, in most cases, has taken no action.

Since the acceptance of the consent decree, the EPA is considering several revisions to this policy (proposed in 43 FR 29588). Among these are (1) a more powerful approach to encouraging upgrading and discouraging downgrading of designated uses and (2) a much more "aggressive" approach to translating federal criteria into standards. It may also consider issuing a list of pollutants for which standards must be promulgated by the states including the toxic pollutants (possibly not all) and the pollutants (possibly not all) contained in Ref. 13. Another possible approach suggested was promulgating water quality standards for this group of pollutants and allowing the states to appeal for less stringent standards, if justifiable. The reader should follow the Federal Register for more up to date information on this proposal. If promulgated, the reader will find the EPA Criteria/Standards Policy in 40 CFR 130.

- Methods Guidelines - "Standard Methods". Two sets of guidelines which establish methods (test procedures) for the analytical determination of pollutants have been promulgated; the latest which appeared in the Federal Register (41 FR 52780, December 1, 1976), gave procedures for 115 parameters. It supercedes the earlier one of October 16, 1973 (38 FR 28758) and appears in Appendix B. The purpose of these guidelines is to establish a set of procedures which will produce uniformly accurate and precise information concerning the quality of water in question. They are discussed further in Part F below.

b. National Interim Primary Drinking Water Standards. National Interim Primary Drinking Water Standards for conventional pollutants were promulgated on March 14, 1975; those for radionuclides were promulgated on July 9, 1976. The reasoning and documentation for the values chosen are found in Ref. 14. Both came into effect on June 24, 1977 and appear as 40 CFR 141 and in Appendix C of this section. National Secondary Drinking Water Regulations (40 CFR 143) were proposed on March 31, 1977 (42 FR 17143) but have not yet been promulgated (10/1/78).

Table 1 compares the standards in effect in 1962, 1968 and 1978. The major changes involve the addition of the mercury standard, the additions of the pesticide standards and the increased list in radioactive substances. Several substances have been omitted from the later standards. This is to prevent overburdening of the monitoring laboratories, in the absence of evidence that certain contaminants are present in U. S. domestic supplies. As their presence is established or new toxicities are found, substances may be added or reintroduced.

The National Interim Primary Drinking Water Regulations are federally enforceable, and monitoring for contaminants or characteristics should take place (for most water suppliers) at least each quarter for which water is supplied to the public. This may vary from state to state and in certain localities, so the schedule should be obtained from the local agency responsible for EPA enforcement. The methods to be used are defined in 40 CFR 141 and are mostly from "Standard Methods" (Ref. 2) and the EPA methods manual (Ref. 15); alternative methods must be approved by the EPA Administrator for each location. The secondary regulations generally concern taste, odor, appearance and several less noxious chemical constituents in the drinking water. Although many of the pollutants governed by the secondary regulations were included in the 1962 regulation, several new parameters have been included: corrosivity, foaming agents, total dissolved solids and hydrogen sulfide. Corrosivity is the only new parameter which has not been covered in the criteria documents and for which no method for determination is readily available. Clearly, a method must be available before the standard will be enforceable. The secondary regulations are not federally enforceable and therefore monitoring is not required, but it is suggested that the parameters be monitored on the same schedule as the primary regulations. The act also provides for regulations to protect underground water sources, primarily through the provisions for a regulation for underground injection, which has not been promulgated (10/1/78).

c. The National Pollution Discharge Elimination System. The National Pollutant Discharge Elimination System (NPDES) has been established and all point-source dischargers into waters of the United States must obtain an NPDES permit which specifies the limits on pollutants which may be discharged. Usually these are based on the effluent limitations (see below Section d.) which have been established for the point source category concerned, although state or local authorities may demand more stringent standards, if necessary, to achieve its water quality goals (Ref. 16). One possible exception to this appears to be the U. S. Bureau of Reclamation, which claims that it does not need to meet state standards, a claim which is currently under appeal (Ref. 17).

The NPDES permit also states the required monitoring and reporting procedures. As yet, after the permit has been issued, qualitative analyses are not generally required. However, before the permit is issued, the effluent of the discharges is analyzed and restrictions are supposed to cover most possible pollutants. Until recently, however, only those pollutants specifically mentioned in the permit were restricted. A revision has been proposed, however, (Ref. 18) which states that any discharge not mentioned in the permit is not allowed. For information on obtaining an NPDES permit the interested person should contact the "Regional Administrator" of the regional EPA, or the state organization which is authorized to handle the issuing of permits, often the State Water Quality Control Board.

• Effect of Toxic Substances Control. On May 23, 1977 partially in response to the "Consent Decree" in the case of Natural Resources Defense Council vs Train, 8 ERC 2120 (D.D.C., 1976), the EPA published clarifications of 40 CFR 124,125 (National Pollution Discharge Elimination System); the clarifications state that for certain industries for which standards have not yet been promulgated, the permit which is issued will say that when limitations or standards are set, then the permit shall be "promptly modified, or, alternatively revoked and reissued in accordance with such effluent standard or limitation...." The 21 major industries affected are listed in Table 3, with the approximate point source categories from Title 40 of the Code of Federal Regulations, which they represent. (Since the consent decree the EPA has added POTW's (Publicly Owned Treatment Works) to the list.) The entire listing as it appeared in 8 ERC 2120, D.D.C. 1976, including the standard industrial classifications involved, appears in Appendix E. The new amendments require within three years after promulgation of an effluent limit for anything added to the list with an outside date of 1987.

d. Effluent Guidelines and Standards. Perhaps the most momentous task for the EPA has been the promulgation of effluent limita-

Table 3. Point Source Categories Affected by the Consent Decree

	Point Source Category	Point Source Cat. # in 40 CFR[a]
1	Timber Products Processing	429
2	Steam Electric Power Plants	423
3	Leather Tanning and Finishing	425
4	Iron and Steel Mfg.	420
5	Petroleum Refining	419
6	Inorganic Chemicals Mfg.	415
7	Textile Mills	410
8	Organic Chemicals Mfg.	414
9	Non-Ferrous Metals Mfg.	421
10	Paving and Roofing Materials (asphalts and tars)	443
11	Paint and Ink Formulation and Printing	446,447
12	Soap and Detergent Mfg.	417
13	Auto and Other Laundries	
14	Plastic and Synthetic Materials Mfg.	416
15	Pulp and Paperboard Mills and Converted Paper Products	430,431
16	Rubber Processing	428
17	Miscellaneous Chemicals	422,439,454,455,457,458,459
18	Machinery and Mechanical Products Mfg.	424
19	Electroplating	413
20	Ore Mining and Dressing	436,440
21	Coal Mining	434

[a]Categories may not be mutually exclusive.

tions or pretreatment standards, and new source performance standards for point source dischargers. In P.L. 92-500, 27 point source categories were established as of July 1, 1972. Currently, there are more than 40 point source categories and innumerable subcategories (see Appendix D for a list of categories and subcategories). For each industry which constitutes a point source category, there may be numerous subcategories, and within the subcategories, there may be further divisions. For each segment, initially the EPA was to promulgate five types of standards and limitations: Best Practicable Control Technology Currently Available Limitations (BPTCA), Best Available Technology Economically Achievable (BATEA) Limitations, New Source Performance Standards (NSPS), Existing Source Pretreatment Standards and New Source Pretreatment Standards. As of the 1977 amendments, (P.L. 95-217), in response to industry concerns and the recommendations of the National Commission on Water Quality, they must also promulgate "Best Conventional Pollutant Control Technology" (BCT) limitations. In Appendix D, the Point Source Categories and Subcategories are listed with an indication of which standards and guidelines have been promulgated, and for each subcategory the substances whose discharge is allowed and the characteristics which may be changed under BPTCA and BATEA guidelines, and the proposed BCT guidelines. The substances whose discharge is allowed by BATEA guidelines are in parentheses if they differ from those allowed by the BPTCA guidelines. A description of and schedule for promulgation of these guidelines and standards is as follows:

- Best Practicable Control Technology Currently Available (BPTCA) Guidelines. This technology represents the "average of the best existing waste treatment currently in use" within the category or subcategory. (Ref. 19). These were to have been in effect by July 1, 1977. Some dischargers may be allowed a variance for meeting these standards until July 1, 1983. Industrial users, showing good faith, can receive waivers until April 1, 1979.

- Best Available Technology Economically Achievable (BATEA) Guidelines represents the best technology which has been developed within a PSC or Subcategory, (Ref. 18). The differences between BPTCA and BATEA are not always universally agreed upon. For non-conventional and toxic pollutants these were to be in effect by July 1, 1983; however, the deadline is now July 1, 1984. For toxic substances, BATEA regulations should be promulgated as soon as possible, with industry in compliance within 3 years (Ref. 20). For so-called conventional pollutants [as of 9-19-78 - pH, fecal coliform, biological oxygen demand (BOD), and total suspended solids (TDS)] best conventional pollutant control technology guidelines may apply (see below). For non-conventional pollutants (those pollutants which are neither toxic pollutants as defined in 43 FR 4108 and later addenda, or conventional pollutants) such as chemical oxygen demand (COD), surfactants, oil and grease, ammonia, and nitrate, modifications of BATEA regulations, may be applied for within 270 days of the promulgation of the applicable guideline, or within 270 days of the promulgation of the Act (12/27/78). Several of these (COD, phosphorus and oil and grease) have been proposed as conventional pollutants, and if they are so promulgated, their regulation will fall under BCT guidelines (below). For further information regarding this modification, the reader is referred to 43 FR 40859, September 13, 1978.

- New Source Performance Standards - "The best available demonstrated controlled technology, processes, operating methods or alternatives including, where practicable, a standard permitting no discharge." These are to be promulgated within a year of an industry's inclusion on the list of Point Source Categories. Same schedule as BATEA for the 65 toxics and 21 industries.

- Exiting Source Pretreatment Standards and New Source Pretreatment Standards. These are designed to assure that the publicly owned treatment works (POTW's) are able to comply with the standards which they are compelled to meet - they must also comply with an NPDES permit. If the POTW is unable to remove certain pollutants or they will disrupt its function or contaminate municipal sludges, the industry must remove them. On the other hand, if the POTW can remove certain pollutants adequately, their discharge into the public system may be allowed. Same schedule as BATEA for the 65 toxics and 21 industries.

- Best Conventional Pollutant Control Technology - BCT is not an additional limitation, but places essentially BATEA controls on conventional pollutants; however, the BCT controls are to be economically reasonable" not merely "achievable". The conventional pollutants so far identified by the EPA are:

  BOD5 - 5-day biological oxygen demand
  TSS - total suspended solids
  Fecal coliform
  pH - log of the hydrogen ion concentrations.

Several more pollutants have been proposed;

  COD - chemical oxygen demand
  Oil and grease
  Total phosphorous.

The least stringent guideline even for conventional pollutants will be the BPTCA guideline. As of September 1, 1978 only two BCT guidelines had been promulgated; however, on August 23, 1978 many were proposed--these are listed in Appendix D.

Appendix D indicates which BPTCA, BATEA, NSPS, ExSPr.S, NSPrS, and BCT regulations had been promulgated or proposed by September 1, 1978. A brief glance at Appendix D clearly demonstrates what a monumental task lies before the EPA. It also indicates that numerous guidelines are not yet available. Each promulgation requires much research, substantiation and appeal. After each set of guidelines is promulgated, a "Development Document" is published, which is available to the public at any EPA library. Specific documents can be obtained from the Superintendent of Documents, U. S. Government Printing Office, Washington, D. C. 20402. While development documents are in draft form, they may be obtained from Distribution Offices, Effluent Guidelines Division, (HW-552), EPA, Washington, D. C. 20460). The reader interested in the process is referred to Ref. 19.

The guidelines as promulgated require some explanation. First, they are not arbitrarily binding - the manufacturer or locality, requesting more stringent or lax regulations, may submit evidence to the regional EPA office or State Control Board (the NPDES administering agency) requesting a variance. There are different kinds of variances. Section 301(g) provides a variance from non-toxic, non-conventional BAT, §301(o) has an economic variance from BAT (not for toxics), and EPA has created an administrative variance ("fundamentally different factors") for BPT (and perhaps others). Secondly, only substances or characteristics which may be discharged or may differ from the ambient water characteristics are specifically mentioned in the guidelines (and in Appendix D). Substances which may not be discharged are not specifically listed. If no discharge is allowed, the regulations state, "There shall be no discharge of process waste water pollutants to navigable waters" (see, for example, Point Source Category 409-Sugar Processing, subcategory E, Florida and Texas Raw Cane Sugar Processing, in Appendix D). The guidelines often provide for some discharge of certain pollutants in the advent of a 10 year, 24 hour rainfall event. For example see Appendix D, Category 412, Feedlots, subcategory A (all subcategories except Ducks), which allows discharge of overflow from such a rainfall or catastrophic event-if the waste water containing facility is designed to hold all generated process waters plus the rainoff from a 10-year, 24-hour rainfall event. For category 415 (Inorganic Chemicals Mfg.) Subcategory M (Potassium Sulfate), any discharge, which occurs as a result of a rainfall event (as described above) is limited to TSS (total suspended solids) - 50 mg/ℓ (maximum for 1 day) and 25 mg/ℓ (average over 30 days), and pH within the range 6.0 - 9.0. Subcategory AA and AB (Borax and Boric Acid Production) of Inorganic Chemicals provides for "no discharge..., except that residual brine and depleted liquor may be returned to the body of water from which the process brine solution was originally drawn".

- Promulgation of Regulations. The promulgation of the effluent guidelines and limitations for BPTCA and BATEA, as well as the Performance and Pretreatment standards is an extremely time-consuming task for the EPA. First contracts must be awarded for technical and impact analysis studies; reports from these studies are sent to all known interested groups (EPA, Industrial, and Professional Association, Governmental Agencies and others). From the initial report and comments, the proposed effluent guidelines, limitations, and standards are developed. After a comment period, the proposed standards, limitations, and guidelines are reviewed and final limitations Guidelines and Standards are promulgated.

As has been mentioned above, the new amendments to the Clean Water Act (P.L. 95-217) provide for extension of deadlines for POTW's, and in some cases for industries which have shown good faith in attempting to comply with the standards. The BATEA regulations for the 65 toxics and also pretreatment and new source performance standards must be developed in accordance with the schedule set down in the settlement agreement for categories of Point Sources. If a toxic (effluent standard) is promulgated, then the industry must comply with that standard within three years if an exception is granted to the usual 1 year period. The original list of 65 toxic substances covered in the consent decree is found in Table 4; since then the EPA has expanded the list to 129 substances.

e. Toxic Chemical Legislation. There has been increasing interest in the past few years in the effect of toxic chemicals in our environment. Recently, the public was shocked by the news that the James River in eastern Virginia was contaminated with kepone, and the subsequent news that cleanup may be improbable for financial reasons. (Ref. 21). Numerous other rivers are polluted; for example, high mercury levels in fish in the Shenandoah (also in Virgina), have caused its closure for fishing (Ref. 22).

The impacts of the latest toxic chemicals control legislation. [The Toxic Substances Control Act (TSCA - P.L. 94-469), The 1977 Amendments to the Federal Clean Water Act (P.L. 95-217), and the NRDC vs. Train Consent Decree] are just beginning to be felt.

Table 4. List of Toxic Substances found in P.L. 95-217, the 1977 Amendments to the Federal Water Pollution Control Act, and the Consent Decree

Acenaphthene
Acrolein
Acrylonitrile
Aldrin/Dieldrin[a]
Antimony and compounds
Arsenic and compounds
Asbestos
Benzene
Benzidine[a]
Beryllium and compounds
Cadmium and compounds
Carbon tetrachloride
Chlordane (technical mixture and metabolites)
Chlorinated benzenes (other than dichlorobenzenes)
Chlorinated ethanes (including 1,2- dichloroethane, 1,1,1-trichloroethane, and hexachloroethane)
Chloroalkyl ethers (chloromethyl, chloroethyl, and mixed ethers)
Chlorinated naphthalene
Chlorinated phenols (other than those listed elsewhere; includes trichlorophenols and chlorinated cresols)
Chloroform
2-Chlorophenol
Chromium and compounds
Copper and compounds
Cyanides
DDT and metabolites[a]
Dichlorobenzenes (1,2-,1,3-, and 1,4-dichlorobenzenes)
Dichlorobenzidene
Dichloroethylenes (1,1-and 1,2-dichloroethylene)
2,4-dichlorophenol
Dichloropropane and dichloropropene
2,4-dimethylphenol
Dinitrotoluene
Diphenylhydrazine
Endosulfan and metabolites
Endrin and metabolites[a]
Ethylbenzene
Fluoranthene
Haloethers (other than those listed elsewhere; includes chlorophenylphenyl ethers, bromophenylphenyl ether, bis(dichloroisopropyl) ether, bis-(dichloroethoxy) methane and polychlorinated diphenyl ethers)
Halomethanes (other than those listed elsewhere; includes methylene chloride methylchloride, methylbromide, bromoform, dichlorobromomethane, dichlorodifluoromethane)
Heptachlor and metabolites
Hexachlorobutadiene
Hexachlorocyclohexane (all isomers)
Hexachlorocyclopentadiene
Isophorone
Lead and compounds
Mercury and compounds
Naphthalene
Nickel and compounds
Nitrobenzene
Nitrophenols (including 2,4-dinitrophenol, dinitrocresol)
Nitrosamines
Pentachlorophenol
Phenol
Phthalate esters
Polychlorinated biphenyls (PCBs)[a]
Polynuclear aromatic hydrocarbons (including benzanthracenes, benzopyrenes, benzofluoranthene, chrysenes, dibenzanthracenes, and indenopyrenes)
Selenium and compounds
Silver and compounds
2,37,8 - Tetrachlorodibenzeo-p-dioxin (TCDD)
Tetrachloroethylene
Thallium and compounds
Toluene
Toxaphene[a]
Trichloroethylene
Vinyl chloride
Zinc and compounds

[a]For these nine compounds: Aldrin/Dieldrin, DDT, DDD and DDE, Endrin, Toxaphene, Benzidine and Polychlorinated Biphenyls, final toxic pollutant effluent standards have been promulgated (40 CFR 129, as of July 1, 1977, promulgations in 42 FR 2588 (1/12/77), 42 FR 2617 (1/12/77) and 42 FR 6555 (2/2/77).

TSCA gives the EPA the right to determine the impact of a toxic substance in the aqueous environment and allows for wide controls of toxic chemicals. It also requires extensive research and rulemaking by the EPA, the extent of which is illustrated by the 2 volumes (over 30,000 entries (Ref. 23) containing the list of chemicals which may be candidates.

The 1977 Clean Water Act Amendments (P.L. 95-217) and the consent decree have set schedules for the promulgation of toxic effluent limitations for 21 major industries initially (the EPA has since added POTW's) under a simplified procedure; however, the list of toxic chemicals was lengthened to 65 families of pollutants in response to the consent decree (list appears in Table 4) and as of September 15, 1978, 129 specific substances will appear on the list. Six toxic effluent regulations (covering nine substances) for the toxics which had already been identified have been promulgated as required by the consent decree. These are summarized in Table 5 and appear in toto in Appendix F.

The EPA therefore must establish guidelines and limitations for the remaining toxics in 22 industries by July 1, 1980 (September 25, 1978, C & EN, p. 41). This is the outside date set by Congress. The Consent Decree requires much earlier promulgation. Before the regulations can be promulgated, the EPA must verify the substances expected in the discharges of the 22 industries. This requires highly sophisticated analytical methodologies for qualitative and semiquantitative analysis [usually GC-MS (gas chromotography followed by mass spectrometry) for organics, electron-microscopy for asbestos, and atomic absorption or spark source mass spectrometry (C & EN, September 25, 1978, p. 41)]. The EPA will then try to provide analytical methodologies for monitoring which a monitoring lab can afford. In promulgating the standards, the EPA must consider also the economics involved and the technology available.

To be up to date as to the status of these standards the reader should watch the Federal Register carefully for notices con-

Table 5. Toxic Substances, Ambient and Effluent Water Standards (from 40 CFR 129)

Substance	Ambient Std.-µg/ℓ	Effluent Stds (µg/ℓ) Manufacturer Calendar Mo. µg/ℓ	Manufacturer kg/kkg Product	Manufacturer Single day µg/ℓ	Formulator (User) Calendar No.	Formulator (User) Single day µg/ℓ
Aldrin/Dieldrin	0.003	discharge prohibited*			discharge prohibited*	
DDT, DDD, DDE	0.001	discharge prohibited*			discharge prohibited*	
Endrin	0.004					
Existing Sources		1.5	0.0006	7.5	discharge prohibited*	
New Sources		0.1	0.00004	0.5		
Toxaphene	0.005					
Existing Sources		1.5	0.0003	7.5	discharge prohibited*	
New Sources		0.1	0.00002	0.5		
Benzidine	0.1					
Existing Sources		10	0.130	50	10	25
New Sources		10	0.130	50	10	25
Polychlorinated Biphenyls	0.001	discharge prohibited*			discharge prohibited*	

*Does not apply to stormwater runoff from areas contaminated only by air emission fallout or to stormwater runoff exceeding a 24 hr-10 yr rainfall event.

cerning proposals, comment periods, public meetings and development documents. The reader if interested in a particular industry should contact the Effluent Guidelines Division of the EPA or the Office of Analysis and Evaluation (EPA).

f. The author wishes to thank R. Stoll and J. T. Banks for their help, criticism and suggestions.

D. Organizations

The number of organizations interested in water quality is very large. The U. S. Geological Survey Digest of the Catalog of Information on Water Data (Ref. 24) lists 12 federal agencies and 159 non-federal agencies which report water-quality data. Several organizations are listed below which are engaged in water-monitoring activities. Additional organizations are listed in Ref. 24.

The Environmental Protection Agency (EPA) was established in 1970 "to assure the protection of the environment by abating and controlling pollution on a systematic basis". The EPA took over the functions of the Federal Water Quality Administration formerly the Federal Water Pollution Control Administration (FWPCA) which had been founded in 1965 to provide research and development grants, increased funds for construction of sewage treatment plants and to establish water quality criteria. The EPA is responsible for water-quality control and management. The Office of Water Programs, the Office of Enforcement and the Office of Research and Monitoring, all located at the Environmental Protection Agency, Washington, D. C. 20460 are responsible for standards and guidelines. EPA laboratories conducting analysis and providing support include the following:

Arctic Environmental Research Laboratory
Environmental Protection Agency
Fairbanks, AK 99701

Analytical Quality Control Laboratory
1014 Broadway
Cincinnati, OH 45260

Gulf Breeze Environmental Research Laboratory
P.O. Box 158
Dauphin Island, AL 36528

National Environmental Research Center
Las Vegas, NV 89114

National Environmental Research Center
Cincinnati, OH 45260

National Environmental Research Center
200 S.W. 35th St.
Corvallis, OH 97330

National Marine Water Quality Laboratory
P.O. Box 277
West Kingston, RI 02892

National Marine Water Quality Laboratory
Bears Bluff Field Site
Box 368
Johns Island, SC 29455

Robert S. Kerr Water Environmental Research Laboratory
P.O. Box 1198
Ada, OK 74820

Southeast Environmental Research Laboratory
College Station Rd.
Athens, GA 30601

The U. S. Public Health Service (USPHS) was founded in 1798; it is the "federal agency specifically charged with promoting and assuring the highest level of health attainable...". The three operating agencies of USPHS are the Food and Drug Administration, the Health Service and Mental Health Administration and National Institutes of Health, all with headquarters in Washington, D. C.

The U. S. Geological Survey (USGS) was established as an agency in the Department of the Interior in 1879. Its activities include the Water Resources Division which is responsible for the appraisal of the quantity and quality of our national water resources and research in the field of hydrology. The USGS shares with state and local water agencies in investigations on both surface and ground water-development conservation and management. Water-quality data are processed through the computerized data file in Washington. The first of the Water Resources Division's Central Laboratories is located in Salt Lake City, UT. Fourteen other water-quality laboratories are located throughout the country. For information contact:

U. S. Geological Survey
18th and F Streets, N.W.
Washington, D.C. 20240

The National Oceanic and Atmospheric Administration (NOAA), among other activities, conducts research related to the oceans and inland waters. It also provides satellite observations of the environment. Address:

National Oceanic and Atmospheric Administration
6010 Executive Blvd.
Rockville, MD 20852
(301) 656-4060

The Bureau of Reclamation is involved in the regulation, conservation and utilization

of water and related land resources in the western states. Address:

Bureau of Reclamation
Department of the Interior
Washington, D. C. 20240
(202) 343-4662

The American Public Health Association (APHA) promotes personal and public health by, among other things, establishing standards, procedures and tabulating facts on the causes of communicable diseases. Address:

American Public Health Association
1015 - 18th St., N.W.
Washington, D. C. 20036
(202) 833-9640

American Water Works Association (AWWA) has interests in water supplies, also water departments and equipment associated with the purifying of water. AWWA issues a monthly journal covering the various aspects of water. Address:

American Water Works Association
2 Park Avenue
New York, N.Y. 10016
(212) 686-2040

The Water Pollution Control Federation (WPCF) is a federation of 50 technical societies. Membership includes chemists and engineers concerned with the collection, treatment and disposal of wastewaters. WPCF publishes a monthly journal. Address:

Water Pollution Control Federation
3900 Wisconsin Ave., N.W.
Washington, D. C. 20016
(202) 362-4100

The main concerns of the American Society for Testing and Materials are performance standards and test methods for materials and the products made from these materials. Part 23 of the Annual Book of ASTM Standards (Ref. 3) is relevant to water and water analysis. The 1972 edition of this volume includes over 150 standards for water and atmospheric analysis. Standards comprise test methods, definitions, recommended practices, classifications and specifications that have been formally adopted by the Society. New editions of Part 23 are published each November. Among the many technical committees is ASTM Committee D-19 on Water. A Journal of Materials is published quarterly. ASTM may be contacted at:

American Society for Testing and
Materials
1916 Race Street
Philadelphia, PA 19103
(215) 569-4200

Battelle Memorial Institute began operations in 1929. It is a non-profit organization with five major research centers engaged in pure and applied research. Among its activities is an interest in many aspects of water quality. Headquarters address:

Battelle Memorial Institute
505 King Avenue
Columbus, OH 43201
(614) 299-3151

E. Information Sources

1. Catalogs

The U. S. Geological Survey publishes an annual Catalog of Information on Water Data, which reports on water-data acquisition activities on streams, lakes, reservoirs, estuaries and ground water. A helpful digest of the catalog information is available (Ref. 24). In the 1970 edition of the Catalog, water-quality activities of both federal and non-federal agencies are reported. Information on water data is listed in one of four indexes: Index to Water-Quality Section, Index to Surface-Water Section (with 23,846 stations reporting), Index to Ground-Water Stations (with 28,964 stations reporting) and Index to Areal Investigations and Miscellaneous Activities. The Catalog information is accessible through data-retrieval methods; however, the actual water data must be obtained from the reporting agencies.

2. Abstracts

The Water Resources Information Center (WRIC) is responsible for publishing Selected Water Resources Abstracts (SWRA). Twice a month abstracts appear in journal articles and reports on the water-related aspects of science and engineering. An annual index is published in two parts: Part 1 is arranged by Author, Organization and Accession Number; Part 2, by Subject. Federal agencies, contractors and grantees in water resources may request the SWRA from the Manager:

Water Resources Scientific Information
Center
Office of Water Resources Research
U. S. Department of Interior
Washington, D. C. 20240

SWRA is also available on subscription from the

National Technical Information Service
U. S. Department of Commerce
Springfield, VA 22151

The Environmental Awareness Reading list (EARL) is a semi-monthly listing of current publications dealing with environmental concerns compiled by the Natural Resources

Library of the U. S. Department of the Interior. These selections are intended to reflect current developments and discussions concerning environmental and natural resource topics appearing in a variety of both popular and technical periodicals. The entries include full bibliographic citations--annotations are added when needed to clarify a title. The arrangement is alphabetical by author or title.

The Environmental Awareness Reading List is a cooperative product of the National Park Service and the Natural Resources Library. Yearly subscriptions are available through:

National Technical Information Service
U. S. Department of Commerce
Springfield, VA 22151

Environmental Information Access is published semi-monthly by:

Environment Information Center, Inc.
124 E. 39th Street
New York, N.Y. 10016

Water Pollution Abstracts cover international literature on water and water collection; the abstracts are published monthly by:

The Department of the Environment
Her Majesty's Stationery Office
London, England

3. Data Bases

Information on water monitoring is being gathered and stored in a number of data bases. A data base may be defined as a collection of information in machine-readable form. Data-base information may be in the form of documents or data. In document form, an abstract or perhaps the entire document is available for re-call. In data form the original data with perhaps some consolidation are available for readout. Several data bases are noted here:

- STORET. In 1961 the staff of the National Water Quality Network in the Division of Water Supply and Pollution Control, U. S. Public Health Service conceived the basic concept of the storage and retrieval of data for water pollution control. In 1966 the STORET System was transferred into the Federal Water Pollution Control Administration; a refinement of the system is now operated by the Division of Applied Technology, EPA. This Water Quality Control Information System is set up to store and retrieve data and information on such topics as water quality, standards, municipal and waste discharges and waste abatement needs. In the U. S. there are now more than 150 terminals with access to STORET. A description on how to use the system is given in the STORET Handbook available from the Water Quality Control Information System (STORET), EPA, Washington, D. C. 20460.

- Water Resources Abstracts is a document form of data base. For information on retrieval, contact:

  Water Resources Information Center
  University of Oklahoma
  Norman, OK 73069

- The National Environmental Research Center maintains a computer-accessed literature file on analytical methods for determining water quality. Also available is a monthly abstract bulletin. Address:

  Analytical Quality Control Laboratory
  National Environmental Research Center, EPA
  1014 Broadway
  Cincinnati, OH 45260

- The Analytical Methodology Information Center (AMIC) is being created for EPA's Analytical Quality Control Laboratory by the Columbus Ohio Laboratories of Battelle Institute. The center plans to gather, analyze, and disseminate technical information on methods for determining water quality and effects of pollutants. Address:

  Battelle Columbus Laboratories
  505 King Avenue
  Columbus, OH 43201

F. Methods of Analysis

1. Standard Methods

Periodically, the EPA (in the Federal Register) publishes a list of methods which are considered "Standard Methods". These become part 136 of the code of Federal Regulations, Title 40, and are the methods which each monitoring laboratory which reports to the EPA must use to determine the "Parameters" mentioned. These appear in Appendix B. Since 1973, the number of parameters and guidelines for their measurement has increased from 71 to 115. Currently, most of the procedures are instrumental.

If a monitoring laboratory decides that it is using a technique which is equivalent to the standard procedure, it may apply to obtain its status "as an alternative method." Evidence must be presented to the regional EPA laboratory showing that the methods are equivalent. This may be done by running samples using both methods simultaneously, or by showing that results obtained using the alternative

method on standards obtained from the EPA lab or NBS (for example) give equivalent or better results. The procedure is somewhat flexible and each laboratory should contact their local EPA to find out the method it prefers.

2. Method Manuals

Methods for the analysis of water quality parameters have progressed significantly during the past three quarters of a century. The first edition of Standard Methods of Water Analysis appeared in 1905. Since then twelve editions have appeared at about 5 year intervals each with refinements and improvements so that the 14th Edition of Standard Methods for the Examination of Water and Wastewater (1975) was immediately accepted as a standard reference work for water analysis in the U. S. The 14th edition is the joint work of the American Public Health Association, the American Water Works Association and the Water Pollution Control Federation. Quoting from the preface, "The methods presented... are the best available and generally accepted procedures for the analysis of water and wastewaters...

"All methods...are 'standard' unless designated 'tentative'... Methods with 'standard' status have been extensively studied and accepted as applicable within the limits of sensitivity, precision and accuracy recorded. 'Tentative' methods are those still under investigation which have not yet been fully evaluated or are not considered sufficiently specific at present to be designated 'standard'...".

In the interim between editions, a new method may be accepted as tentative or standard by the Joint Editorial Board. Details of such action will be published in the journal of one of the three sponsoring agencies and an announcement made in the journals of the other two. The advantage of the above procedure is that each technique has been repeated a great many times and its operation quite well understood before consideration as a standard. A disadvantage is that a great deal of time must elapse before a really new technique is accepted on a wide-spread basis.

The ASTM Standards Part 31, Water; Atmospheric Analysis (1975) includes water sampling and analytical methods, corrosivity test and methods of reporting. These standards, which are revised annually, represent a background of wide technical experience and analytical ability. The standards are used extensively in the examination of industrial waters and waste waters.

The EPA is responsible for the analytical procedures for measuring water quality. Methods for Chemical Analysis of Water and Waste 1974 (Ref. 15) lists several criteria for choosing the analytical procedures to be followed by the EPA Water Quality Office (WQO) laboratories:

"(1) The method should measure the desired constitutent with precision and accuracy sufficient to meet the data needs of WQO in the presence of the interferences normally encountered in polluted waters.

"(2) The procedures should utilize the equipment and skills normally available in the typical water pollution control laboratory.

"(3) The selected methods are in use in many laboratories or have been sufficiently tested to establish their validity.

"(4) The methods should be sufficiently rapid to permit routine use for the examination of a large number of samples."

EPA is to be commended for its emphasis that "instrumental methods have been selected in preference to wet chemical procedures because of the improved speed, precision and accuracy."

The U. S. Geological Survey has prepared a series of manuals on techniques for water-quality investigations. The material is divided into subject headings called books and subdivided into sections and chapters. Section A of Book 5 deals with water analysis. Chapter 1 is entitled, "Methods for Collection and Analysis of Water Samples for Dissolved Minerals and Gases," (Ref. 25). The manual contains methods used by the Survey to collect, preserve, and analyze water samples for their content of dissolved minerals and gases. Also discussed are laboratory equipment and instrumental techniques, accuracy and precision of analysis, and methods of reporting results. Seventy-six analytical procedures are given for determining 55 water properties. The instrumental methods include atomic absorption for 19 metals and the ion-specific electrode method for fluoride. Chapter 3 is "Methods for Analysis of Organic Substances in Water." (Ref. 26).

In summary, current knowledge about pollutants and their sources ranges from comprehensive reports on many of the pollutants to sparse or nonexistent information on other potential ones. Likewise, analysis techniques are well established for many of the pollutants; yet for several others the techniques are still in various stages of development, and commercially available instruments do not

exist. In addition to the references mentioned above, Refs. 1, 4, 6, 9 and 26-30 offer very useful information on water analysis and techniques.

3. Water-Monitoring Instrumentation

The use of automated water-monitoring instrumentation is increasing and in many areas it is replacing manual analytical techniques. The shift toward automated methods results from 1) the need to record data continuously, 2) the availability of data processing equipment to provide more rapid analysis of samples, 3) the accuracy provided by well-calibrated equipment, 4) the ease of determining results from well-designed instrumentation and 5) the potential for lower manpower requirements. Instruments are usually designed with field or laboratory service in mind; both types of equipment are included in this Survey and are treated separately.

When designing a system for a specific monitoring problem, several factors must be considered. At the core of such a system is an instrument or technique for analysis of the constituent of concern. Constituents and the instrumental techniques used for their detection are listed in Table 6. This list places emphasis on instruments and analyzers and does not attempt to list all of the several hundred manual methods of analysis. The number of analytical techniques is certainly not complete; however, the table should give an indication of the complexity and magnitude of the monitoring problem. It must be emphasized that the analytical instrument or technique alone does not complete the monitoring system.

Systems used for measuring water parameters may include the following steps (but not necessarily always in this order):

1. Sampling - including taking of the actual sample and sample preservation (or placing of a continuous monitor).
2. Sample pretreatment or preconcentration - including pollutant separation, premeasurement chemical reaction(s) and concentration adjustments.
3. Calibration
4. Pollutant or parameter measurement.
5. Data acquisition and reduction.

General techniques for performing steps 3 and 5 are described at the end of the introduction to this volume. A section on sampling is still in preparation. Calibration and data aquisition are also discussed individually where they affect the performance of that instrument. Instrumentation discussed in this Survey is divided into three classes according to the steps required for final measurement: (a) Continuous-Sensor-type instruments which follow steps 4 and 5 (b) Batch-Sampling type instruments which follow the sequence 1, 3, 4 and 5, and (c) Laboratory Analysis Instrumentation which follows the entire sequence 1 through 5.

a. Continuous-Sensor Type Instruments measure a constituent or parameter on an uninterrupted basis. Instruments in this class may be further subdivided into 1) those which do not require pretreatment of the sample (e.g. the addition of reagents), and 2) those normally employing pretreatment, such as added pH buffers and decomplexing agents for ion-specific electrodes. Water-quality parameters of the first category measured include pH, temperature, turbidity, conductivity, and dissolved oxygen and residual chlorine. An example of sensors in the second category are ion-selective electrodes for monitoring of some anions.

b. Batch-Sampling Type Instruments measure a constituent or parameter on an interrupted or intermittent sampled basis; the analysis is then performed on this discrete sample. Instruments in this class may be further subdivided into 1) those which are operated manually and 2) automated devices. A number of systems with multiparameter capabilities fall into this latter category. These include monitors for such diverse pollutants as Cu, cyanide, Cr, phenol and residual chlorine and parameters including pH, and conductivity. Systems are also available for measuring one pollutant at a time.

c. Laboratory Analysis Instrumentation ordinarily operates in the laboratory due to the constraints imposed by the need for operator intervention, operational environments, fragility or high maintenance requirements. Instruments in this category include Gas Chromatographs/Mass Spectrometers, Atomic Absorption Spectrometers, X-Ray Fluorescence Analyzers, Emission Spectrometers and neutron-Activation Analyzers.

Of primary concern are the realiability, durability, and ruggedness of a complete monitoring system. These nebulous qualities, which are more desirable than extremely high accuracy and other quantitative characteristics, determine the required degree of inspection, maintenance, and repair. This is especially important in on-site monitoring in which the operating conditions may be quite hostile. Depending upon the desired frequency of data, available manpower, and accessibility, one might also appreciate the capability of unattended operation for extended periods.

Table 6. Instrumental Techniques for Water Monitoring

METALS (all forms)	
All Metals Listed Herein:	Atomic Absorption Spectrophotometry Emission Spectrometry Molecular Absorption Spectrophotometry (except Ca, Na, Ti)
Aluminum:	Spark Source Mass Spectrometry
Antimony:	
Arsenic:	
Barium:	
Beryllium:	
Boron:	Direct Reading Emission Spectrometry Potentiometric
Cadmium:	Atomic Fluorescence Electrochemical
Calcium:	Atomic (Flame) Emission Spark Source Mass Spectrometry X-Ray Fluorescence
Chromium:	Chemiluminescence Electrochemical Spark Source Mass Spectrometry X-Ray Fluorescnece
Cobalt:	
Copper:	Atomic Fluorescence Electrochemical Spark Source Mass Spectrometry X-Ray Fluorescence
Gold:	
Iridium:	
Iron:	Atomic Fluorescence Chemiluminescence Spark Source Mass Spectrometry
Lead:	Electrochemical Spark Source Mass Spectrometry X-Ray Fluorescence
Magnesium:	Spark Source Mass Spectrometry
Manganese:	Direct Reading Emission Spectrometry Spark Source Mass Spectrometry
Mercury:	Atomic Fluorescence Neutron Activation X-Ray Fluorescence
Molybdenium:	
Nickel:	Polarographic Spark Source Mass Spectrometry X-Ray Fluorescence
Osmium:	
Palladium:	
Platinum:	
Potassium:	Atomic (Flame) Emission Ion Selective Electrode Spark Source Mass Spectrometry X-Ray Fluorescence
Rhodium:	
Ruthemium:	
Selenium:	Molecular Fluorescence
Silicon:	
Silver:	X-Ray Fluorescence
Sodium:	Atomic (Flame) Emission Ion Selective Electrode Spark Source Mass Spectrometry
Strontium:	Atomic (Flame) Emission
Thallium:	Electrochemical Techniques
Tin:	

METALS (Continued)

Titanium:	Spark Source Mass Spectrometry X-Ray Fluorescence
Vanadium:	Neutron Activation Spark Source Mass Spectrometry
Zinc:	Atomic Fluorescence Electrochemical Spark Source Mass Spectrometry X-Ray Fluorescence

HALIDES AND CYANIDE

Fluoride:	Ion Selective Electrode Molecular Absorption (Coloroimetric) Potentiometric (Ag-AgCl Electrode)
Bromide:	Molecular Absorption (Colorimetric)
Iodide:	Ion Selective Electrode Molecular Absorption (Colori-Metric)
Cyanide:	Ion Selective Electrode Molecular Absorption (Colorimetric)

NITROGEN, PHOSPHORUS, SULFUR

Ammonia:	Activation Analysis Automated Colorimetric Colorimetric Ion Selective Electrode
Nitrate:	Activation Analysis Automated Colorimetric Colorimetric UV Absorption
Nitrite:	Activation Analysis Automated Colorimetric Colorimetric Ion Selective Electrode
Organic Nitrogen:	Activation Analysis Automated Colorimetric Colorimetric
Total Nitrogen:	Activation Analysis Automated Colorimetric Colorimetric
Phosphate:	Automated Colorimetric Colorimetric (All Phosphorus) Continuous Colorimetric (Phosphate)
Sulfide:	Colorimetric Ion Selective Electrode
Sulfite:	Colorimetric

PHYSICAL AND CHEMICAL PARAMETERS

Conductivity:	Conductance Bridge
Hardness:	Automated Colorimetric Ion Selective Electrode
Salinity:	Conductance
pH:	Electrochemical
Alkalinity:	Automated Colorimetric Colorimetric Electrochemical
Acidity:	Colorimetric
Temperature:	Thermometer Thermistor Thermocouple
Turbidity:	Nephelometer Turbidimeter

BIOLOGICAL PARAMETERS

Biochemical Oxygen Demand (BOD):	DO Probe Respirometry/Manometric
Chemical Oxygen Demand (COD):	Colorimetric
Dissolved Oxygen (DO):	Membrane Probe
Total Organic Carbon:	Combustion Analyzer
Bacteria and Viruses:	Colony Counters Fluorescent Antibody Technique

DISSOLVED GASES

Chlorine:	Colorimetric Electrochemical
Hydrogen Sulfide:	Colorimetric Iodometric

PESTICIDES: INSECTICIDES, HERBICIDES, FUNGICIDES, TRACE TOXIC COMPOUNDS

Chlorinated Hydrocarbons:
- Gas Chromatography
- Gas Chromatography/Mass Spectrometry/Computer

PHENOLICS
- Gas Chromatography
- Gas Chromatography/Mass Spectrometry/Computer
- Thin-Layer Chromatography

OIL AND GREASE
- Atomic Absorption Spectrophotometry
- Gas Chromatography
- IR Spectrophotometry
- Reflectance
- Sensors
- Thin-Layer Chromatography
- UV Spectrophotometry

Versatility of the system is of concern if several pollutants are to be monitored. Multiparameter capability of major portions of a system can save considerable expenditure.

d. Automated Instruments. Instruments that operate automatically exhibit several advantages over manually operated instrumentation: There is less likelihood of random error in performing the analysis; large volumes of data are handled more efficiently, one obtains faster turnaround time in data reduction; and operating personnel may be released for other tasks. The disadvantages of automated instruments are that they are more time consuming to set up initially (the effort is usually not worthwhile unless at least 50 samples are analyzed in the same time span), the equipment is more complicated to maintain and the initial cost is considerably greater. At present, trade-offs favor automated instrumentation when a multiplicity of measurements of the same nature are to be performed, e.g. a number of batch samples analyzed as rapidly as possible or a single water-quality parameter measured continually.

Proper calibration of instrumentation systems is important; unreliable data are almost worse than no data at all. This is of special importance if real-time information is used in the decision making process, for example, immediate corrective action for downstream receiving waters. A section on calibration is now included at the end of the introduction of this volume. There follows a list of units generally considered acceptable in reporting results.

Units

m = meter	g = gram
cm = centimeter	mg = milligram
µm = micrometer	g = microgram
nm = nanometer	ng = nanogram
µl = liter	pg = picogram
ml = milliliter	ppb = parts per billion
µl = microliter	ppm = parts per million

M, molar solution = 1 gram molecular weight per liter (moles per liter)

N, normal solution = 1 gram equivalent weight per liter

n, molal solution = 1 gram molecular weight per 1000 g of water

Conversion Units (assuming one liter of water weighs one kg)

ppm = mg/l	g = 1000 mg
ppb = µg/l	mg = 1000 µg
mg/l = µg/ml	µg = 1000 ng
ppm = 1000 ppb	ng = 1000 pg

$m = 10^9$ nm

Some automatic environmental monitoring systems are capable of collecting data in computer compatible format. Data are recorded continuously at the monitoring site on punched paper tape or reusable magnetic tape. After an appropriate recording period tapes are transported to the computer center for analysis. An example is a Westinghouse system which can record water parameters such as flow, level, temperature, pH, DO and conductivity.

The use of an on-line computer to control data-acquisition activities is in its infancy in water monitoring. With the decreased cost of mini-computers and the availability of commercially available equipment to interface water monitors to computers, significant progress is being made.

Users of this Survey are invited to comment on and criticise its contents. These comments will hopefully help insure the accuracy and completeness of the Survey. Such information should be communicated to the Environmental Instrumentation Survey Group, Lawrence Berkeley Laboratory, Berkeley, CA 94720.

G. Explanation of Instrument Notes

In the following sections are the Instrument Notes for those instruments either commercially available or expected to become so shortly. For each group of pollutants or parameters, e.g. Metals, the notes are divided into two sections: Field Monitors (for water-

monitoring at streams, reservoirs, estuaries, etc.) and Laboratory Monitors. The descriptor in the upper right-hand corner identifies the type of use. Some instruments fall into both types of use. The notes are arranged alphabetically by manufacturer and each model has been assigned a number. The reader is referred to the Indexing Method for an understanding of descriptors in the upper right-hand corner of the notes, and to the Glossary for an understanding of the terms used in the Instrument Notes. The Table of Instruments in each group summarizes the information contained in the Instrument Notes and may serve as a preliminary guide.

The manufacturer's specifications are shown if available, and we gratefully acknowledge those manufacturers who have assisted in the compilation of their notes. Specifications and comments reported by independent workers are also shown and are footnoted and referenced. All information not footnoted has been supplied by the manufacturer, either from brochures and manuals or by private communication. If no information is given for a particular specification for an instrument, there is none available.

The Instrument Notes should not be used as separate entities in themselves. The reader should first refer to the discussion sections preceding the Instrument Notes.

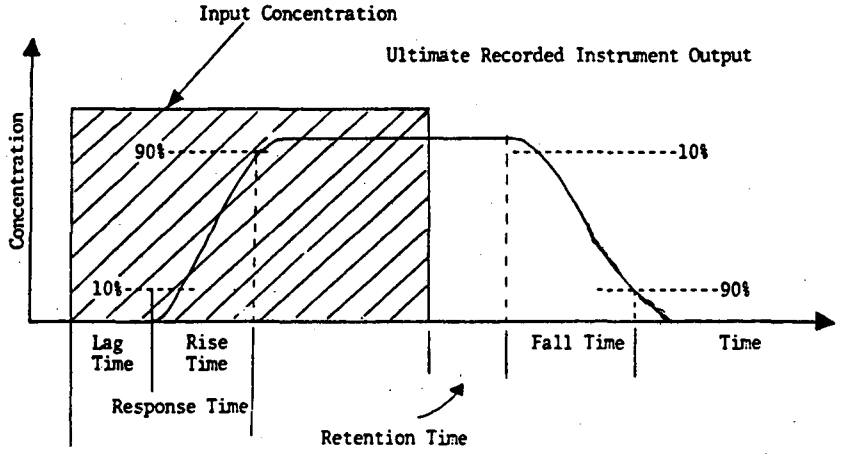
The technical information in these notes has been compiled from the best available sources and is believed to be correct and up-to-date. These notes will be continually updated, and additional information and comments are certainly solicited.

H. Glossary

1. Terms Related to Instrument Notes

Class	Continuous-Sensor Type Instruments measure a constituent or parameter on an uninterrupted basis. These instruments may be used in the field or laboratory. Batch-Sampling Type Instruments measure a constituent or parameter on an interrupted or discrete sampled basis; the analysis is then performed on this sample. These instruments are usually used in the laboratory, but may be used in the field. Laboratory Analysis Instrumentation ordinarily operates in the laboratory due to the constraints of operator intervention, operational environment, fragility or high maintenance requirements.
Type of Use	Field operation usually denotes the use of portable equipment capable of analysis under a wide range of environmental conditions. Laboratory operation usually denotes use of fixed equipment capable of analysis only under restricted environmental conditions, this may include mobile laboratories used in the field.
Minimum Detectable Sensitivity	(Detection Limit) Concentration that produces a reading equal to twice the standard deviation of a series of measurements near the blank level.
Range	The minimum and maximum measurement limits (the minimum limit is usually reported as 0 µg/l; this is somewhat misleading, and it would be better to report it as the true minimum measurement limit).
Interferences	Any substance or species which causes a deviation of instrument output from the value which would result from the presence of only the desired constituent under test. Appreciable interferences are those greater than 10%. Moderate interferences are those between 5% and 10%. Slight or no interferences are those less than 5%. Where the interference percent is: $\frac{(X) - (C)}{(I)} \times 100 = \%$ interference and (X) = total response due to constituent and interference (C) = response due to constituent under test (I) = concentration of interference The unit of response or concentration must be common to all parameters and should be indicated.
Multiparameter Capability	Ability to measure other constituents or parameters
Sampling	Specified either as continuous or batch
Accuracy	The correctness in comparison to an independent or reference method. Generally calibration of the instrument involves adjustment of the instrument output to the value determined by the independent or reference method.
Reproducibility	The precision of the measurements - the degree of agreement between repeated measurements of the same concentration.
Linearity	The maximum deviation between an actual instrument reading and the reading predicted by drawing a straight line between the upper and lower calibration points.

Noise	Spontaneous deviation from a mean output not caused by input concentration changes.
Lag Time	The time interval from a step change in the input concentration at the instrument inlet to the first corresponding change in the instrument output.
Rise Time	The time interval between the initial response and a 90% response (unless otherwise specified) after a step increase in the inlet concentration.
Retention Time	The time interval from a step decrease in the input concentration at the instrument inlet to the first corresponding change in the instrument output.
Response Time	The time interval from a step change in the input concentration at the instrument inlet to a reading of 90% (unless otherwise specified) of the ultimate recorded output. This measurement is the same as the sum of lag time and rise time.
Fall Time	The time interval between the initial response and a 90% response (unless otherwise specified) after a step decrease in the inlet concentration. This measurement is usually, but not necessarily, the same as the rise time.



Zero Drift	The charge with time in instrument output over a stated time period of unadjusted continuous operation when the input concentration is zero.
Span Drift	The change with time in instrument output over a stated time period of unadjusted continuous operation when the input concentration is a stated value other than zero.
References	Published or unpublished information pertaining to instrument specifications and performance characteristics.
Categories of Water	Applicability of the instrumentation to the analysis of a pollutant or parameter in Fresh, Waste, and/or Saline water samples.

2. Terms Related to Water Monitoring

The following are some terms related to water monitoring. Definitions have been altered in some cases from those found in the references.

Absent	The most sensitive analytical procedure in Standard Methods for the Examination of Water and Wastewater, 13th edition (or other approved procedure), does not show the presence of the subject constituent.
Acclimated	Adapted to environmental change.
Acclimated Organism(s)	Seed organism(s) especially grown to cope with bio-oxidation-resistant organic wastes.
Acidity	The quantitative capacity of aqueous solutions to react with hydroxyl ions. It is measured by titration with a standard solution of a base to a specified end point. Usually expressed as milligrams per liter of calcium carbonate; that is, the amount of calcium carbonate that would be required to exactly neutralize the sample. (Ref. 31)
Activated-Carbon Filter	A filter used to remove dissolved organic matter from water for taste and odor control. Dissolved gases, liquids and finely divided solids may also be removed.
Activated Sludge	A gelatinous matrix imbedded with filamentous and unicellular bacteria which serve as food for protozoa. The bacterial genera which predominate depend on the characteristics of the wastewater being treated. The activated sludge treatment of wastewater purification is one of the most common secondary waste treatment processes.
Aeration	The bringing about of intimate contact between air and water by methods including: (a) spraying water into the air over a collecting basin or, (b) causing water to flow over baffles. (Ref. 4)
Aerobic	In the presence of air (or oxygen); an aerobic organism requires oxygen for respiration.
Aerobic Bacteria	Bacteria that require free elemental oxygen for their growth. Their metabolic demands can severely deplete the dissolved oxygen. (Ref. 4)
Aerobic Organotrophy	Organism which utilizes organic materials under aerobic conditions for its growth.
Aerobic Oxidation	Decomposition of organic matter by aerobic organisms.
Algae	Simple plants, many microscopic, containing chlorophyll. Freshwater algae are diverse in shape, color, size, and habitat. They are the basic link in the conversion of inorganic constituents in water into organic constituents. (Ref. 4)
Algicide	A specific chemical highly toxic to algae. Algicides are often applied to water to control nuisance algal blooms.
Alkalinity	The capacity of water to neutralize acids, a property imparted by the water's content of carbonates, bicarbonates, hydroxides, and occasionally borates, silicates and phosphates. It is expressed in milligrams per liter of equivalent calcium carbonate. (Ref. 31)
Anabolic	Relating to the growth portion of the metabolic process; e.g., new cell formation
Anaerobic Bacteria	Bacteria that grow only in the absence of free elemental oxygen. (Ref. 31)
Anaerobic Organism	An organism that thrives in the absence of oxygen.

Anaerobic Stabilization	Decomposition of waste by an anaerobic microbic population in the continuous absence of oxygen.
Aquatic Biota	Animal and plant life, or fauna and flora, of a stream or other water. (Ref. 31)
Assimilation Capacity	The extent to which a body of water can receive wastes without significant deterioration of beneficial uses. Suitability for a given use is defined in terms of quality criteria, and these are still to some extent arbitrarily designated. The criterion most widely used is dissolved oxygen, although that parameter is by no means always relevant.
ATP (Adenosine Triphosphate)	A high energy biochemical intermediary in enzyme catalyzed processes.
Auto-Oxidation	A self-induced or internally catalyzed oxidation process.
Autotrophic Organism	An organism capable of constructing organic matter from inorganic substances. (Ref. 4)
Bacteria	A group of universally distributed, rigid, essentially unicellular microscopic organisms lacking chlorophyll. Bacteria usually appear as spheroid, rod-like, or curved entities, but occasionally appear as sheets, chains, or branched filaments. Bacteria are usually regarded as plants. Some bacteria are the primary nuisance-type growths in rivers, lakes, and ponds, where the growths they produce can clog fishing nets and create unsightly conditions. (See aerobic bacteria; anaerobic bacteria.) (Ref. 4 and 31)
Bacteriocide	A substance which kills bacteria.
Bacteriostat	A substance which inactivates bacteria.
Benthic Region	The bottom of a body of water. This region supports the benthos, a type of life that not only lives upon but contributes to the character of the bottom. (Ref. 4 and 31)
Benthos	Aquatic bottom-dwelling organisms. These include: (1) sessile animals, such as the sponges, barnacles, mussels, oysters, some of the worms, and many attached algae; (2) creeping forms, such as insects, snails, and certain clams; and (3) burrowing forms, which include most clams and worms.
Bioassay	(1) An assay method using a change in biological activity as a qualitative or quantitative means of analyzing a material's response to biological treatment. (2) A method of determining toxic effects of industrial wastes and other wastewaters by using viable organisms as test organisms. (Ref. 31)
Biochemical Oxygen Demand (BOD)	"The quantity of oxygen required, expressed in mg/ , for the biological and chemical oxidation of water-borne substances under conditions of test." (Ref. 3, 4, BOD) BOD represents oxygen utilized in energy reactions which support synthesis of organic material into new cell material. For a given organic substance BOD is the summation of oxygen utilization in energy reactions. (Ref. 42, BOD)
Biological Stabilization	Occurs when the initially available substrate has been utilized by the bacteria in a bio-system to produce relatively stable, oxidation-resistant cellular end products. At this point the BOD curve approaches zero slope (in the absence of nitrification).
Biologically Available	Utilizable as a nutrient by the biota in the environment.
Biomass	The weight of all life in a specified unit of environment or an expression of the total mass or weight of a given population, both plant and animal.
Biostat	A substance which inhibits the biological activity (growth) of bacteria.
Biota	All living organisms of a region. (Ref. 4)

Bloom	Large, readily visible masses of microscopic and macroscopic plant life, such as green algae, occurring in bodies of water. (Ref. 31)
BOD	See Biochemical Oxygen Demand.
BOD Exertion	Oxygen requirement of a bio-system; biochemical oxygen demand equivalent.
Brackish	Saline, unpalatable.
Brackish Water	Water having a mineral content in the general range between fresh water and seawater. Water containing from 1,000 to 10,000 mg/l of dissolved solids. (Ref. 31)
Carbonaceous Oxygen Demand (Carbonaceous OD)	Oxygen demand exerted by organic carbon compounds present; oxygen required to convert organic carbon to CO_2.
Carbonate Hardness	Hardness caused by the presence of carbonates and bicarbonates of calcium and magnesium in water. Such hardness may be removed to the limit of solubility by boiling the water. When the hardness in numerically greater than the sum of the carbonate alkalinity and the bicarbonate alkalinity, that amount of hardness which is equivalent to the total alkalinity is called carbonate hardness. See hardness. (Ref. 31)
Cell Stabilization	See Biological Stabilization.
Chemical Oxygen Demand (COD)	A measure of the oxygen-consuming capacity of inorganic and organic matter present in water or wastewater. It is expressed as the amount of oxygen consumed from a chemical oxidant in a specific test. It does not differentiate between stable and unstable organic matter and thus does not necessarily correlate with biochemical oxygen demand. Also known as OC and DOC, oxygen consumed and dichromate oxygen consumed, respectively. (Ref. 31)
Chlorine Demand	The difference between the amount of chlorine added to water or wastewater and the amount of residual chlorine remaining at the end of a specified contact period. (Ref. 31)
Chromogen	A reagent which produces a colored product.
Coenzyme	The non-protein moitié of an enzyme system.
Cold-Blooded Animals (Poikilothermic Animals)	Animals that lack a temperature regulating mechanism that offsets external temperature changes. Their temperature fluctuates to a large degree with that of their environment. Examples are fish, shellfish, and aquatic insects.
Coliform-Group Bacteria	A group of bacteria predominantly inhabiting the intestines of man or animal, but also occasionally found elsewhere. It includes all aerobic and facultative anaerobic, Gram-negative, non-spore-forming bacilli that ferment lactose with production of gas. Also included are all bacteria that produce a dark, purplish-green colony with metallic sheen by the membrane-filter techniques used for coliform identification. The two groups are not always identical, but they are generally of equal sanitary significance. (Ref. 31)
Colorimetry	See molecular absorption spectrophotometry.
Composite Sample	A combination of individual samples of water or wastewater taken at selected intervals, generally hourly for some specified period, to minimize the effect of the variability of the individual sample. Individual samples may have equal volume or may be proportioned to the flow at time of sampling. (Ref. 31)
Constituent	Organic or inorganic material, dissolved gas, debris or organisms present in fresh, saline or wastewater.
Contaminant	A potentially harmful pollutant or constituent.

Cotton Kier Liquors	Waste liquors from cotton processing.
Detection Limit	Concentration in mg/l that produces a reading equal to twice the standard deviation of a series of measurements near the blank level. See sensitivity.
Detritus	(1) The coarse cellular debris carried by wastewater. (2) The heavier mineral debris moved by natural watercourses, usually in bed-load form. (Ref. 31)
Dichromate Oxygen Consumed (DOC)	See COD.
Dissolved Oxygen (DO)	Oxygen present in solution in a chemically available form. In unpolluted water, oxygen is usually present in amounts of 10 μg/1 or less. Adequate dissolved oxygen is necessary for the life of fish and other aquatic organisms. About 3-5 μg/1 is the lowest limit for support of fish life over a long period of time. (Ref. 32)
Dissolved Solids (DS)	The total amount of dissolved material, organic and inorganic, contained in water or wastes. Excessive dissolved solids can make water unsuitable for industrial uses, unpalatable for drinking, and even cathartic . . . (Ref. 32) Also called Filterable Residue.
Diurnal Cycle	Daily variation in the photosynthesis-respiration pattern of aquatic flora resulting in a dissolved oxygen maximum during the day and a minimum at night -- usually just before dawn.
DPN (NAD)	Diphosphopyridine Nucleotide (nicotinamide adenine dinucleotide). A coenzyme necessary for the alcoholic fermentation of glucose.
Ecology	The science of the interrelations between living organisms and their environment.
Ecosystem	That set of ecological relationships resulting from a primary focus on an organism, group of organisms, or a portion of the earth's surface.
Effluent	(1) A liquid which flows out of a containing space. (2) Wastewater or other liquid, partially or completely treated, or in its natural state, flowing out of a reservoir, basin, treatment plant, or industrial treatment plant, or part thereof. (3) An outflowing branch of a main stream or lake. (Ref. 31)
Emergent Aquatic Plants	Plants that are rooted at the bottom but project above the water surface. Examples are cattails and bulrushes.
Endogenous	(Gr.) *endo* = within; *genesis* = growth. The growth of bacterial cultures eventually becomes *endogenous* as the result of environmental constraints imposed on the system (e.g., disappearance of nutrient substrate, enzymes, etc.).
Endogenous State	The state of continuous physiological activity in a stationary phase, which may eventually enter a declining phase.
Endpoint Filtrate COD	That point at which the filtrate COD has become constant (in the Mass Culture Aeration BOD method).
Energy Oxygen	Oxygen utilized by biota during their exponential growth phase for the synthesis of new cellular materials or biologically stable organic substances.
Environment	The sum of all external influences and conditions affecting the life and the development of an organism.

Enzyme	A class of complex proteinaceous substances produced by living cells and essential to life processes. They act similarly to catalysts in that they promote a variety of usually reversible cellular reactions (e.g., oxidation, hydrolysis) at cell temperature without themselves undergoing permanent change. Frequently the presence of activators such as metal ions or coenzymes is required for reaction to occur.
Epilimnion	That region of a body of water that extends from the surface to the thermocline and does not have a permanent temperature stratification.
Epiphyton	A non-parasitic secondary plant growth.
Estuary	Commonly an arm of the sea at the lower end of a river. Estuaries are often enclosed by land except at channel entrance points.
Eulittoral Zone	The shore zone of a body of water between the limits of water-level fluctuation.
Euphotic Zone	The lighted region that extends vertically from the water surface to the level at which photosynthesis fails to occur because of ineffective light penetration.
Eurytopic Organisms	Organisms with a wide range of tolerance to a particular environmental factor. Examples are sludgeworms and bloodworms.
Eutrophic Lake	Lake or other contained water body rich in nutrient. Characterized by a large quantity of planktonic algae, low water transparency with high dissolved oxygen in upper layer, zero dissolved oxygen in deep layers during summer months, and large organic deposits colored brown or black. Hydrogen sulfide often present in water and deposits. (Ref. 31)
Eutrophication	The normally slow aging process by which a lake evolves into marsh and ultimately becomes completely filled with detritus and disappears. In the course of this process the lake becomes overly rich in dissolved nutrients (for example, nitrogen and phosphorus), so that an excessive development of algae results. First the water becomes murky, then noxious odors and unsightly scums appear. In the lower layers dissolved oxygen levels become depressed, and bottom-dwelling fauna change from clean-water forms to pollution-tolerant forms. (Ref. 32)
Extractable Metals	The concentration of metals in an unfiltered sample following digestion with hot dilute mineral acid. (Ref. 15)
Facultative Aerobe	An organism that, although fundamentally an anaerobe, can grow in the presence of free oxygen.
Facultative Anaerobe	An organism that although fundamentally an aerobe can grow in the absence of free oxygen.
Fauna	The entire animal life of a region.
Filterable (Dissolved) Metals	Those metals which will pass through a 0.45 μm membrane filter. (Ref. 15)
Floating Aquatic Plants	Plants that wholly or in part float on the surface of the water. Examples are water lilies, water shields, and duckweeds.
Flora	The entire plant life of a region.
Formazan (Triphenyltetrazolium chloride)	A color indicator used in the quantitative estimation of oxidation-reduction equilibria involving hydrogen transfer.
F = SLR	Sludge loading ratio: Parameter used in activated sludge treatment systems to estimate imposed waste demand. It is expressed in BOD/day/lb MLVSS (Mixed liquor volatile suspended solids).

Fungi	Small non-chlorophyll-bearing plants which lack roots, stems, or leaves, which occur (among other places) in water, wastewater, or wastewater effluents and grow best in the absence of light. Their decomposition after death may cause disagreeable tastes and odors in water; in some wastewater treatment processes they are helpful and in others they are detrimental. (Ref. 31)
Fungicide	Substances or a mixture of substances intended to prevent, destroy, or mitigate any fungi. (Ref. 4)
Game Fish	Those species of fish considered to possess sporting qualities on fishing tackle. These fish may be classified as undesirable, depending on their usefulness. Examples of fresh water game fish are salmon, trout, grayling, black bass, muskellunge, walleye.
Gasometric	Pertaining to measurement of a gas parameter.
Grab Sample	A single sample of wastewater taken at neither set time nor flow. (Ref. 31)
Green Algae	Algae that have pigments similar in color to those of higher green plants. Common forms produce algal mats or floating "moss" in lakes.
Groundwater	Subsurface water occupying the saturation zone, from which wells and springs are fed. In a strict sense the term applies only to water below the water table. Also called phraetic water, plerotic water. (Ref. 31)
Hardness	A characteristic of water, imparted by salts of calcium, magnesium, and iron such as bicarbonates, carbonates, sulfates, chlorides and nitrates, that causes curdling of soap and increased consumption of soap, deposition of scale in boilers, damage in some industrial processes and sometimes objectionable taste. It may be determined by a standard laboratory procedure or computed from the amounts of calcium and magnesium as well as iron, aluminum, manganese, barium, strontium, and zinc, and is expressed as equivalent calcium carbonate. See carbonate hardness. (Ref. 31)
Herbicide	Substances or a mixture of substances intended to control or destroy any vegetation. (Ref. 4)
Herbivore	An organism that feeds on vegetation.
Heterotrophic Organisms	Organisms that are dependent on organic matter for food.
Higher Aquatic Plants	Flowering aquatic plants. (These are separately categorized as Emergent, Floating, and Submerged Aquatic Plants.)
Homeostatic Plateau	Point or place at which homeostasis occurs.
Homeostatis	(*homeo*: same; *stasis*: condition) Condition of equilibrium or stability.
Hydrology	The applied science concerned with the waters of the earth in all their states--their occurrence, distribution, and circulation through the unending hydrologic cycle of precipitation, consequent runoff, streamflow, infiltration, and storage, eventual evaporation, and reprecipitation. It is concerned with the physical, chemical, and physiological reactions of water with the rest of the earth and its relation to the life of the earth. (Ref. 31)
Hypereutrophy	Excessively enriched with nutrients. A hypereutrophic body of water may be inundated with algae, and is generally oxygen-deficient.
Hypolimnion	The region of a body of water that extends from the thermocline to the bottom of the lake and is removed from surface influence.
Immediate Dissolved Oxygen Demand (IDOD)	The OD of reduced forms of N, P, S, some metallic species and some easily oxidizable organic compounds (e.g., formaldehyde: CH_2O).
Invertebrates	Animals without backbones.

Isobestic Point	Wavelength at which the % transmission or optical density of a substance is independent of the isomeric form or oxidation state: a point of intersection for all spectral curves of the compound independent of the concentrations of its forms. For each pair of forms there will be one such isosbestic point.
Lethal Dose (LD)	A measured quantity administrated to test fish or animals. For direct feeding experiments or injections, the median toxic dosage is noted as LD_{50}, or the lethal dose for 50% of the animals. The time of observation may or may not be a criterion for single feedings or injections. (Ref. 1)
Life Cycle	The series of stages in the form and mode of life of an organism; i.e., the stages between successive recurrences of a certain primary stage such as the spore, fertilized egg, seed, or resting cell.
Limnetic Zone	The open-water region of a lake. This region supports plankton and fish as the principal plants and animals.
Limnology	The study of the physical, chemical, and biological aspects of inland waters.
Lithosphere	The outer part of the solid earth composed of rock essentially like that explored at the surface and believed to be about 50 miles in thickness.
Littoral Zone	The shoreward region of a body of water.
Macro-Organisms	Plants, animals, or fungal organisms visible to the unaided eye.
Median Lethal Dose (LD_{50})	The dose lethal to 50% of a group of test organisms for a specified period. The dose material may be ingested or injected.
Median Tolerance Limit (TL_m)	The concentration of the tested material in a suitable diluent (experimental water) at which just 50% of the test animals are able to survive for a specified period of exposure.
Membrane Filtration	A method of quantitative or qualitative analysis of bacterial or particulate matter in a water sample by filtration through a membrane capable of retaining bacteria. (Ref. 31)
Meromictic Lakes	Lakes in which dissolved substances create a gradient of density differences in depth, preventing complete mixing or circulation of the water.
Metabolizable	May be utilized by organisms in respiratory and/or growth processes.
Microorganism	Any minute organism invisible or barely visible to the unaided eye.
MLVSS	Mixed liquor volatile suspended solids.
Molecular Absorption Spectrometry (Colorimetry)	The measurement of color naturally present in samples or developed therein by the addition of reagents. (Ref. 31)
Mollusk (Mollusca)	A large animal group including those forms popularly called shellfish (but not including crustaceans). All have a soft unsegmented body protected in most instances by a calcareous shell. Examples are snails, mussels, clams, and oysters.
Moss	Any bryophytic plant characterized by small, leafy, often tufted stems bearing sex organs at the tips.
Motile	Exhibiting or capable of spontaneous movement.
Mycology	The study of fungi.
Nematoda	Unsegmented roundworms or threadworms. Some are free living in soil, fresh water, and salt water; some are found living in plant tissue; others live in animal tissue as parasites.
Nephelometer	An instrument for comparing turbidities of solutions by passing a beam of

light through a transparent tube and measuring the ratio of the intensity of the scattered light to that of the incident light. (Ref. 31)

Nitrification — Bacterial oxidation of ammonia and nitrites to nitrates.

Nutrients — Substances essential to bacterial growth and function. Chief among these are carbon, nitrogen, phosphorus, and sulfur, but a number of trace elements have been shown to be essential to growth (K, Ca, Mg, Fe, Mn, Zn, Co, Cu, and Mo). (Ref. 32)

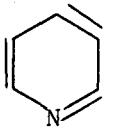
Nonfilterable (Suspended) Metals — Those metals which are retained by a 0.45 μm membrane filter. (Ref. 15)

Oceanography — The study of the physical, chemical, geological, and biological aspects of the sea.

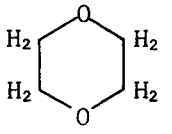
Oligotrophic Waters — Waters with a small supply of nutrients; thus, they support little organic production.

Organic Detritus — The particulate remains of disintegrated plants and animals. (Ref. 4)

Organic Heterocyclic Compounds — Organic ring structures containing atom(s) other than carbon (e.g., N, O, S) associated with the ring carbons. For example:



pyridine



1,4-dioxane

Osmole — The standard unit for expressing osmotic pressure. One osmole is the osmotic pressure exerted by a one-molar solution of an ideal solute.

Oxidation-Reduction Potential (ORP) — The emf developed by a platinum electrode immersed in water, referred to the Standard Hydrogen Electrode.

Oxygen Debt — A phenomenon that occurs in an organism when available oxygen is inadequate to supply the respiratory demand. During such a period the metabolic processes result in the accumulation of breakdown products that are not oxidized until sufficient oxygen becomes available.

Oxygen Tension — Partial pressure of oxygen in solution.

Partial Molal Free Energy — Free energy of a system expressed as the summation of component free energies:

$$dF = \left(\frac{\partial F}{\partial T}\right) dT + \left(\frac{\partial F}{\partial p}\right) dp + \Sigma\, \mu_i d_{n_i}$$

Pathogenic Bacteria — Bacteria inimical to man's welfare.

Pelagic Zone — The free-water region of a sea. (Pelagic refers to the sea, limnetic refers to bodies of fresh water.

Periphyton — The association of aquatic organisms attached or clinging to stems and leaves of rooted plants or other surfaces projecting above the bottom

Pesticide — Substances or a mixture of substances intended to prevent, destroy or repel plant or animal pests. (Ref. 31)

Photometer — An instrument that measures the intensity of light or the degree of light absorption. (Ref. 31)

Photosynthesis — The process by which simple sugars and starches are produced from carbon

	dioxide and water by living plant cells, with the aid of chlorophyll and in the presence of light.
Phototrophism	Movement in response to a light gradient; for example, a movement towards light is *positive* phototrophism.
Phytoplankton	Plant plankton that live unattached in water.
Piscicide	Substances or a mixture of substances intended to destroy or control fish populations
Plankton (Plankter)	Aquatic organisms of relatively small size mostly microscopic, that have either relatively small powers of locomotion or that drift in the water with waves, currents, and other water motion.
Poising Index	The increment of oxidizing agent (in equivalents/ℓ) divided by the incremental change in Eh. A measure of the electrical stability of a system subjected to ORP measurement.
Polarography	Automatic electroanalysis of a solution, usually by means of the dropping mercury electrode, by measuring current flow with voltage changes. (Ref. 31)
Pollutant	The term "pollutant" refers to any matter discharged into a body of water, or entering it from the air or soil, which is not normally a component of that particular ecosystem. The pollutant in question may, or may not, result in immediately obvious deleterious changes in the aquasystem.
Pollution	". . . the accidental or intentional discharge, directly or indirectly, of any liquid, gaseous, thermal and/or solid substance into water. These added pollutants may constitute a nuisance or be actually injurious to the health and well-being of man, animals, birds, and aquatic life forms such as fish and plants." (Ref. 72a, BOD)
Pollution (of Water)	Contamination or other alteration of the physical, chemical, or biological properties of water, including changes in temperature, taste, color, or odor of the water, or the discharge into the water of any liquid, gaseous radioactive, solid, or other substance that may create a nuisance or render such water detrimental or injurious to public health, safety, or welfare. Broadly, pollution means any change in water quality that impairs it for the subsequent user. (Ref. 32)
Pool Zone	The deep-water area of a stream, where the velocity of current is reduced. The reduced velocity provides a favorable habitat for plankton. Silt and other loose materials that settle to the bottom of this zone are favorable for burrowing forms of benthos.
Porifera	See Sponges.
Potable Water	Water that does not contain objectional pollution, contamination, minerals, or infective agents and is considered satisfactory for domestic consumption. (Ref. 31)
Potassium Dichromate ($K_2Cr_2O_7$)	Oxidizing agent commonly used in the determination of *Chemical Oxygen Demand (COD)*. In acid solution this salt is reduced from Cr^{+6} to the Cr^{+3} valence state in the presence of organic and/or inorganic reducing agents. The color change from yellow (Cr^{+6}) to green (Cr^{+3}) forms the basis of a spectrophotometric analytical method of COD determination.
Potassium Permanganate ($KMnO_4$)	Oxidizing agent formerly employed in COD analyses. In this country it has been largely superseded by the (silver catalyzed) dichromate procedure.

Precision	(1) Relative or apparent nearness to the truth. In physical measurements, it should not be confused with accuracy, which denotes absolute nearness to the truth. (2) In analytical chemistry, a measure of the reproducibility of a method when repeated on a homogeneous sample, regardless of whether the observed values are widely displaced from the true value as a result of systematic or constant errors present throughout the measurements. It may be expressed in terms of the standard deviation. (Ref. 2 and 31)
Producers	Organisms, for example, plants, that synthesize their own organic substances from inorganic substances.
Production (Productivity)	A time-rate unit of the total amount of organism grown.
Profundal Zone	The deep and bottom-water area beyond the depth of effective light penetration. All of the lake floor beneath the hypolimnion.
Protozoa	Organism consisting either of a single cell or of aggregates of cells, each of which performs all the essential functions in life. They are mostly microscopic in size and largely aquatic
Rapids Zone	The shallow-water area of a stream, where velocity of current is great enough to keep the bottom clear of silt and other loose materials, thus providing a firm bottom. This zone is occupied largely by specialized benthic or periphytic organisms that are firmly attached to or cling to a firm substrate.
Receiving Waters	The bodies of water that receive effluent wastewater from treatment plants.
Red Tide	A visible red-to-orange coloration of an area of the sea caused by the presence of a bloom of certain "armored" flagellates.
Redd	A type of fish-spawning area associated with running water and clean gravel. Fish moving upstream sequentially dig a pocket, deposit and fertilize eggs and then cover the spawn with gravel from the next upstream pocket. Fishes that utilize this type of spawning area include some trouts, salmons, and minnows.
Reducers	Organisms that digest food outside the cell wall by means of enzymes secreted for this purpose. Soluble food is then absorbed into the cell and reduced to a mineral condition. Examples are fungi, bacteria, protozoa, and nonpigmented algae.
Rheotropism	Movement in response to the stimulus of a current gradient in water.
Riffle	A section of a stream in which the water is usually shallower and the current of greater velocity than in the connecting pools; a riffle is smaller than a rapid and shallower than a chute.
Rotifers (Rotatoria)	Microscopic aquatic animals, primarily free-living, fresh water forms that occur in a variety of habitats. Approximately 75% of the known species occur in the littoral zone of lakes and ponds. The more dense populations are associated with the presence of submerged aquatic vegetation. Most forms ingest fine organic detritus for food, whereas others are predaceous.
Saline Water	Water containing dissolved salts -- usually from 10,000 to 33,000 mg/1. (Ref. 31)
Salinity	The weight in vacuo of solids which can be obtained when all organic matter has been oxidized, all bromides and iodides have been replaced by chlorides, all carbonates converted to oxides and the residue has been dried to constant weight at 480° C with appropriate correction for loss of volatile halide during drying.
Scavenger	An organism that feeds upon decomposing organic matter.

Scuds (Amphipods)	Macroscopic aquatic crustaceans that are laterally compressed. Most are marine and estuarine. Dense populations are associated with aquatic vegetation. Great numbers are consumed by fish.
Secchi Disc	A device used to measure visibility depths in water. The upper surface of a circular metal plate, 20 centimeters in diameter, is divided into four quadrants and so painted that two quadrants directly opposite each other are black and the intervening ones white. When suspended to various depths of water by means of a graduated line, its point of disappearance indicates the limit of visibility.
Sediment	(1) Solid material settled from suspension in a liquid. (2) Mineral or organic solid material that is being transported or has been moved from its site of origin by air, water, or ice and has come to rest on the earth's surface either above or below sea level. (3) Inorganic or organic particles originating from weathering, chemical precipitation, or biological activity. (Ref. 31)
Seed	Viable organisms, usually obtained from settled sewage, and known to be effective in promoting oxidation of organics. Seeding is generally carried out prior to the BOD measurement of effluents containing bio-inhibitors.
Self Purification	(a) The partial or complete restoration by natural processes, of a stream's pristine condition following the introduction of foreign matter sufficient in quality and quantity to cause a measurable change in physical, chemical and/or biological characteristics. Lee defined self-purification in terms of reactions producing "transformations that result in the production of a chemical compound that has a less deleterious effect on water quality than the parent compound." He divided reactions into 8 types: acid-base, precipitation, gas transfer, complex formation, oxidation-reduction, photochemical reactions, sorption, and biochemical reactions. (Ref. 39, vol. 1, chapter 4, BOD) (b) Process whereby a stream rids itself of impurities, generally forfeiting DO.
Sensitivity	Concentration in mg/l that produces a reading of 1%. The term is used often in metals analysis. See detection limit. (Ref. 15)
Sessile Organisms	Organisms that sit directly on a base without support, attached or merely resting unattached on a substrate.
Shellfish Poison (Mussel Poison)	A poison present in shellfish that have fed upon certain small marine phytoplankters in which the toxic principles exist. The shellfish concentrates the poison without harmful effects to itself, but man is poisoned through consumption of the toxic flesh.
Sludge	(1) The accumulated solids separated from liquids, such as water or wastewater, during processing, or deposits on bottoms of streams or other bodies of water. (2) The precipitate resulting from chemical treatment, coagulation, or sedimentation of water or wastewater. (Ref. 31)
Sludge Bulking	Flocculation: problem which arises in the Activated Sludge (AS) treatment of wastes.
Sludge Loading Ratio (SLR)	Parameter used in AS treatment systems. It is expressed in lbs BOD/day/lb MLVSS.
Specific Conductance (of Water)	Measure of a water's capacity to convey an electric current. This property is related to the total concentration of the ionized substances in the water and the temperature of the water. Most inorganic acids, which dissociate readily in aqueous solution, will conduct an electric current well, while organic compounds (such as sucrose and benzene), which do not dissociate in aqueous solution, will conduct a current poorly if at all. (Ref. 32)

Spectrophotometry	Quantitative measurement with a photometer of the quantity of light of any specific wavelength absorbed by a colored solution or emitted by a sample excited by a flame, arc, or spark. (Ref. 31)
Sphaerotilus	(a) A genus of bacteria having filaments that exhibit false branching, and reproducing by both conidia and swarmers. (b) A slime-producing, nonmotile, sheathed, filamentous, attached bacterium. Great masses are often broken from their "holdfasts" by currents and are carried floating downstream in gelatinous flocks.
Sponges (Porifera)	One of the sessile animals that fasten to piers, pilings, shells, rocks, etc. Most live in the sea.
Spore	The reproductive cell of a protozoan, fungus, alga, or bryophyte. In bacteria, spores are specialized resting cells.
Spring Overturn	A physical phenomenon that may take place in a body of water during the early spring. The sequence of events leading to spring overturn include: (1) melting of ice cover, (2) warming of surface waters, (3) density change in surface waters producing convection currents from top to bottom, (4) circulation of the total water volume by wind action, and (5) vertical temperature equality. The overturn results in a uniformity of the physical and chemical properties of the water.
SS	Suspended solids.
Stabilization Oxygen Demand	Oxygen consumed in energy reactions through the point where death of microorganisms is essentially complete and only relatively stable organic end products remain
Standing Crop	The biota present in an environment on a selected date.
Stenotopic Organisms	Organisms with a narrow range of tolerance for a particular environmental factor. Examples are trout, stonefly nymphs, etc.
STOD	Short Term Oxygen Demand.
STP	Standard temperature & pressure (0° C, 760 mm).
Sublittoral Zone	The part of the shore from the lowest water level to the lower boundary of plant growth.
Submerged Aquatic Plant	A plant that is continuously submerged beneath the surface of the water. Examples are the pondweed and coontail.
Surface Water	(1) All water on the surface, as distinguished from ground water. (2) Water appearing on the surface in a diffused state, with no permanent source of supply or regular course for any considerable time, as distinguished from water appearing in watercourses, lakes, or ponds. (Ref. 31)
Suspended Solids	Solids suspended in waste water. The amount of suspended solids is a measure of the strength of sewage. (Ref. 32)
Swimbladder	An internal, membranous, gas-filled organ of many fishes. It may function as a hydrostatic or sense organ, or as part of the respiratory system.
Swimmers' Itch	A rash produced on bathers by a parasitic flatworm in the cercarial stage of its life cycle. The organism is killed by the human body as soon as it penetrates the skin; however, the rash may persist for a period of about 2 weeks.
Symbiosis	Two organisms of different species living together, one or both of which may benefit and neither is harmed.

Systematics	The science of organism classification.
TBOD	Total Biological Oxygen Demand
Thermocline	That layer in a body of water where the temperature difference is greatest per unit depth. It is the layer in which the drop in temperature equals or exceeds 1° C (1.8° F) per meter (39.37 inches).
TL_m	See Median Tolerance Limit.
TOD	Total Oxygen Demand.
Tolerance Limit (TL)	Term used in designating a level of any measurable lethal agent, including physical parameters such as high and low temperatures, pH, and the like. As an example, a bioassay 96-hour TL_{50} of a toxic substance is that concentration in which 50% of the fish survive for 96 hours. TL_{50} is equivalent to the median tolerance limit (TL_m). (Ref. 2)
Tolerant Association	An association of organisms capable of withstanding adverse conditions within the habitat. It is usually characterized by a reduction in species (from a clean water association) and an increase in individuals representing a particular species.
Total Metals	The concentration of metals determined on an unfiltered sample following vigorous digestion or the sum of the concentrations of metals in both the filterable and nonfilterable fractions. (Ref. 15)
Toxic	Poisonous; deleterious to the survival of living organisms (see median tolerance limit).
Toxic Substance	A substance that either directly poisons living things or alters their environment so that they die. Examples are cyanides found in plating and steel mill wastes, phenols from coke and chemical operations, pesticides and herbicides, and some heavy metal salts. Another broad group includes oxygen-consuming substances that upset the balance of nature, such as organic matter from food plants, pulp and paper mills, chemical plants, and textile plants. Still another group are sulfides, produced by oil refineries, smelters, and chemical plants. (Ref. 32)
TPTZ	Triphenyltetrazolium chloride -- see Formazan.
Trickling Filter	Rock or gravel bed used in the treatment of sewage.
Trophogenic Region	The superficial layer of a lake in which organic synthesis from mineral substances occurs in the presence of light energy.
Tropholytic Region	The deep layer of a lake, where organic dissimilation predominates because of light deficiency.
Turbidimeter	An instrument for measurement of turbidity, in which a standard suspension usually is used for reference. (Ref. 31)
Turbidity	An empirical measure of the optical property of the particles of mud, clay, silt, finely divided organic matter, or microscopic organisms suspended in water that interfere with light transmission, causing the light to be scattered and absorbed rather than transmitted through the water in straight lines. (Ref. 32)
Ultimate Biochemical Oxygen Demand	The relatively stable end products from stabilization oxygen demand slowly continue to be degraded. The ultimate achievement of essentially complete oxidation to CO_2, water, and inorganic end products is termed the ultimate biochemical oxygen demand.
Ultimate Carbonaceous BOD	The maximum value attainable by complete oxidation of all organic constituents in the solution.
Vertebrate	Animals with backbones.

Virus	The smallest (10-300 mμ in diameter) form capable of producing infection and diseases in man or other large species. Occurring in a variety of shapes, viruses consist of a nucleic acid core surrounded by an outer shell (capsid) which consists of numerous protein subunits (capsomeres). Some of the larger viruses contain additional chemical substances. The true viruses are insensitive to antibiotics. They multiply only in living cells where they are assembled as complex macromolecules utilizing the cells' biochemical systems. They do not multiply by division as do intracellular bacteria. (Ref.31)
Virtually Absent	The subject constituent is present in very low concentrations, and is not objectionable in these barely detectable concentrations. (Ref. 4)
VSS	Volatile suspended solids.
Warm and Cold-Water Fish	Warm-water fish include black bass, sunfish, catfish, gar and others; whereas cold-water fish include salmon and trout, whitefish, miller's thumb, and blackfish. The temperature factor determining distribution is set by adaptation of the eggs to warm or cold water.
Wastewater	The spent water of a community. From the standpoint of source, it may be a combination of the liquid and water-carried wastes from residences, commercial buildings, industrial plants, and institutions, together with any groundwater, surface water, and storm water that may be present. In recent years, the word wastewater has taken precedence over the word sewage. (Ref. 31)
Water	(1) A transparent, odorless, tasteless liquid, a compound of hydrogen and oxygen, H_2O, freezing at 32° F or 0° C and boiling at 212° F or 100° C, which in more or less impure state, constitutes rain, oceans, lakes, rivers, and other such bodies; it contains 11.188 percent hydrogen and 88.812 percent oxygen, by weight. It may exist as a solid, liquid, or gas and, as normally found in the lithosphere, hydrosphere, and atmosphere, may have other solid, gaseous, or liquid materials in solution or suspension. (2) To wet, supply, or irrigate with water. (Ref. 31)
Waterfleas (Daphnia)	Mostly microscopic swimming crustaceans, often forming a major portion of the zooplankton population. The second antennae are very large and are used for swimming.
Water Quality	The chemical, physical, and biological characteristics of water with respect to its suitability for a particular purpose. The same water may be of good quality for one purpose or use, and bad for another, depending on its characteristics and the requirements for the particular use.
Zooglea	Bacteria embedded in a jellylike matrix formed as the result of metabolic activities.
Zooplankton	Protozoa and other animal microorganisms living unattached in water. These include small crustacea, such as daphnia and cyclops.

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INSTRUMENTATION
FOR ENVIRONMENTAL
MONITORING

APPENDIX A. CURRENTLY APPLICABLE WATER CRITERIA

This appendix relies on two references:

a. National Academy of Sciences/ National Academy of Engineers, report to the EPA, Water Quality Criteria, 1972, U. S. Environmental Protection Agency, Washington, D.C. 20460, EPA Report No. EPA-R3-033, March 1973. Hereafter, references to this report use the short form NAS and

b. U. S. Environmental Protection Agency, Quality Criteria for Water, July 1976, U. S. Environmental Protection Agency, Washington, D.C. 20460, 1976. Hereafter, references to this report use the short form EPA.

First in the Appendix is Table A-1 which includes the water criteria which are amenable to tabulation. If the criterion could not be tabulated, the space in the table has a ¶ reference to the textual material which appears at the end of the table. The criteria which appear as textual material are as they appear in the reports, verbatim. Changes which have been made are indicated by diacritical marks and have been made only to make table and page references conform with the appendix.

In three cases, Mixing Zones, ¶5, Plankton, ¶10, some of Radioactivity, ¶17, it has been necessary to include some of the textual material from the report, and in several cases, tables are referred to in the criteria. These have been taken verbatim (except where indicated with diacritical marks). We are grateful to the U.S. Environmental Protection Agency and the National Academy of Sciences for the use of these excellent texts.

Table A-1. Water Quality Criteria[a]

Water Quality Characteristic or Substance	General Surface Waters (Recreational Aesthetic Purpose)	Domestic (Public) Water Supplies	Freshwater Aquatic Life and Wildlife	Marine Aquatic Life Wildlife	Agriculture Uses	
					Livestock	Irrigation
	µg/ℓ unless noted	µg/ℓ unless noted	µg/ℓ unless noted	µg/ℓ unless noted	µg/ℓ unless noted	µg/ℓ unless noted
Physical Characteristics						
Aesthetic Qualities	¶ 1[b](1.1)		¶ 2[b]	¶ 2[b]		
Color	virtually free of color[b]	75 color units[b]				
Odor		essentially free from				
Temperature (and heat)	¶ 1 (1.2)	¶ 3 (3.1)	¶ 3 (3.2)[b] (WL-avoid changes in freezing pattern)	¶ 3[b] (3.2)		
Turbidity (clarity light penetration)	¶ 1 (1.2)		¶ 4[b]			
Total Suspended (settleable) solids	¶ 1 (1.3)		¶ 4[b](WL-minimized to support water fowl)			may improve soils
Mixing Zones	¶ 5[b](5.1)		¶ 5(5.2)			
Microbiological Characteristics	¶ 6					
Botulism						
Coliform Organisms (total)		20,000/100mml	¶ 7			
Fecal Coliform	¶ 8[b]	20,000/100ml	¶ 8[b]	¶ 8[b]		
Microorganisms (Microbial Pathogens)					keep livestock out of infected areas	¶ 9
Parasitic Organisms						
Plant Pathogens						
Plankton		¶ 10				
Toxic Algae					waters with blue green algae should be avoided	
Viruses		insufficient information				

Table A-1. Water Quality Criteria (continued)

Water Quality Characteristic or Substance	General Surface Waters (Recreational Aesthetic Purpose)	Domestic (Public) Water Supplies	Freshwater Aquatic Life and Wildlife	Marine Aquatic Life Wildlife	Agriculture Uses	
					Livestock	Irrigation
	µg/ℓ unless noted	µg/ℓ unless noted	µg/ℓ unless noted	µg/ℓ unless noted	µg/ℓ unless noted	µg/ℓ unless noted
Inorganic Chemicals (other than metals)						
Acidity			(WL-see bicarbonate)			
Alkalinity		no recommendation	20,000 (as $CaCO_3$, except where natural conc. is less[b]			
Ammonia		500	20[b] (WL-0.1×96 hr LC50)			
Bicarbonate			(WL-between 30,000-130,000 fluctuations < 50000)		depends on soil conditions	
Bromine (Bromide)				free-100, bromide 100,000		
Chlorine (chloride)		chloride: 250,000 (welfare)[b]	total resd. chlorine-2(salmonids), 10(others)[b]	total resd. chlorine 10[b]		
Cyanide			5[b]	5[b]		
Dissolved Gases (total)		no recommendation	<110% saturation valve[b]	<110% saturation value		
Dis. oxygen (DO)			minimum: 50,000 also 50,0000 in gravel (salmonids)	¶11		
Dis. carbon dioxide			¶12			
Florine (Floride)		floride: ¶13			2,000	1000[c]; 15,000[d]
Hardness		no recommendation	¶14(14.1)			

Table A-1. Water Quality Criteria (continued)

Water Quality Characteristic or Substance	General Surface Waters (Recreational Aesthetic Purpose)	Domestic (Public) Water Supplies	Freshwater Aquatic Life and Wildlife	Marine Aquatic Life Wildlife	Agriculture Uses	
					Livestock	Irrigation
	µg/ℓ unless noted	µg/ℓ unless noted	µg/ℓ unless noted	µg/ℓ unless noted	µg/ℓ unless noted	µg/ℓ unless noted
Nutrients	¶15					
Nitrates and Nitrites		10,000(as N-health)[b]			both - <100ppm, NO_2(N) <10ppm	Not necessary
Phosphates		no recommendation				
pH		5-9 (welfare)[b]	6.5-9.0[b](WL-7.0-9.2; plants)	6.5-8.5(not > 0.2 outside normal)[b]		4.5-9.0
Salinity						¶16
Sulfates		250,000 (welfare)[b]				
Sulfide (hydrogen sulfide)			H_2S: 2[b]	H_2S: 2[b]		
Total Dissolved Solids		see sulfates, chloride[b]	¶14(14.1)			¶14(14.2)
Metals	Same as for Domestic Water Supplies					
Aluminum	↓		careful exam. if Al^{n+} suspected	0.01×96 hr LC50	5000	5,000[c] 20,000[d]
Antimony				0.02×96 hr LC50		
Arsenic		50 (health)[b]		0.01×96 hr LC50	200	100[b]
Barium		1000 (health)[b]		0.05×96 hr LC50		
Beryllium			11 (soft water);[b] 1100 (hard water)[b]	0.01×96 hr LC50	insufficient data	100[c],500[a]
Bismuth				insufficient data		
Boron				<5000	5000	750 (long term, sensitive crops)

Table A-1. Water Quality Criteria (continued)

Water Quality Characteristic or Substance	General Surface Waters (Recreational Aesthetic Purpose)	Domestic (Public) Water Supplies	Freshwater Aquatic Life and Wildlife	Marine Aquatic Life Wildlife	Agriculture Uses	
					Livestock	Irrigation
	µg/ℓ unless noted	µg/ℓ unless noted	µg/ℓ unless noted	µg/ℓ unless noted	µg/ℓ unless noted	µg/ℓ unless noted
Cadmium	Same as for Domestic Water Supplies	10 (health)[b]	0.4 (soft), 1.2 (hard) salmonids, cladocerans;[b] 4.0 (soft, 12 (hard) others[b]	5.0[b]	50	10[c], 50[d]
Chromium		50 (health)[b]	100[b]	0.01×96 hr LC50	1000	100[c],1000[d]
Cobalt					1000	50[c],5000[d]
Copper		1000 (welfare)[b]		0.1×96 hr LC50	500	200[c],5000[d]
Iron		300 (welfare)[b]	1000[b]	<300	not necessary	5,000[c], 20,000[d]
Lead		50 (health)[b]	0.01× 6 hr LC50 (soluble lead) (WL: avoid lead shot)]	0.02×96 hr LC50 0.01×96 hr LC50, if 24 hr.aver. (WL: use non-toxic shot)	100	5,000[c] 10,000[d]
Lithium						2,500 (all soils), 25 (citrus crops)
Manganese		50 (welfare)[b]	0.1×96 hr LC50[b]	100 (mollusks)[b]		200[c],5000[d]
Mercury		2 (health)[b]	0.05[b]	0.1[b]	10	
Molybdenum				0.05×96 hr LC50	insufficient data	10 (all soils), 50 (short term use)
Nickel			0.01×96 hr LC50[b]	0.01×96 hr LC50[b]		200[c],2000[d]
Phosphorus				0.10 (yellow)[b]		

Table A-1. Water Quality Criteria (continued)

Water Quality Characteristic or Substance	General Surface Waters (Recreational Aesthetic Purpose)	Domestic (Public) Water Supplies	Freshwater Aquatic Life and Wildlife	Marine Aquatic Life Wildlife	Agriculture Uses	
					Livestock	Irrigation
	µg/ℓ unless noted	µg/ℓ unless noted	µg/ℓ unless noted	µg/ℓ unless noted	µg/ℓ unless noted	µg/ℓ unless noted
Selenium	Same as for Domestic Water Supplies	10 (health)[b]	0.01×96 hr LC50[b]	0.01×96 hr LC50[b]	50	20[c]
Silver		50 (health)[b]	0.01×96 hr LC50[b]	0.01×96 hr LC50[b]		
Sodium		no recommended limit				
Thallium				0.05×20 day, sub-lethal effects		
Tin						insuffi-
Titanium						cient data
Uranium (Uranyl Ion)		see taste, color gross α		0.01×96 hr LC50		
Vanadium				0.05×96 hr LC50		100[c],1000[d]
Zinc		5,000 (welfare)[b]	0.01×96 hr LC50[b]	0.01×96 hr LC50		2,000 (pH 6, continuous) 10,000 (neut.alk) soils
Radioactive Materials						
Gross α Gross β Radionuclides Iodine 131 Radium 226 Strontium-89,90		¶17(17.1)		¶17(17.2)	drinking water standards apply	drinking water standards apply

Table A-1. Water Quality Criteria (continued)

Water Quality Characteristic or Substance	General Surface Waters (Recreational Aesthetic Purpose)	Domestic (Public) Water Supplies	Freshwater Aquatic Life and Wildlife	Marine Aquatic Life Wildlife	Agriculture Uses	
					Livestock	Irrigation
	µg/ℓ unless noted	µg/ℓ unless noted	µg/ℓ unless noted	µg/ℓ unless noted	µg/ℓ unless noted	µg/ℓ unless noted
Organic Chemical (except Pesticides)						
Carbon Adsorbable Extract		¶18				
Detergents (Foaming Sub., Methylene Blue Active Substances, MBAs)	¶19 (Foaming Subst.)	MBA: 500	Detergents: 0.05×96 hr LC50			
Nitrilotriactate (NTA)		no recommendation (insufficient data)				
Oil and Grease	¶20[b]	virtually free[b]	¶20[b]	¶20[b]		
Phenols		1 (welfare)	1 (prevent tainting)[b]	1 (prevent tainting)		
Phthalate Esters		insufficient data	3[b]			
Polychlorinated Biphenyls		¶21	0.001[b] (¶21)	(WL: ¶22)		
Tainting Substances			¶23	¶23		
Toxic Organic				(WL: ¶24)		
Pesticides[e]						
Chlorinated Hydrocarbons						
Aldrin/Diedrin		¶21[b]	0.003[b]	0.003[b] (WL: ¶25)		
Chlordane		¶21[b]	0.01[b]	0.004[b] (WL: ¶26)		
DDT (DDD,DDE)		¶21	0.001[b] (WL: <1mg/kg wet wt.)	0.001[b] (WL: ¶27)		
Endrin		0.2 (health)[b]	0.004[b]	0.004[b] (WL: ¶25)		
Heptachlor (Heptachlor epoxide)		¶21[b]	0.001[b]	0.001[b] (WL: ¶25)		
Lindane		4.0 (health)[b]	0.01[b]	0.004[b] (WL: ¶26)		
		1000	0.03[b]	0.03[b] (WL: ¶26)		
		5 (health)[b]	0.005[b]	0.005[b] (WL: ¶26)		

Table A-1. Water Quality Criteria (continued)

Water Quality Characteristic or Substance	General Surface Waters (Recreational Aesthetic Purpose)	Domestic (Public) Water Supplies	Freshwater Aquatic Life and Wildlife	Marine Aquatic Life Wildlife	Agriculture Uses	
					Livestock	Irrigation
	µg/ℓ unless noted	µg/ℓ unless noted	µg/ℓ unless noted	µg/ℓ unless noted	µg/ℓ unless noted	µg/ℓ unless noted
Chlorophenoxy Herbicides						
2,4-D		100 (health)[b]				
2,4,5-T		2				
2,4,5-TP		10 (health)[b]				
Mirex		100 (health)[b]	0.001[b]	0.001[b] (WL: ¶ 26)		
Organic Phosphates, Carbamates		100 (total)				
Demeton			0.1[b]	0.1[b]		
Endosulfur			0.003[b]	0.001[b] (WL: ¶ 26)		
Guthion			0.01[b]	0.01[b]		
Malathion			0.01[b]	0.01[b]		
Parathion			0.04[b]	0.04[b]		
Other Pesticides			¶ 28	¶ 26		
Pesticide Residues						¶ 29
Sewage				¶ 30(30.1)	Public Water Criteria	¶ 30(30.2)
Toxic Wastes				¶ 31		

Footnotes for Table A-1.

[a]The Water Quality Criteria presented are largely from the National Academy of Sciences/National Academy of Engineers, Report for the U. S. Environmental Protection Agency, Water Quality Criteria, 1972. EPA Report-EPA.R3.033. March 1973, unless marked with a superscrit b.

[b]Water quality criteria marked with a superscript b are from the U. S. Environmental Protection Agency, Quality Criteria for Water, July 1976, U. S. EPA, Washington, D. C. 20460.

[c]Criteria marked with a superscript c, are for irrigation waters used continuously on all soils.

[d]Criteria marked with a superscript d are for irrigation waters for use on line textured soils of pH 60-8.5.

[e]The chemical formulations of the pesticides are (as reported in Ref. b):
Aldrin - 1,2,3,4,10,10-hexachloro-1,4,4a,5,8,8a-hexahydro-1,4,endo-5,8-exo-dimethanonaphthalene.
Dieldrin - 1,2,3,4,10,10-hexachloro-6,7-epoxy-1,4,4a,5,6,7,8,8a-octahydro-1,4-endo-5,8-exo-dimethanonapthalene
Chlordane - 1,2,4,5,6,7,8,8-octachloro-2,3,3a,4,7,7a-hexahydro-4,7-methanoindene
2,4-D - 2,4-dichlorophenoxyacetic acid
2,4,5-TP, silvex - 2,4,5-trichlorophenoxyproprionic acid.
DDT - 1,1,1-Trichloro-2,3-bis(p-chlorophenyl)ethane
Demeton - 0,0-Diethyl 0-2-(diethylthio)ethyl phosphorothiate. 0,0-diethyl S-2-(ethylthio)ethyl phosphorothiate
Endosulfan - 6,7,8,9,10-Hexachloro-1,5,5a,6,9,9a-hexahydro-6,9-methano-2,4,3-benzo-dioxathiepin 3-oxide
Endrin - 1,2,3,4,10,10-Hexachloro-6,7-epoxy-1,4,4a,5,6,7,8,8a-octahydro-1,4-endo-5,8-endo-dimethanonaphthalene
Guthion - 0.0-Dimethyl S-[4-oxo-1,2,3-benzo-triazin-3(4H)-ylmethyl]-phosphoroithioate
Heptachlor - 1,4,5,6,7,8,8-Heptachloro-3a,4,7,7a-tetrahydro-4,7-methanoindene
Lindane - Gamma isomer of 1,2,3,4,5,6-Hexachlorocyclohexane
Malathion - 0,0-Dimethyl S-(1,2-dicarbethoxyethyl)dithiophosphate
Methoxychlor - 1,1,1-Trichloro-2,2-bis(p-methoxyphenyl)ethane
Mirex - Dodecachlorooctahydro-1,3,4-metheno-2H-cyclobuto(cd)pentalene
Parathion - 0,0-Diethyl O-p-nitrophenyl phosphorothioate
Toxaphene - Mixture of various chlorinated camphenes (C_{10} H_{10} Cl_8)

¶1 AESTHETIC USES, PHYSICAL CHARACTERISTICS

1.1 Aesthetic Qualities (General Surface Waters)
1.2 Debris, Oil, Color, Odor, Taste, Turbidity (Aesthetic Uses)
1.3 Settleable and Suspended Solids (Aesthetic Uses)

1.1 Aesthetic Qualities (General Surface Waters)

CRITERIA

All waters free from substances attributable to wastewater of other discharges that:

(1) settle to form objectionable deposits;
(2) float as debris, scum, oil, or other matter to form nuisances;
(3) produce objectional color, odor, taste, or burbidity;
(4) injure or are toxic or produce adverse physiological responses in humans, animals or plants; and
(5) produce undesirable or nuisance aquatic life. EPA (Ref.1), p. 6

1.2 Debris, Oil, Color, Odor, Taste, Turbidity (Aesthetic Uses)

Recommendations

Surface waters will be aesthetically pleasing if they are virtually free of substances attributable to discharges or waste as follows:

- materials that will settle to form objectionable deposits;
- floating debris, oil, scum, and other matter;
- substances producing objectionable color, odor, taste, or turbidity;
- substances and conditions or combinations thereof in concentrations which produce undesirable aquatic life. NAS (Ref.2), p. 12.

1.3 Settleable and Suspended Solids (Aesthetic Uses)

Recommendation

Clear waters are normally preferred for recreation. Because sediment-laden water reduces water clarity, inhibits the growth of plants, displaces water volume as sediments settle, and contributes to the fouling of the bottom, prevention of unnatural quantities of suspended sediments or deposit of sediments is desirable. Individual waters vary in the natural amounts of suspended sediments they carry; therefore, no fixed recommendation can be made. Management decisions should be developed with reference to historical based line data concerning the individual body of water.
NAS, p.17

¶2 COLOR (Freshwater and Marine Aquatic Life)

CRITERION

Increased color (in combination with turbidity) should not reduce the depth of the compensation point for photosynthetic activity by more than 10 percent from the seasonally established norm for aquatic life.
EPA, p.51

¶3 TEMPERATURE

3.1 Temperature (Public Water Supplies)
3.2 Temperature (Freshwater and Marine Aquatic Life)

3.1 Temperature (Public Water Supplies)

Recommendation

No temperature change that detracts from the potability of public water supplies and no temperatures change that adversely affects the standard treatment process are suggested guidelines for temperature in public water supply sources.
NAS, p.89.

3.2 Temperature (Freshwater and Marine Aquatic Life)

CRITERIA

Freshwater Aquatic Life

For any time of year, there are two upper limiting temperatures for a location (based on the important sensitive species found there at that time):

1. One limit consists of a maximum temperature for short exposures that is time dependent and is given by the species-specific equation:

$$\text{Temperature } (°C) = 1/b[\log_{10}(\text{time in minutes}) - a] - 2$$

Where:

a = intercept on the "y" or logarithmic axis of the line fitted to experimental data which are available for some species from Appendix II-C, NAS, 1974.

b = slope of the line fitted to experimental data which are available for some species from Appendix II-C, NAS, 1974.

2. The second value is a limit on the weekly average temperature that:

a. in the cooler months (mid-October to mid-April in the north and December to February in the south) will protect against mortality of important species if the elevated plume temperature is suddenly dropped to the ambient temperature, with the limit being the acclimation temperature minus 2°C when the lower lethal threshold temperature equals the ambient water temperature (in some regions this limitation may also be applicable in summer); or

b. in the warmer months (April through October in the north and March through November in the south) is determined by adding to the physiological optimum temperature (usually for growth) a factor calculated as one-third of the difference between the ultimate upper incipient lethal temperature and the optimum temperature for the most sensitive important species (and appropriate life state) that normally is found at that location and time; or

c. during reproductive seasons (generally April through June and September through October in the north and March through May and October through November in the south) meets site-specific requirements for successful migration, spawning, egg incubation, fry rearing, and other reproductive functions of important species. These local requirements should supersede all other requirements when they are applicable; or

d. is a site-specific limit that is found necessary to preserve normal species diversity or prevent appearance of nuisance organisms.

Marine Aquatic Life

In order to assure protection of the characteristic indigenous marine community of a water body segment from adverse thermal effects:

1. the maximum acceptable increase in the weekly average temperature due to artificial sources is 1°C (18°F) during all seasons of the year, providing the summer maxima are not exceeded; and

2. daily temperature cycles characteristic of the water body segment should not be altered in either amplitude of frequency. Summer thermal maxima, which define the upper thermal limits for the communities of the discharge area, should be established on a site-specific basis. Existing studies suggest the regional limits expressed in Table [A-2]. Baseline thermal conditions should be measured at a site where there is no unnatural thermal addition from any source, which is in reasonable proximity to the thermal discharge (within 5 miles) and which has similar by hydrography to that of the receiving waters at the discharge.

EPA, pp.218-9

Table [A-2]

	Short term maximum	Maximum true daily mean *
Sub-tropical Regions (south of Cape Canaveral and Tampa Bay, Fla., and Hawaii)	32.2°C (90°F)	29.4°C (85°F)
Cape Hatteras, N.C., to Cape Canaveral, Fla.	32.2°C (90°F)	29.4°C (85°F)
Long Island (south shore) to Cape Hatteras, N.C.	30.6°C (87°F)	27.8°C (82°F)

*True daily mean = average of 24 hourly temperature readings.

¶4 TOTAL SUSPENDED AND SETTLEABLE SOLIDS, and TURBIDITY (Freshwater Aquatic Life)

CRITERION

Freshwater fish and other aquatic life:

Settleable and suspended solids should not reduce the depth of the compensation point for photosynthetic activity by more then 10 percent from the seasonally established norm for aquatic life.
EPA, p. 210

¶5 MIXING ZONES

5.1 Mixing Zones (General Surface Waters)
5.2 Mixing Zones (Freshwater Aquatic Life)

5.1 Mixing Zones (General Surface Waters)

Introduction

A mixing zone is an area contiguous to a discharge where receiving water quality may meet neither all quality criteria nor requirements otherwise applicable to the receiving water. It is obvious that any time an effluent is added to a receiving waterway, where the effluent is poorer in quality, there will be a zone of mixing. The mixing zone should be considered as a place where wastes and water mix and not as a place where effluents are treated.

Rationale

Because damage to the aquatic resource can occur when quality standards are violated, the permissible size of a mixing zone is dependent upon the acceptable amount of damage. The permissible size depends in part on the size of the particular receiving water; the larger the water body, the larger the mixing zone may be without violating quality standards in more that a given percentage of the total area or volume of the receiving water. Likewise, the greater number of mixing zones within a reach of river or within a water body, the smaller each must be in order to maintain an appropriate mixing zone to water body ratio. Future industrial and population growths must be considered in designating such areas for wastes' admixture.

As a guideline, the quality for life within a mixing zone should be such that the 96-hour LC_{50} for biota significant to the indigenous aquatic community is not exceeded; the mixing zone should be free from effluent substances that will settle to form objectionable deposits, free from effluent-associated materials that float to form unsightly masses, and free from effluent-associated substances that produce objectionable color, odor, or turbidity.

A prime purpose in designating the location, size, and area constraints of a mixing zone is to protect the aquatic life within the receiving waterway. Shallow water areas, generally, are the nursery areas for aquatic ecosystems. Designating offshore mixing areas or providing a larger available volume or area for mixing offshore as a viable alternative to a smaller shoreside area has a lesser potential for adverse biotic effects than a comparable discharge area in shallow water. Offshore, diffusion will tend to occur in all directions and not be constrained by a land barrier. Mixing zones may be less harmful biologically when located deep within the receiving water and, wherever possible, beneath the light-penetration area where photosynthesis occurs and algae and associated protozoa and other organisms provide the extensive base for the aquatic food web.

An axiom of environmental quality is that different areas vary in ecological importance. Generally the highest importance, and therefore the greatest protection, must be placed on shallow-water shoreline areas of rivers, lakes, and coastal zones and on the Nation's wetlands. These are commonly the areas that protect the young and supply the food not only for the animals that live in open waters but also for those animals that depend upon water in some measure for their existence. Likewise, one local aquatic area may have a higher social or ecological value than another, and the higher that value the greater the protection from degradation that is warranted within a waste mixing area.

Mixing zones should be located in such a manner that they do not form a barrier to the migratory routes of aquatic species. On a given reach of a stream or river, it would be good practice to limit the total mixing area to one-third of the receiving water width. In the same fashion, the combined areas of all mixing zones within a lake should not exceed 10 percent of the lake surface area. In some cases, this maximum should be reduced depending on lake volume and other local conditions. Within an estuary, the maximal dimension of the mixing area should not exceed 10 percent of the cross-sectional area of the waterway. It is not the objective of this rationale to outline limits for effluents, but to provide the reader with some of the general biological and physical considerations necessary for the establishment of mixing zones.

In essence, the positioning of mixing zones should be accomplished in a manner that will provide the greatest protection to aquatic life and for the various uses of water. Generally, shoreline and surface areas for waste admixture should be discouraged in preference to deep water, offshore designations. The relative social and ecological values of the aquatic life that may inhabit a particular waterway area should be given due consideration in zone definition (Fetterolf, 1973; NAS, 1974). The designation of particular mixing zones is a task that should follow the biological, physical, and chemical appraisal of the receiving waterway.

References Cited

Fetterolf, C. M., Jr. 1973. Mixing zone concepts: biological methods for the assessment of water quality, ASTM STP-528. American Society for Testing and Materials, pp. 31-45.

National Academy of Sciences, National Academy of Engineering, 1974. Water quality criteria, 1972. U.S. Government Printing Office, Washington, D.C. EPA, pp. 104-105.

5.2 Mixing Zones (Freshwater Aquatic Life)

Recommendation

Although water quality characteristics in mixing zones may differ from those in receiving systems, to protect uses in both regions it is recommended that mixing zones be free of substances attributable to discharges or wastes as follows:

- materials which form objectionable deposits;
- scum, oil and floating debris;
- substances producing objectionable color, odor, taste, or turbidity;
- conditions which produce objectionable growth of nuisance plants and animals.

General Physical Considerations - Recommendation

To avoid potential biological damage or interference with other uses of the receiving system it is recommended that mixing zone characteristics be defined on a case-by-case basis after determination that the assimilative capacity of the receiving system can safely accommodate the discharge taking into consideration the physical, chemical, and biological characteristics of the discharge and the receiving system, the life history and behavior of organisms in the receiving system, and desired uses of the waters.

General Biological Considerations - Recommendation

To protect populations of nonmobile benthic and sessile organisms in mixing zones it is recommended that the area of their habitat exposed to water quality poorer than recommended receiving system quality be minimized by discharge location and design or that intermittent time-exposure history relationships be defined for the organisms' well-being.

To protect drifting and both weak and strong swimming organisms in mixing zones it is recommended that scientifically valid data be developed to demonstrate that the organisms can survive without irreversible damage, the integrated time-exposure history to be based on maximum expected residence time so that deleterious effects on populations of important species do not occur.

Overlapping Mixing Zones - Recommendation

When two plumes are contiguous or overlap and synergistic effects do not occur, protection for aquatic life should be provided if the sum of the fractions of integrated time exposure effects for each plume total ≤ 0.5. Alternatively, protection should be provided if the sum of the fractions for both plumes (or more than two contiguous or overlapping plumes) is ≤ 1.

Proportional Relationship of Mixing Zones to Receiving Systems - Recommendation

It is recommended that the total area or volume of a receiving system assigned to mixing zones be limited to that which will: (1) not interfere with biological communities or populations of important species to a degree which is damaging to the ecosystem; (2) not diminish other beneficial uses disproportionately.

Zones of Passage

In river systems, reservoirs, lakes, estuaries, and coastal waters, zones of passage are continuous water routes of such volume, area, and quality as to allow passage of free-swimming and drifting organisms so that no significant effects are produced on their populations....

Recommendation

Because of varying local physical and chemical conditions and biological phenomena, no single-value recommendation can be made on the percentage of river width necessary to allow passage of critical free-swimming and drifting organisms so that negligible or no effects are produced on their populations. As a guideline no more than 2/3 the width of a

water-body should be devoted to mixing zones thus leaving at least 1/3 free as a zone of passage.
NAS, pp. 112-115

¶6 MICROBIOLOGICAL CHARACTERISTICS (Aesthetic and Recreational Uses)

The role of water quality in either limiting or augmenting the production of vector and nuisance organisms involves many interrelationships which are not clearly understood. Since organic wastes generally directly or indirectly increase biomass production there may be an attendant increase in vector or nuisance organisms. Some wastes favor their production by creating water quality or habit at conditions that limit their predators and competitors. Increased production of vector and nuisance organisms may degrade a healthy and desirable human environment and be accompanied by a lessening of recreational and aesthetic values.
NAS, p. 19.

¶7 BOTULISM (Freshwater Wildlife)

Recommendation

Outbreaks of botulism poisoning tend to be associated with, or affected by insect die-offs, water temperature above 70°F, fluctuatine water levels, and elevated concentrations of dissolved solids. Management of these factors may reduce outbreaks of botulism poisoning.
NAS, p. 197.

¶8 FECAL COLIFORM BACTERIA (Recreational Uses, Freshwater and Marine Aquatic Life)

CRITERIA

Bathing Waters

Based on a minimum of five samples taken over a 30-day period, the fecal coliform bacterial level should not exceed a log mean of 200 per 100 ml, nor should more than 10 percent of the total samples taken during any 30-day period exceed 400 per 100 ml.

Shellfish Harvesting Waters

The median fecal coliform bacterial concentration should not exceed 14 MPN per 100 ml with not more than 10 percent of samples exceeding 43 MPN per 100 ml for the taking of shellfish.
EPA, p. 42.

¶9 PLANT PATHOGENS (Agricultural Uses, Irrigation and Livestock Watering

Recommendation

Irrigation waters below the fecal coliform density of 1,000/100 ml should contain sufficiently low concentrations of pathogenic microorganisms that no hazards to animals or man result from their use or from consumption of raw crops irrigated with such waters.
NAS, p. 371

¶10 PLANKTON (Public Water Supplies)

The quality of public water supplies may be drastically affected by the presence of planktonic organisms. Plankton may be defined as a community of motile or nonmotile microscopic plants and animals that are suspended in water. The species diversity and density of the plankton community are important water quality characteristics that should be monitored in all public water supplies. Several methods for counting plankton as number of organisms per aliquot of sample rather than biomass. Since various species of algae are much larger than other species, plankton counts that simply enumerate cells, colonies, or filaments do not indicate accurately the true plankton content of the water (Standard Methods 1971).

Plankters are primarily important in public water supply sources for their contribution to taste and odor problems, pH alteration, or filter clogging. To aid operators in interpreting plankton data, the algae counted should be listed under applicable categories that show the predominance or absence of certain groups of organisms at any given time. The categories used should include green algae, blue-green algae, diatoms, flagellated forms, Protozoa, microcrustaceans and Rotifera, as well as related Protista.

Data from plankton counts can be very useful to water treatment operators (Silvey et al. 1972). Counts of blue-green algae which exceed 50 per cent of the total plankton community usually indicate potential taste and odor problems. So long as the green algae comprise 75 per cent of the total plankton count, it is not likely that serious taste and odor problems will arise. The diatom

population of the plankton community is also important. During some diatom blooms, the pH of the water increases enough to require the addition of more alum or iron than would normally be used to achieve the desired pH in the distribution system. Some blooms of planktonic green algae cause the pH of the water to rise from 7.6 to as high as 10. There are apparently no plankters that tend to reduce pH or remove minerals in sufficient quantities to alter conditions.

The role which plankton plays in the productivity of a lake or reservoir is important. The relationship between productivity and respiration may frequently be used as a pollution index. In many instances, plankton studies are more revealing than bacterial studies. A ratio of productivity to respiration amounting to one or more indicates that the algae are producing more oxygen than is being consumed by the bacteria. If the ratio drops below one for significant periods, an undesirable condition exists that may cause problems with anaerobic organisms.

¶11 DISSOLVED OXYGEN (Marine Aquatic Life)

Recommendation

Each proposed change in the dissolved oxygen concentration in estuaries and coastal waters should be reviewed for risk of damage to aquatic life. The limited laboratory data and field observations on marine organisms suggest that easily observed effects, which are in many cases deleterious, occur with dissolved oxygen concentrations of 4 to 5 mg/ℓ as daily minimum values for periods of several days. As a guideline, therefore, reduction of the dissolved oxygen concentration to values below 4 mg/l can be expected to change the kinds and abundances of the aquatic organisms in the affected volume of water and area of bottom. Particular attention should be directed toward identifying species with restricted spawning and nursery areas and conservatism should be used in applying guidelines to these areas. ...

NAS, p. 270

¶12 CARBON DIOXIDE (Freshwater Aquatic Life)

Recommendation

Concentrations of free carbon dioxide above 20 mg/ℓ occur rarely. Fish acclimatize to increases in carbon dioxide levels as high as 60 mg/ℓ with little effect. However, fish are able to detect and respond to slight gradients and many avoid free carbon dioxide levels as low as 1.0 to 6.0 mg/ℓ.

NAS, p. 139

¶13 FLUORIDE (Public Water Supplies)

Recommendation

Because of adverse physiological effects and because the defined treatment process does nothing to reduce excessive fluoride concentrations, it is recommended that the maximum levels shown in Table [A-3] not be exceeded in public water supply sources.

Table [A-3] Fluoride Recommendation

Annual average of maximum daily air temperatures[a] fahrenheit	Fluoride maximum [µg/1]
80-91	[1,400]
72-79	[1,600]
65-71	[1,800]
59-64	[2,000]
55-58	[2,200]
50-54	[2,400]

[a]Based on temperature data obtained for a minimum of five years.

NAS, p.66.

¶14 TOTAL DISSOLVED SOLIDS AND HARDNESS

14.1 Total Dissolved Solids and Hardness (Freshwater Aquatic Life)
14.2 Total Dissolved Solids (Agricultural Uses)

14.1 Total Dissolved Solids and Hardness (Freshwater Aquatic Life)

Recommendation

Total dissolved materials should not be changed to the extent that the biological communities characteristic of particular habitats are signficantly changed. When dissolved materials are altered, bioassays and field

studies can determine the limits that may be tolerated without endangering the structure and function of the aquatic ecosystem.
NAS, p. 143

14.2 Total Dissolved Solids (Agricultural Uses)

Recommendation

In spite of the facts that (1) any TDS limits used in classifying the salinity hazard of waters are somewhat arbitrary; (2) the hazard is related not only to the TDS but also to the individual ions involved; and (3) no exact hazard can be assessed unless the soil, crop, and acceptable yield reductions are known, Table [A-4] suggests classifications for general purposes for arid and semiarid regions.
NAS, p. 335.

Table [A-4]. Recommended Guidelines for Salinity in Irrigation Water

Classification	TDS mg/ℓ	EC mmhos/cm
Water for which no detrimental effects are usually noticed.....	500	0.75
Water that can have detrimental effects on sensitive crops.....	500-1,000	0.75-1.50
Water that can have adverse effects on many crops; requires careful management practices	1,000-2,000	1.50-3.00
Water that can be used for tolerant plants on permeable soils with careful management practices	2,000-5,000	3.00-7.50

¶15 NUTRIENTS (Recreational and Aesthetic Uses)

Recommendations

The principal recommendations for aesthetic and recreational uses of lakes, ponds, rivers, estuaries, and near-shore coastal waters are that these uses continue to be pleasing and undiminished by effects of cultural activities that increase plant nutrients. The trophic level and natural rate of eutrophication that exists, or would exist, in these waters in the absence of man's activities is considered the reference level and the commonly desirable level to be maintained. Such water should not have a demonstrable accelerated production of algae growth in excess of rates normally expected for the same type of waterbody in nature without man-made influences.

The concentrations of phosphorus and nitrogen mentioned in the text [of NAS pp.19-23] as leading to accelerated eutrophication were developed from studies for certain aquatic systems: maintenance of lower concentrations may or may not prevent eutrophic conditions. All the factors causing nuisance plant growths and the level of each which should not be exceeded are not known. However, nuisance growths will be limited if the addition of all wastes such as sewage, food processing, cannery, and industrial wastes containing nutrients, vitamins, trace elements, and growth stimulants are carefully controlled and nothing is added that causes a slow overall decrease of average dissolved oxygen concentration in the hypolimnion and an increase in the extent and duration of anaerobic conditions.
NAS, p. 23.

¶16 SALINITY (Agricultural Purposes, Irrigation)

Recommendation

Crops vary considerably in their tolerance to soil salinity in the root zone, and the factors affecting the soil solution and

crop tolerance are varied and complex. Therefore, no recommendation can be given for these. For specific crops, however, it is recommended that the salt tolerance values (EC_e) for a saturation extract established by the U. S. Salinity Laboratory Staff be used as a guide for production.

NAS, pp. 327-338.

¶17 RADIOACTIVITY

17.1 Radioactivity (Public Water Supplies)
17.2 Radioactivity (Marine Aquatic Life and Wildlife)

17.1 Radioactivity (Public Water Supplies)

The effects of radiation on human beings are viewed as harmful, and any unecessary exposure to radiation should be avoided. The U.S. Federal Radiation Council* (1961a) provided guidance for federal agencies to limit exposure of individuals to radiation from radiactive materials in the environment. The following statement by the U. S. Federal Radiation Council (1960) is considered especially pertinent in applying the recommendations of this report:

> There can be no single permissible or acceptable level of exposure without regard to the reason for permitting the exposure. It should be general practice to reduce exposure to radiation, and positive effort should be carried out to fulfill the sense of these recommendations. It is basic that exposure to radiation should result from a real determination of its necessity.

The U. S. Federal Radiation Council criteria (1960, 1961a) have been used in establishing the limits for radioactivity recommended here. It should be noted that these guidelines apply to normal peacetime operations. They are predicted upon three ranges of daily intake of radioactivity as seen in Table [A-5].

The recommended radionuclide intake derives from the sum of radioactivity from air, food, and water. Daily intakes were prescribed with the provision that dose rates be averaged over a period of one year. The range for specific radionuclides recommended by the U. S. Federal Radiation Council (1961a) are shown in the following tables: [Tables A-5, and A-6].

For each range, a measure of control was defined, which represented a graded scale of control procedures.

The U. S. Federal Radiation Council (1961b) further defined the action to be taken by stating that "Routine control of useful applications of radiation and atomic energy should be such that expected average exposures of suitable samples of an exposed population group will not exceed the upper value of Range II." Furthermore, they recommended, with respect to Range III, that "Control actions would be designed to reduce the levels to Range II or lower, and to provide stability at lower levels."

It has not been considered necessary to prescribe criteria for iodine-131 or strontium-89 for surface waters. Iodine-131 has never been a problem in water supplies and does not appear likely to be, and strontium-89 levels should not be significant if strontium-90 levels are kept satisfactorily low. Using the midpoint of Range I, Table [A-6], for transient rates of intake recommended by the U. S. Federal Radiation Council, and assuming a 2 liter per day consumption, the radium-226 limit is 0.5 Pc/day and strontium-90 limit is 5 Pc/day. These levels are not currently being exceeded in any surface water supply in the United States, although a number of ground water supplies have more than 0.5 pCi/ℓ of radium-226.

Because tritium (hydrogen-3) may be discharged from nuclear power reactors and fuel reprocessing plants, and because it would not be detected in normal analysis of water samples, it has been considered desirable to include a limit on this low energy radionuclide. The Federal Radiation Council has not provided guidance on tritium intake. A tentative limit of 3,000 pCi/ℓ of tritrium has been proposed for the revised edition of Drinking Water Standards. This relatively conservative limit has been suggested because of uncertainty in the potential genetic effects of tritium incorporated into body tissues as tritiated water. It is a generally attainable level based on data from the Environmental Protection Agency Tritium Surveillance System. These data indicate that of 70 United States cities surveyed in 1970, none had an annual average tritium activity in tap water exceeding 3,000 pCi/ℓ, the highest annual average value being 1,900 pCi/ℓ. Levels in surface water collected downstream from nuclear facilities showed only two of 34 locations having tritium activity exceeding 3,000 pCi/ℓ. Precipitation samples taken

*The functions of the U.S. Federal Radiation Council have been transferred to EPA, Office of Radiation Programs.

Table [A-5]. Ranges of Transient Rates of Intake (pCi/day) for use in Graded Scale of Action[a]

	Range I	Range II	Range III
Radium-226	0-2	2-20	20-200
Iodine-131[b]	0-10	10-100	100-1000
Strontium-90	0-20	20-200	200-2000
Strontium-89	0-200	200-2000	2000-20,000

[a]See Table [A-6].

[b]In the case of iodine-131, the suitable sample would include only small children. For adults, the radiation protection guide for the thyroid would not be exceeded by rates of intake higher by a factor of 10 than those applicable to small children.

Table [A-6]. Graded Scale of Action

Ranges of transient rates of daily intake	
Range I	Periodic confirmatory surveillance as necessary
Range II	Quantitative surveillance and routine control
Range III	Evaluation and application of additional control measures as necessary

during 1970 at locations within the United States indicated less than 700 pCi/ℓ.

Although a large number of other radionuclides may be present in water, it has not been considered necessary to include specific limits for other than the three mentioned above. If other nuclides are likely to be present, it is recommended that permissible limits be held to 1/150 of the limit for continuous occupational exposure set by the International Commission on Radiological Protection (1960).

Gross radioactivity limits provide screening techniques and guides to an increased level of radiochemical analysis. If the gross alpha and gross beta concentrations in a sample are less than certain minimum concentrations, no additional radiochemical or radiophysical analysers are required.

Gross Alpha Radioactivity. Gross alpha limits or investigation levels are keyed to the concentration limit for radium-226 (the alpha emitter with the most restrictive intake limit). A typical scheme is the following: [see Table A-7]

Gross Beta Radioactivity. Two beta emitting radionuclides with the most restrictive maximum permissible concentrations are lead-210 and radium-228. However, since it is extremely unlikely that either radionuclide will ever be present in a significant concentration in a raw water source, the investigation levels for gross beta radioactivity are keyed to strontium-90 and isotopes of radioiodine [see Table A-8].

The radionuclide concentration limits proposed in the above tables should not be considered as absolute maxima that, if exceeded, constitute grounds for rejection of a drinking water supply source. Instead, the concentration limits should be considered guidelines that should not be exceeded unless there is good reason. The constraints that should be imposed are based on: (1) a determination by the appropriate regulatory agencies that the higher level of radioactivity is as low as can be practicably achieved, and (2) quantitative surveillance of all intake pathways to demonstrate that total dose to a suitable sample of the exposed population is with Radiation Protection Guidelines levels. To permit variances in radio-

Table [A-7]. Typical Scheme of Gross Alpha Concentration

	Gross Alpha Concentration (pCi/1	Required action
(a)	Not exceeding 0.5 pCi/1	None
(b)	Greater than 0.5 but not exceeding 5 pCi/1	Radiochemical analysis for radium-226
(c)	Greater than 5 pCi/1	Comprehensive radiochemical analysis

Table [A-8]. Gross Beta Radioactivity to Strontium-90 and Isotopes of Radioiodine

Gross beta concentration excluding Potassium-40		Required action
(a)	Not greater than 5 pCi/1	None (with knowledge that lead-210 and radium-228 are essentially absent)
(b)	Greater than 5, but less than 50 pCi/1	Analyses for strontium-90, iodine-129, and iodine-131
(c)	Greater than 50 pCi/1	

nuclide concentrations in water depending on concentrations in other environmental media and dietary habits is consistent with the guidance and recommendations of the U. S. Federal Radiation Council, the National Council on Radiation Protection and Measurement, and the International Commission on Radiological Protection.

Recommendation

Because the defined treatment process has uncertain effects in the removal of soluble radionuclides and because of the effects of radiation on humans, it is recommended that the limits related to the guidelines presented above be accepted in the context of the discussion for application to sources of public water supply.

NAS, pp. 84-5.

17.2 Radioactivity (Marine Aquatic-life and Wildlife)

Recommendation

Aquatic organisms concentrate radioisotopes to various degrees in their tissues. The concentration in sea water should be low enough so that the concentration in any aquatic species will not exceed Radiation Protection Guides of the U. S. Federal Radiation Council (1961) for organisms harvested for use as human food. This recommendation is based upon the assumption that radiation levels which are acceptable as human food will not injure the aquatic organisms including wildlife.

NAS, p. 274

¶18 CARBON ADSORBABLE EXTRACT (Public Water Supplies)

Recommendation

Because large values of CCE [carbon-chloroform extract] and CAE [carbon-alcohol extract] are aesthetically undesirable and represent unacceptable levels of unidentified organic compounds that may have adverse physiological effects, and because the defined treatment process has little or no effect on the removal of these organics, it is recommended that organics-carbon adsorbable as measured by the Low-Flow Sampler (Standard Methods 1971) not exceed 0.3 mg/ℓ CCE and 1.5 mg/ℓ CAE in public water supply sources.

NAS, p. 75.

¶19 FOAMING SUBSTANCES (Aesthetic Uses)

Recommendation

To avoid undesirable aesthetic effects and because the defined treatment process does little or nothing to reduce the level of foaming agents, it is recommended that foaming agents determined as methylene blue active substances not exceed 0.5 mg/ℓ in public water supply sources.
NAS, p. 67.

¶20 OIL AND GREASE (Surface Waters, Domestic Water Supply and Freshwater and Marine Aquatic Life)

CRITERIA

[Domestic Water Supply] ... Virtually free from oil and grease, particularly from the tastes and odors that emanate from petroleum products.

[Aquatic Life]

(1) Levels of individual petrochemicals in the water column should not exceed 0.01 of the lowest continuous flow 96-hour LC_{50} to several important freshwater or marine species, each having a demonstrated high susceptibility to oils and petrochemicals;

(2) Levels of oils or petrochemicals in the sediment which cause deleterious effects to the biota should not be allowed;

(3) Surface waters shall be virtually free from floating nonpetroleum oils of vegetable or animal origin, as well as petroleum derived oils.

EPA, p.111.

¶21 The criteria suggest, in every case where ¶21 is cited that exposure to these pollutants should be minimized. Furthermore where ¶21 is referred to in the freshwater and marine aquatic life column, the criteria are to protect aquatic life and the "consumers thereof."
EPA

¶22 POLYCHLORINATED BIPHENYLS (Marine Wildlife)

Recommendation

It is recommended the PCB concentrations in any sample consisting of a homogenate of 25 or more whole fish of any species that is consumed by fish-eating birds and mammals, within the same size range as the fish consumed by any bird or mammal, be no greater than 0.5 mg/kg of the wet weight.

In the absence of a standardized methodology for the determination of PCB in environmental samples, it is recommended that estimates of PCB concentrations be based on the commercial Aroclor® preparation which it most closely resembles in chlorine composition. If the PCB composition should resemble a mixture of more than one Aroclor, Aroclor®, it should be considered a mixture for the basis of quantitation, and the PCB concentration reported should be the sum of the component Aroclor® equivalents.s.
NAS, p. 226

¶23 TAINTING SUBSTANCES (Freshwater and Marine Aquatic Life)

CRITERION

Materials should not be present in concentrations that individually or in combination produce undesirable flavors which are detectable by organoleptic tests performed on the edible portions of aquatic organisms.
EPA, p. 216

¶24 TOXIC ORGANICS (Marine Aquatic Life)

The recommendations listed here in Table A-9 apply if not superseded by the EPA document. Any new criteria appear in Table A-1, under the specific name of the compound.

Recommendations

In general, marine life with the exception of fish-eating birds and mammals should be protected where the maximum concentration of the chemical in the water does not exceed one one-hundredth (0.01) of the LC50 values listed in Column 7, [Table A-9]. If new data indicate that an ecosystem can adequately degrade a

TABLE A-9—Presence and Toxicity of Organic Chemicals in the Marine System

Chemical (1)	U.S. production pounds, gal. yr (2)	Presence in sea water or marine organisms (3)	Trophic accumulation (4)	Most sensitive organisms tested (5)	Formulation (6)	Conc. (ppb active ingredient in water) (7)	Method of assessment (8)	Test procedure (9)	Reference (10)
PESTICIDES. Total	1.1×10⁹ lb	...	...	...					
Fungicides									
Fungicides, total	1.4×10⁶	...	...	...					
Pentachlorophenol	4.6×10⁷	Expected	Unknown	Insufficient data for marine organisms					
2,4,5-Trichlorophenol	Not available (1969) 2.8×10⁷ (1968)	Unknown	Unknown	Crassostrea virginica American oyster	.....	600	TLM	48 hr static lab bioassay	Davis and Hidu 1969[354]
Nabam (Ethylene bis[dithiocarbamic acid], disodium salt)	1.9×10⁶	Unlikely	Unlikely	Dunaliella tertiolecta	.....	100	.270. O. D. expt/O.D. control	10 day growth test	Ukeles 1962[376]
Hexachlorobenzene	Not available	Expected	Detected in birds (Vos et al., 1968)[378] Koeman and Genderen, 1970)[363]	Insufficient data for marine organisms					
Herbicides									
Herbicides, total	3.9×10⁶	...	...	...					
Amitrole (3-amino-1,2,4-triazole)	Not available	Unlikely	Unlikely	Insufficient data					
Chloramben (3-amino-2,5-dichlorobenzoic acid, sodium salt)	Not available	Unlikely	Unlikely	Chlorococcum sp	Methyl ester	2.5×10³	50% decrease in growth	Growth measured as ABS. (525 mu) after 10 days	Walsh 1972[379]
				Phaeodactylum tricornutum					
Picloram (4-amino-3,5,6-trichloropicolinic acid) (Tordon[11])	Not available	Unlikely	Unlikely	Isochrysis galbana	.....	1×10⁶	50% decrease in O_2 evolution*	.....	Walsh 1972[379]
					.....	5×10⁴	50% decrease in growth	Measured as ABS. (525 mu) after 10 dys	Walsh 1972[379]
Simazine [2-chloro-4,6-bis-(ethylamino)-s-triazine]	Not available	Unlikely	Unlikely	Isochrysis galbana	Technical acid	500	50% decrease in growth	Measured as ABS. (525 mu) after 10 days	Walsh 1972[379]
				Phaeodactylum tricornutum	Technical aid	500	50% decrease in growth	Measured as ABS. (525 mu) after 10 days	Walsh 1972[379]
Atrazine [2-chloro-4-ethylamino-6-isopropyl-amino-s-triazine]	Not available	Unlikely	Unlikely	Chlorococcum sp., Chlamydomonas sp., Monochrysis lutheri	Technical acid	100	50% decrease in growth	Measured as ABS. (525 mu) after 10 days	Walsh 1972[379]
				Isochrysis galbana	Technical acid	100	50% decrease in O_2 evolution*	.....	Walsh 1972[379]
				Phaeodactylum tricornutum	Technical acid	100	50% decrease in O_2 evolution*	.....	Walsh 1972[379]
Monuron [3-(p-chlorophenyl)-1,1-dimethylurea]	Not available	Unlikely	Unlikely	Protococcus sp.	.....	20	.00 OPT. DEN. expt/opt DEN control	10 day growth test	Ukeles 1962[376]
				Dunaliella tertiolecta	.....	20	.00 OPT. DEN. expt/opt DEN control	10 day growth test	Walsh 1972[379]
				Phaeodactylum tricornutum	.....	20	.00 OPT. DEN. expt/opt DEN control	10 day growth test	Ukeles 1962[376]
Diuron [3-(3,4,-dichlorophenyl)-1,1-dimethylurea]	Not available	Unlikely	Unlikely	Protococcus	.....	0.02	.52 OPT. DEN. expt/opt DEN control	10 day growth test	Ukeles 1962[376]
				Monochrysis lutheri	.....	0.02	.00 OPT. DEN. expt/opt DEN control	10 day growth test	Ukeles 1962[376]
Maleic hydrazide [1,2-dihydropyridazine-3,6-dione]	2.8×10⁶ lb.	Unlikely	Unlikely	Insufficient data					
Fenuron [1,1-dimethyl-3-phenylurea]	Not available	Unlikely	Unlikely	Chlorococcum sp.	Technical acid	750	50% decrease in growth	10 day growth test	Walsh 1972[379]
				Isochrysis galbana	Technical acid	750	50% decrease in growth	10 day growth test	Walsh 1972[379]
				Monochrysis lutheri	.....	280	.67 OPT. DEN. expt/opt DEN control	10 day growth test	Ukeles 1962[376]
Ametryne [2-ethylamino-4-isopropylamino-6-methyl-mercapto-s-triazine]	Not available	Unlikely	Unlikely	Chlorococcum sp.	Technical acid	10	50% decrease in growth	Measured as ABS. (525 mu) after 10 days	Walsh 1972[379]
				Isochrysis galbana	Technical acid	10	50% decrease in O_2 evolution*	.....	Walsh 1972[379]
				Monochrysis lutheri Phaeodactylum tricornutum	Technical acid	10	50% decrease in O_2 evolution*	.....	Walsh 1972[379]

*, O_2 evolution measured by Gilson differential respirometer on 4 ml of culture in log phase. Length of test 90 minutes.

TABLE A-9—Presence and Toxicity of Organic Chemicals in the Marine System—Continued

Chemical (1)	U.S. production pounds, gal./yr (2)	Presence in sea water or marine organisms (3)	Trophic accumulation (4)	Most sensitive organisms tested (5)	Formulation (6)	Conc. (ppb active ingredient in water) (7)	Method of assessment (8)	Test procedure (9)	Reference (10)
Herbicides, cont.									
Endothal [7-oxabicyclo-(2.2.1) heptane-2,3-dicarboxylic acid, disodium salt]	Not available	Unlikely	Unlikely	Mercenaria mercenaria Hard clam		1.25×10^4	TLM	12 day static lab bioassay	Davis and Hidu 1969[354]
MCPA [4-chloro-2-methylphenoxyacetic acid]	Not available	Unlikely	Unlikely	Crassostrea virginica American oyster		1.56×10^4	TLM	48 hr static lab bioassay	Davis and Hidu 1969[354]
2,4-D & derivatives	1.0×10^8 lb	Unknown	Unknown	Crassostrea virginica American oyster	Ester	740	TLM	14 day static lab bioassay	Davis and Hidu 1969[354]
				Dunaliella tertiolecta					
2,4,5-T & derivatives [2,4,5-trichlorophenoxyacetic acid]	2.8×10^7 lb	Unknown	Unknown	Isochrysis galbana	Technical acid	5×10^4	50% decrease in O_2 evolution*		Walsh 1972[379]
				Phaeodactylum tricornutum	Technical acid	5×10^4	50% decrease in growth	Measured as ABS. (525 mu) after 10 days	Walsh 1972[379]
Silvex [2-(2,4,5-trichlorophenoxy)propionic acid]	1.6×10^6	Unlikely	Unlikely	Crassostrea virginica American oyster		710	TLM	14 day static lab bioassay	Davis and Hidu 1969[354]
				Dunaliella tertiolecta					
Diquat [6,7-Dihydrodipyrido (1,2-a:2',1'-c)pyrazidinium dibromide	Not available	Unlikely	Unlikely	Chlorococcum sp.	Dibromide	5×10^6	50% decrease in O_2 evolution*		Walsh 1972[379]
				Dunaliella tertiolecta	Dibromide	5×10^6	50% decrease in O_2 evolution*		Walsh 1972[379]
				Isochrysis galbana	Dibromide	1.5×10^4	50% decrease in growth	Measured as ABS. (525 mu) after 10 days	Walsh 1972[379]
				Phaeodactylum tricornutum	Dibromide	5×10^6	50% decrease in O_2 evolution*		Walsh 1972[379]
Paraquat [1,1'-dimethyl-4,4'-dipyridilium dichloride]	Not available	Unlikely	Unlikely	Dunaliella tertiolecta	Dichloride	5×10^6	50% decrease in O_2 evolution*		Walsh 1972[379]
				Isochrysis galbana	Dichloride	5×10^5	50% decrease in growth	Measured as ABS. (525 mu) after 10 days	Walsh 1972[379]
Trifluralin[α,α,α-Trifluoro-2,6-dirtino-N, N-dipropyl-p-toluidine]	Not available	Unlikely	Unlikely	Chlorococcum sp.	Technical acid	2.5×10^3	50% decrease in growth	Measured as ABS. (525 mu) after 10 days	Walsh 1972[379]
				Isochrysis galbana	Technical acid	2.5×10^3	50% decrease in growth	Measured as ABS. (525 mu) after 10 days	Walsh 1972[379]
				Phaeodactylum tricornutum	Technical acid	2.5×10^3	50% decrease in growth	Measured as ABS. (525 mu) after 10 days	Walsh 1972[379]
Cacodylic acid [Hydroxydimethyl arsine oxide]	Not available	Unlikely	Unlikely	Insufficient data					
Insecticides									
Insecticides, total (includes rodenticides)	5.7×10^8 lb								
Heptachlor [Heptachlorotetrahydro-endo-methanoindene] (includes heptachlor epoxide)	Not available	Oysters (Bugg et al. 1967)[350]	Bald Eagles (Krantz et al. 1970)[365]	Thalassoma bifasciatum Bluehead	100%	0.8	LC-50	96 hr static lab bioassay	Eisler 1970b[357]
Endrin [Hexachloro-epoxyoctahydro-endo-endo-dimethanonaphthalene]	Not available	Oysters (Bugg et al. 1967,[350] Casper, 1967,[352] Rowe et al. 1971)[372]	Brown Pelican (Schreiber and Risebrough 1972,[374] Risebrough et al. 1968)[371]	Mugil cephalus Striped mullet	100%	0.3	LC-50	96 hr static lab bioassay	Eisler 1970b[357]
				Menidia menidia Atlantic silverside	100%	0.05	LC-50	96 hr static lab bioassay	Eisler 1970b[357]
Dieldrin [Hexachloro-epoxyoctahydro-endo-exo-dimethanonaphthalene]	Not available	Oysters (Bugg et al. 1967,[350] Casper, 1967,[352] Rowe et al. 1971)[372]	Bald eagles (Krantz et al. 1970)[365] Grey Whale, Sperm Whale (Wolman and Wilson 1970)[380] Brown Pelican (Schreiber and Risebrough 1972)[374]	Anguilla rostrata American eel	100%	0.9	LC-50	96 hr static lab bioassay	Eisler 1970b[357]
Aldrin [Hexachloro-hexahydro-endo-exo-dimethanonaphthalene]	Not available	Oysters (Bugg et al. 1967)[350]	Unlikely, converts to dieldrin (Korschgen 1970)[364]	Palaemon macrodactylus Korean shrimp	Technical	0.74 (0.51–1.08)	TL-50	96 hr static lab bioassay	Earnest (unpublished)[382]
Chlordane [Octochlorohexahydro-methanoindene]	Not available	Oysters (Bugg et al. 1967)[350]	Expected	Palaemon macrodactylus Korean shrimp	100%	18 (10–38)	TL-50	96 hr static lab bioassay	Earnest (unpublished)[382]

* O_2 evolution measured by Gilson differential respirometer on 4 ml of culture in log phase. Length of test 90 minutes.

TABLE A-9—Presence and Toxicity of Organic Chemicals in the Marine System—Continued

Chemical (1)	U.S. production pounds, gal. yr (2)	Presence in sea water or marine organisms (3)	Trophic accumulation (4)	Most sensitive organisms tested (5)	Formulation (6)	Conc. (ppb active ingredient in water) (7)	Method of assessment (8)	Test procedure (9)	Reference (10)
Insecticides, cont.									
Strobane® [polychlorinated terpenes]	Not available	Expected	Expected	Insufficient data for marine species					
Toxaphene [Chlorinated camphene]	Not available	Bay mussel (Modin, 1969);[367] Oysters (Bugg et al. 1967)[350]	Expected	Gasterosteus aculeatus threespine stickle-back	100%	7.8	TLM	96 hr static lab bioassay	Katz 1961[362]
DDT compounds	1.2×10^{8} lb.	Jensen et al. 1969,[360] Risebrough et al. 1968[371]							
p,p'-DDT [1,1,1-Trichloro-2,2-bis(p-chlorophenyl) ethane		(References cited above)		Penaeus duorarum Pink shrimp	Technical 77%	0.12 0.17 (0.09–0.32)	TL-50 TL-50	28 day bioassay 96 hr intermittent flow lab bioassay	Nimmo et al. 1970[369] Earnest (unpublished)[382]
p,p'-DDD(p,p'-TDE) [1,1-Dichloro-2,2-bis (p-chlorophenyl)ethane				Palaemon macrodactylus	99%	2.5 (1.6–4.0)	TL-50	96 hr intermittent flow lab bioassay	Earnest (unpublished)[382]
p,p'-DDE [1,1-Dichloro-2,2-bis(p-chlorophenyl) ethylene		(References cited above)		Falco peregrinus Peregrine Falcon			Eggshell thinning	DDE in eggs highly correlated with shell thinning	Cade et al. 1970[351]
Mirex [Dodecachloro-octahydro-1,3,4-metheno-2H-cyclobuta[cd]pentalene]	Not available	Expected	Expected	Penaeus duorarum Pink shrimp	Technical	1.0	100% paralysis/death in 11 days	Flowing water bioassay	Lowe et al 1971[366]
Benzene hexachloride [Hexachlorocyclohexane]	Not available	Southern hemisphere sea birds (Tatton and Ruzicka 1967)[375]		Penaeus setiferus White shrimp	8.1%	2.8	TLM	24 hr static lab bioassay	Chin and Allen 1958[353]
Lindane [gamma-hexachlorocyclohexane]	Not available	Oysters (Bugg et al. 1967,[350] Casper 1967)[352]	Expected	Crangon septemspinosa Sand shrimp	100%	5	LC-50	96 hr static lab bioassay	Eisler 1969[355]
				Pagurus longicarpus Hermit crab	100%	5	LC-50	96 hr static lab bioassay	Eisler 1969[355]
Endosulfan [Hexachlorohexahydro-methano-benzo-dioxathiepin-3-oxide] (Thiodan®)	Not available	Bay mussel (Koeman and Genderen 1970)[363]	Sandwich Tern, Common Eider (Koeman and Genderen 1970)[363]	Palaemon macrodactylus Korean shrimp	96%	3.4 (1.8–6.5)	TL-50	96 hr intermittent flow lab bioassay	Earnest (unpublished)[382]
Methoxychlor [1,1,1-Trichloro-2,2-bis(p-methoxy-phenyl)ethane]	Not available	Oysters (Bugg et al. 1967)[350]	Unlikely	Palaemon macrodactylus	89.5%	0.44 (0.21–0.93)	TL-50	96 hr static lab bioassay	Earnest (unpublished)[382]
Carbaryl (Sevin) [1-naphthyl-N-methylcarbamate]	Not available	Unlikely	Unlikely	Palaemon macrodactylus	100%	7.0 (1.5–28)	TL-50	96 hr intermittent bioassay	Earnest (unpublished)[382]
				Cancer magister Dungeness crab	80%	6	Prevention of hatching and molting	24 hr static lab bioassay	Buchanan et al. 1970[349]
Coumaphos (Co-ral) [O,O-Diethyl-O-(3-chloro-4-methyl-2-oxo-2H-1-benzopyran-7-yl)-phosphorothioate]	Not available	Unlikely	Unlikely	Crassostrea virginica American oyster		110	TLM	48 hr static lab bioassay	Davis and Hidu 1969[354]
Diazinon [O,O-Diethyl-O-(2-isopropyl-4-methyl-6-pyrimidinyl)phosphorothioate]	Not available	Unlikely	Unlikely	Insufficient data					
Parathion [O,O-Diethyl-O-p-nitrophenyl-phosphorothioate]	Not available	Unlikely	Unlikely	Cyprinodon variegatus Sheepshead minnow		10	Acetylcholinesterase activity in control vs. expt groups. Control = 1.36; Expt. 0.120	72 hr static exposure	Coppage (unpublished)[381]
Dursban [O,O Diethyl-O-3,5,6-trichloro-2-pyridyl-phosphorothioate]	Not available	Unlikely	Unlikely	Palaemon macrodactylus Korean shrimp		0.01 (0.002–0.046)	TL-50	96 hr intermittent flow bioassay	Earnest (unpublished)[382]
Fenthion [O,O-Dimethyl-O-(4-methylthio-m-tolyl) phosphorothioate] (Baytex)	Not available	Unlikely	Unlikely	Palaemon macrodactylus		3.0 (1.5–60)	TL-50	96 hr intermittent flow bioassay	Earnest (unpublished)[382]
Methyl parathion [O,O,-Dimethyl-O-p-nitrophenyl-phosphorothioate]	5.1×10^{7} lb	Unlikely	Unlikely	Crangon septemspinosa Sand shrimp	100%	2	LC-50	96 hr static lab bioassay	Eisler 1969[355]
Guthion [O,O-Dimethyl-S-(4-oxo-1,2,3-benzotriazino-3-methyl)phosphorodithioate]	Not available	Unlikely	Unlikely	Gasterosteus aculeatus threespine stickle-back	93%	4.8	TLM	96 hr static lab bioassay	Katz 1961[362]
Dioxathion (Delnav) [2,3-p-Dioxane-S,S-bis(O,O-diethylphosphorodithioate]	Not available	Unlikely	Unlikely	Crangon septemspinosa Sand shrimp	100%	38	LC-50	96 hr static lab bioassay	Eisler 1969[355]
				Fundulus heteroclitus Mummichog	100%	6	LC-50	96 hr static lab bioassay	Eisler 1970a[356]
				Menidia menidia Atlantic silverside	100%	6	LC-50	96 hr static lab bioassay	Eisler 1970b[357]

TABLE A-9—Presence and Toxicity of Organic Chemicals in the Marine System—Continued

Chemical (1)	U.S. production pounds, gal./yr (2)	Presence in sea water or marine organisms (3)	Trophic accumulation (4)	Most sensitive organisms tested (5)	Formulation (6)	Conc. (ppb active ingredient in water) (7)	Method of assessment (8)	Test procedure (9)	Reference (10)
Insecticides, cont.									
Phosdrin [1-methoxycarbonyl-1-propen-2-yl dimethylphosphate]	Not available	Unlikely	Unlikely	Crangon sepemspinosa Sand shrimp	100%	11	LC-50	96 hr static lab bioassay	Eisler 1969[355]
Malathion [S-(1,2-dicarbethoxyethyl)-O, O-dimethyldithiophosphate]	Not available	Unlikely	Unlikely	Thalasomma bifasciatum Bluehead	100%	27	LC-50	96 hr static lab bioassay	Eisler 1970b[357]
Phosphamidon [2-Chloro-N, N-diethyl-3-hydroxy-crotonamide dimethyl phosphate]	Not available	Unlikely	Unlikely	Insufficient data					
Phorate [O, O Diethyl-S-([Ethylthio]methyl)-phosphorodithioate]	Not available	Unlikely	Unlikely	Cyprinodon variegatus Sheepshead minnow	.....	5	Acetylcholinesterase activity** in control vs expt. groups. Control=1.36; Expt.=0.086	72 hr static exposure	Coppage (unpublished)[381]
DDVP [O, O-Dimethyl-O-(2,2-dichlorovinyl)phosphate]	Not available	Unlikely	Unlikely	Crangon septemspinosa Sand shrimp	.....	4	LC-50	96 hr static lab bioassay	Eisler 1969[355]
Trichlorfon [O, O-Dimethyl-1-hydroxy-2,2,2-trichloroethylphosphonate] (Dipterex)	Not available	Unlikely	Unlikely	Crassostrea virginica American oyster	.....	1,000	TLM	48 hr static lab bioassay	Davis and Hidu 1969[354]
TEPP [Tetraethyl pyrophosphate]	Not available	Unlikely	Unlikely	Crassostrea virginica	.....	>1×10⁴	TLM	14 day static lab bioassay	Davis and Hidu 1969[354]
Related products									
DBCP [1,2-Dibromo-3-chloropropane] (Nemagon®)	8.6×10⁶ lb	Unknown	Unknown	Mercenaria mercenaria Hard clam	.....	780	TLM	12 day static lab bioassay	Davis and Hidu 1969[354]
Methyl bromide	2.0×10⁷ lb	Unknown	Unknown	Insufficient data					
TAR AND TAR CRUDES									
Benzene	1.2×10⁹ gal.	Unknown	Unknown	Insufficient data					
Toluene	7.6×10⁸ gal.	Unknown	Unknown	Insufficient data					
Xylene	3.8×10⁸ gal.	Unknown	Unknown	Insufficient data					
Naphthalene	8.5×10⁸ gal.	Unknown	Unknown	Insufficient data					
PLASTICIZERS									
Phthalic anhydride esters, total	8.8×10⁸ lb.	Expected	Unknown	Insufficient data					
Adipid acid esters, total	6.6×10⁷	Unknown	Unknown	Insufficient data					
SURFACE-ACTIVE AGENTS									
Dodecylbenzenesulfonates, total	5.7×10⁸ lb. (1968)	Unknown	Unlikely	Insufficient data					
Ligninsulfonates, total	4.4×10⁸ lb.	Unknown	Unknown	Insufficient data					
Nitrilotriacetic acid	Not available	Unknown	Unlikely	Cyclotella nana	Monohydrated sodium salt	5×10³	38% growth as compared to controls	72 hr static lab bioassay	Erickson et al. 1950[358]
				Homarus americanus American lobster	Monohydrated sodium salt	1×10⁵	100% mortality	7 day static lab bioassay	NMWQL 1970[358]
HALOGENATED HYDROCARBONS									
Carbon tetrachloride	7.6×10⁸ lb (1968)	Unknown	Unlikely	Insufficient data					
Dichlorodifluoromethane	3.3×10⁸ (1968)	Unknown	Unlikely	Insufficient data					
Ethylene dichloride	4.8×10⁹ (1968)	Expected	Unlikely	Insufficient data					
Aliphatic chlorinated hydrocarbon wastes of vinyl chloride production	3×10⁷ lb (estimated as 1% of vinyl chloride production)	Surface waters and marine organisms of North Atlantic and North Sea (Jensen et al. 1970)[361]	Unknown	Gadus morrhua Cod	67% 1,1,2-trichloroethane, 20% 1,2-diethane	10,000	LC-50	10 hr lab bioassay	Jensen et al. 1970[361]
Polychlorinated biphenyl	Not available	Jensen et al. 1969[360], Risebrough et al. 1968[372]	.....	Penaeus duorarum Pink shrimp	Aroclor 1254	0.94	51% mortality	15 day chronic exposure in flowing seawater	Nimmo et al. 1971[370]
Polychlorinated terphenyl	Not available	Expected	Expected	Insufficient data					
Brominated biphenyls	Not available	Unknown	Expected	Insufficient data					
CYCLIC INTERMEDIATES									
Monochlorobenzene	6.0×10⁸ lb	Expected	Unlikely	Insufficient data					
Phenol	1.7×10⁹ lb	Expected	Unlikely	Mercenaria mercenaria Hard Clam	.....	5.3×10⁴	TLM	48 hr static lab bioassay	Davis and Hidu 1969[354]
MISCELLANEOUS CHEMICALS									
Tetraethyl lead	4.9×10⁸	Unlikely	Unlikely	Insufficient data					

** ACh hydrolysed/hr/mg brain.

particular pollutant, a higher application factor for this pollutant may be used.

In order to maintain the integrity of the ecosystem to the fullest possible extent, it is essential to consider effects on all non-target organisms when applying pesticides to estuarine habitats in order to control one or more of the noxious species. For those occasions when chemicals must be used, the following guidelines are offered:

- a compound which is the most specific for the intended purpose should be preferred over a compound that has broad spectrum effects;
- a compound of low persistence should be used in preference to a compound of greater persistence;
- a compound of lower toxicity to non-target organisms should be used in preference to one of higher toxicity;
- water samples to be analyzed should include all suspended particulate and solid material: residues associated with these should therefore be considered as present in the water;
- when a derivative such as p,p'-DDE or 1-naphthol is measured with or instead of the parent compound, the toxicity of the derivative should be considered separately: if the toxicity of a derivative such as an ionic species of a pesticide is considered equivalent to that of the original parent compound, concentrations should be expressed as equivalents of the parent compound.

It is recommended that the chemicals listed in Table [A-9] and all chemicals subsequently added to this list be considered as toxic organic compounds potentially harmful to the marine environment. It is emphasized that the data in Table [A-9] are not sufficient in themselves for final evaluation of the environmental significance of each compound.

¶25 ALDRIN, DIELDRIN, ENDRIN AND HEPTACHLOR EPOXIDE (Marine Wildlife)

Recommendation

It is recommended that the sum of the concentrations of aldrin, dieldrin, endrin, and heptachlor epoxide in any sample consisting of a homogenate of 25 or more whole fish of any species that is consumed by fish-eating birds and mammals, within the size range consumed by any bird or mammal, be no greater than 5 µg/kg of the wet weight.
NAS, p. 227.

¶26 LINDANE, CHLORDANE, ENDOSULFAN, METHOXYCHLOR, MIREX, TOXAPHENE HEXACHLOROBENZENE AND OTHER CHLORIATED HYDROCARBON PESTICIDES (Marine Wildlife)

Recommendation

It is recommended that the concentration of any of these chlorinated hydrocarbon insecticides, including lindane, chlordane, endosulfan, methoxychlor, mirex, and toxaphene, and of hexachlorobenzene, in any sample consisting of a homogenate of 25 or more whole fish of any species that is consumed by fish-eating birds and mammals, with the size range that is consumed by any bird or mammal, be no greater than 50 µg/kg of the wet weight.
NAS, p. 227.

¶27 DDT COMPOUNDS (Marine Wildlife)

Recommendation

It is recommended that DDT concentrations in any sample consisting of a homogenate of 25 or more fish of any species that is consumed by fish-eating birds and mammals, within the same size range as the fish consumed by any bird or mammal, be no greater than 50 µg/kg of the wet weight. DDT residues are defined as the sum of the concentrations of p,p'-DDT, p,p'-DDD, p,p'-DDE and their ortho-para isomers.
NAS, p. 226

¶28 OTHER PESTICIDES (Freshwater Aquatic Life)

The recommended maximum concentrations of pesticides in freshwater are listed in Table [A-10] except that where pesticides are applied to water to kill undesirable aquatic life, the values will be higher. In the latter instances, care should be taken to avoid indiscriminate use and to insure that application of the pesticide follows the prescribed methods.

¶29 PESTICIDE RESIDUES (Agricultural Purposes, Irrigation)

Recommendation

Pesticide residues in irrigation waters are variable depending upon land and crop management practices. Recent data indicate pesticide residues are declining in irrigation waters, with concentrations less than 1.0 µg/l being detected. To date there have been no documented toxic effects on crops

TABLE A-10—Recommended Maximum Concentrations of Other Pesticides in Whole (Unfiltered) Water, Sampled at Any Time and Any Place.[a]

Organophosphate insecticides	Recommended maximum concentration (μg/l)
Abate	(b)
Azinphosmethyl	0.001
Azinphosethyl	(b)
Carbophenothion	(b)
Chlorothion	(b)
Ciodrin	0.1
Coumaphos	0.001
Demeton	(b)
Diazinon	0.009
Dichlorvos	0.001
Dioxathion	0.09
Disulfonton	0.05
Dursban	0.001
Ethion	0.02
EPN	0.06
Fenthion	0.006
Malathion	0.008
Methyl Parathion	(b)
Mevinphos	0.002
Naled	0.004
Oxydemeton methyl	0.4
Parathion	0.0004
Phorate	(b)
Phosphamidon	0.03
Ronnel	(b)
TEPP	0.4
Trichlorophon	0.002

Carbamate insecticides	Recommended maximum concentrations (μg/l)
Aminocarb	(b)
Bayer	(b)
Baygon	(b)
Carbaryl	0.02
Zectran	0.1

Herbicides, fungicides and defoliants	Recommended maximum concentrations (μg/l)
Acrolein	(b)
Aminotriazole	300.0
Balan	(b)
Bensulide	(b)
Choroxuron	(b)
CIPC	(b)
Dacthal	(b)
Dalapon	110.0
DEF	(b)
Dexon	(b)

Herbicides, fungicide and defoliants	Reccommended maximum concentration (μ/l)
Dicamba	200
Dichlobenil	37.0
Dichlone	0.2
Diquat	0.5
Diuron	1.6
Difolitan	(b)
Dinitrobutyl phenol	(b)
Diphenamid	(b)
2,4-D (PGBE)	(b)
2,4-D (BEE)	4.0
2,4-D (IOE)	(b)
2,4-D (Diethylamine salts)	(b)
Endothal (Disodium salt)	(b)
Endothal (Dipotassium salt)	(b)
Eptam	(b)
Fenac (Sodium salt)	45.0
Hyamine-1622	(b)
Hyamine-2389	(b)
Hydrothal-47	(b)
Hydrothal-191	(b)
Hydrothal plus	(b)
IPC	(b)
MCPA	(b)
Molinate	(b)
Monuron	(b)
Paraquat	(b)
Pebulate	(b)
Picloram	(b)
Propanil	(b)
Silvex (BEE)	2.5
Silvex (PGBE)	2.0
Silvex (IOE)	(b)
Silvex (Potassium salt)	(b)
Simazine	10.0
Trifluarafin	(b)
Vernolate	(b)

Botanicals	Recommended maximum concentrations (μg/l)
Allethrin	0.002
Pyrethrum	0.01
Rotenone	10.0

NAS, p. 186-187

[a] Concentrations were determined by multiplying the acute toxicity values for the more sensitive species (Appendix II-D) by an application factor of 0.01 except where an experimentally derived application fact or is indicated.
[b] Insufficient data to determine safe concentrations.

irrigated with waters containing insecticide residues. Because of these factors and the marked variability in cross sensitivity, no recommendation is given for insecticide residues in irrigation waters. For selected herbicides in irrigation water, it is recommended that levels at the crop not exceed the recommended maximum concentration listed in Table [A-11].

¶30 SEWAGE

30.1 Sewage (Marine Aquatic Life)
30.2 Sewage (Agricultural Uses, Irrigation)

30.1 Sewage (Marine Aquatic Life)

Table [A-11]. Maximum Levels of Herbicide Residues Found in Irrigation Water as a Result of Ditchbank Treatment[a]

Herbicide and canal treated	Treatment rate, lb/A	Water flow in cfs	Maximum concentration of residue, µg/ℓ
DALAPON			
Five-mile Lateral	20	15	365[b]
Lateral No. 4	6.7	290	23
Manard Lateral	9.6	37	39
Yolo Lateral	10.5	26	162
TCA			
Lateral No. 4	3.8	290	12
Manard Lateral	5.4	37	20
Yolo Lateral	5.9	26	69
2,4-D AMINE SALT			
Lateral No. 4	1.9	290	5
Manard Lateral	2.7	17	13
Yolo Lateral	3.0	26	36

[a]Frank et al. (1970).
[b]High level of residue probably due to atypical treatment.

NAS, p. 353.

Recommendations

- Untreated or treated municipal sewage discharges should be recognized as a major source of toxic substances. Recommendations for these constituents will limit the amount of sewage effluent that can be dispersed into estuaries. Reduced degradation rates of highly dispersed materials should be considered if the effluent contains refractory organic material. Undegradable synthetic organic compounds do not cause oxygen depletion but can still adversely affect the ecosystem. Maintenance of dissolved oxygen standards will not prevent the potentially harmful buildup of these materials. Specific quantitative analyses should be done to identify and assess the abundance of these compounds.

- The addition of any organic waste to the marine environmental should be carefully controlled to avoid decomposition which would reduce the oxygen content of the water below the levels specified in the recommendations for oxygen.

- Neither organic matter nor fertilizers should be added that will induce the production of organic matter by normal biota to an extent causing an increase in the size of any natural anoxic zone in the deeper waters of any estuary.

- The natural ratios of available nitrogen to total phosphorus should be evaluated under each condition, and the element actually limiting plant production should be determined. Control of the amount of the limiting element added to the water will generally control enrichment.

- If the maximum amounts of available nitrogen and phosphorus in domestic waste increase the concentration in receiving waters to levels of 50 micrograms per liter of phosphorus and 360 micrograms per liter of nitrogen, enough organic matter would be produced to exhaust the oxygen content of the water, at the warmest time of the year under conditions of poor circulation, to levels

below those recommended.... These concentrations of nutrients are clearly excessive.

• The potential presence of pathogenic bacteria and viruses must be considered in waters receiving untreated or treated municipal sewage effluents. The present quality stnadards for fecal coliform counts... should be observed. The procedures for the examination of seawater and shellfish as recommended by Hosty et al. (1970) should be used.

• Disposal of sludge into coastal waters may adversely affect aquatic organisms, especially the bottom fauna. Periodic examination samples should determine the spread of such an operation to aid in the control of local waste material loads. The probable transport by currents should be carefully considered. The dumping of sludge into marine waters should be recognized as a temporary practice.

• Disposal of organic wastes into the deep-sea is not recommended until further studies on their fate, their effect on the deep-sea-fauna, and the controllability of such a procedure have been completed.
NAS, pp. 277-278.

30.2 Sewage (Agricultural Uses, Irrigation)

Recommendations

• Raw sewage should not be used in the United States for irrigation or land disposal.

• Sewage water that has received primary treatment may be used on crops not used for human consumption. Primary effluents should be free of phytotoxic materials.

• Sewage water that has received secondary treatment may also be used to irrigate crops that are canned or similarly processed before sale.

• Fecal coliform standard for unrestricted irrigation water should be a maximum of 1,000/100 ml.

• The amount of wastewater that can be applied is determined by balancing the nutrient load of the wastewater against the nutrient removal capacity of the soil.

• The amount of wastewater that can be applied is determined by balancing the nutrient load of the wastewater against the nutrient removal capacity of the soil.

• Phosphorus will probably not limit sewage application because of the tremendous adsorption capacity of the soil.

• The nitrogen load should be balanced against crop removal within 30 per cent unless additional removal can be demonstrated.
NAS, p. 353.

¶31 TOXIC WASTES

Recommendations

The disposal of waste materials at sea, or the transport of materials for the purpose of disposal at sea should be controlled. Such disposal should be permitted only when reasonable evidence is presented that the proposed disposal will not seriously damage the marine biota, interfere with fisheries operations or with other uses of the marine environment such as navigation and recreation, or cause hazards to human health and welfare. The following guidelines are suggested:

• Disposal sea at of potentially hazardous materials such as highly radioactive material or agents of chemical or biological warfare should be avoided.

• Toxic wastes should not be discharged at sea in a way which would adversely affect the marine biota. The toxicity of such materials should be established by bioassay tests and the concentrations produced should conform to the conditions specified in the discussion of mixing zones....

• Disposal of materials containing settleable solids or substances that may precipitate out in quantities adversely affecting the biota should be avoided in estuarine or coastal waters.

• Solid waste disposal at sea should be avoided if floating material might accumulate in harbors or on the beaches or if such materials might accumulate on the bottom or in the water column in a manner that will deleteriously affect deep sea biota.

In connection with dredging operations or other physical modifications of harbors and estuaries which would increase the suspended sediment load, the following types of investigations should be undertaken:

• Evaluation of the range and types of particles to be resuspended and transported, where they will settle, and what substratum changes or modifications may be created by the proposed activities in both the dredged and the disposal areas.

• Determination of the biological activity of the water column, the sediment-water interface, and the substrate material to depths which contain burrowing organisms.

• Estimation of the potential release into the water column of sediments, those substances originally dissolved or complexed in the interstitial water of the sediments, and the beneficial or detrimental chemicals sorbed or otherwise associated with particles which may be released wholly or partially after resuspension.

• Establish the expected relationship between properties of the suspended load and the permanent resident species of the area and their ability to repopulate the area, and the transitory species which use the area only at certain seasons of the years.

NAS, pp. 282-283.

APPENDIX B

List of Approved Test Procedures for Determination of Water Quality Pollutants and Characteristics as of July 1, 1977 (Reproduced from Code of Federal Regulations 40 CFR 136).

PART 136—GUIDELINES ESTABLISHING TEST PROCEDURES FOR THE ANALYSIS OF POLLUTANTS

Sec.

AUTHORITY: Sec. 304(g) of Federal Water Pollution Control Act Amendments of 1972 86 Stat. 816, et seq., Pub. L. 92-500).

§ 136.1 Applicability.

The procedures prescribed herein shall, except as noted in § 136.5, be used to perform the measurements indicated whenever the waste constituent specified is required to be measured for:

(a) An application submitted to the Administrator, or to a State having an approved NPDES program, for a permit under section 402 of the Federal Water Pollution Control Act as amended (FWPCA), and,

(b) Reports required to be submitted by dischargers under the NPDES established by Parts 124 and 125 of this chapter, and,

(c) Certifications issued by States pursuant to section 401 of the FWPCA, as amended.

[38 FR 28758, Oct. 16, 1973]

§ 136.2 Definitions.

As used in this part, the term:

(a) "Act" means the Federal Water Pollution Control Act, as amended, 33 U.S.C. 1314, et seq.

(b) "Administrator" means the Administrator of the U.S. Environmental Protection Agency.

(c) "Regional Administrator" means one of the EPA Regional Administrators.

(d) "Director" means the Director of the State Agency authorized to carry out an approved National Pollutant Discharge Elimination System Program under section 402 of the Act.

(e) "National Pollutant Discharge Elimination System (NPDES)" means the national system for the issuance of permits under section 402 of the Act and includes any State or interstate program which has been approved by the Administrator, in whole or in part, pursuant to section 402 of the Act.

(f) "Standard Methods" means *Standard Methods for the Examination of Water and Waste Water,* 14th Edition, 1976. This publication is available from the American Public Health Association, 1015 18th Street, N.W., Washington, D.C. 20036.

(g) "ASTM" means *Annual Book of Standards, Part 31, Water, 1975.* This publication is available from the American Society for Testing and Materials, 1916 Race Street, Philadelphia, Pennsylvania 19103.

(h) "EPA Methods" means *Methods for Chemical Analysis of Water and Waste, 1974.* Methods Development and Quality Assurance Research Laboratory, National Environmental Research Center, Cincinnati, Ohio 45268; U.S. Environmental Protection Agency, Office of Technology Transfer, Industrial Environmental Research Laboratory, Cincinnati, Ohio 45268. This publication is available from the Office of Technology Transfer.

[38 FR 28758, Oct. 16, 1973, as amended at 41 FR 52781, Dec. 1, 1976]

§ 136.3 Identification of test procedures.

(a) Every parameter or pollutant for which an effluent limitation is now specified pursuant to sections 401 and 402 of the Act is named together with test descriptions and references in Table I. The discharge parameter values for which reports are required must be determined by one of the standard analytical methods cited and described in Table I, or under certain circumstances by other methods that may be more advantageous to use when such other methods have been previously approved by the Regional Administrator of the Region in which the discharge will occur, and providing that the Director of the State in which such discharge will occur does not object to the use of such alternate test procedures.

(b) Under certain circumstances the Regional Administrator or the Director in the Region or State where the discharge will occur may determine for a particular discharge that additional parameters or pollutants must be reported. Under such circumstances, additional test procedures for analysis of pollutants may be specified by the Regional Administrator, or the Director upon the recommendation of the Director of the Environmental Monitoring and Support Laboratory, Cincinnati.

(c) Under certain circumstances, the Administrator may approve, upon recommendation by the Director, Environmental Monitoring and Support Laboratory, Cincinnati, additional alternate test procedures for nationwide use.

TABLE I.—*List of approved test procedures*[1]

Parameter and units	Method	References (page nos.) 1974 EPA methods	14th ed. standard methods	Pt. 31 1975 ASTM	USGS methods[2]	Other approved methods
1. Acidity, as $CaCO_3$, milligrams per liter.	Electrometric end point (pH of 8.2) or phenolphthalein end point.	1	273(4d)	116	40	[3](607)
2. Alkalinity, as $CaCO_3$, milligrams per liter.	Electrometric titration (only to pH 4.5) manual or automated, or equivalent automated methods.	3 5	278	111	41	[3](607)
3. Ammonia (as N), milligrams per liter.	Manual distillation[4] (at pH 9.5) followed by nesslerization, titration, electrode, Automated phenolate.	--- 159 165 168	410 412 616	237	116	[3](614)
BACTERIA						
4. Coliform (fecal)[5], number per 100 ml.	MPN;[6] membrane filter	--- ---	922 937	--- ---	--- [7](45)	--- ---
5. Coliform (fecal)[5] in presence of chlorine, number per 100 ml.	-----do.[6 8]	--- ---	922 928, 937	--- ---	--- ---	--- ---
6. Coliform (total),[5] number per 100 ml.	-----do.[6]	--- ---	916 928	--- ---	--- [7](35)	--- ---
7. Coliform (total)[5] in presence of chlorine, number per 100 ml.	MPN;[6] membrane filter with enrichment.	--- ---	916 933	--- ---	--- ---	--- ---
8. Fecal streptococci,[5] number per 100 ml.	MPN;[6] membrane filter; plate count.	--- --- ---	943 944 947	--- ---	--- [7](50)	--- ---
9. Benzidine, milligrams per liter.	Oxidation—colorimetric[9]					
10. Biochemical oxygen demand, 5-d (BOD_5), milligrams per liter.	Winkler (Azide modification) or electrode method.	---	543	---	[7](50)	[10](17)
11. Bromide, milligrams per liter.	Titrimetric, iodine-iodate	14	---	323	58	---
12. Chemical oxygen demand (COD), milligrams per liter.	Dichromate reflux	20	550	472	124	[3](610) [10](17)
13. Chloride, milligrams per liter.	Silver nitrate; mercuric nitrate; or automated colorimetric-ferricyanide.	--- 29 31	303 304 613	267 265 ---	--- --- [11](46)	--- [3](615) ---
14. Chlorinated organic compounds (except pesticides), milligrams per liter.	Gas chromatography[12]					
15. Chlorine—total residual, milligrams per liter.	Iodometric titration, amperometric or starch-iodine end-point; DPD colorimetric or Titrimetric methods (these last 2 are interim methods pending laboratory testing).	--- 35 --- ---	318 322 332 329	--- 278 --- ---	--- --- --- ---	--- --- --- ---
16. Color, platinum cobalt units or dominant wave length, hue, luminance, purity.	Colorimetric; spectrophotometric; or ADMI procedure.[13]	36 39	64 66	---	82	---

See footnotes at end of table.

TABLE I.—*List of approved test procedures* [1]—Continued

Parameter and units	Method	1974 EPA methods	14th ed. standard methods	References (page nos.) Pt. 31 1975 ASTM	References (page nos.) USGS methods [2]	Other approved methods
BACTERIA—Continued						
17. Cyanide, total,[14] milligrams per liter.	Distillation followed by silver nitrate titration or pyridine pyrazolone (or barbituric acid) colorimetric.	40	361	503	85	[10](22)
18. Cyanide amenable to chlorination, milligrams per liter.	----do----	49	376	505	----	----
19. Dissolved oxygen, milligrams per liter.	Winkler (Azide modification) or electrode method.	51 56	443 450	368	126	[3](609) ----
20. Fluoride, milligrams per liter.	Distillation [4] followed by ion electrode; SPADNS; or automated complexone.	---- 65 59 61	389 391 393 614	 307 305 ----	 93 ----	---- ---- ---- ----
21. Hardness—Total, as $CaCO_3$, milligrams per liter.	EDTA titration; automated colorimetric; or atomic absorption (sum of Ca and Mg as their respective carbonates).	68 70 ----	202 ----	161 ----	94 ----	[3](617) ----
22. Hydrogen ion (pH), pH units.	Electrometric measurement.	239	460	178	129	[3](606)
23. Kjeldahl nitrogen (as N), milligrams per liter.	Digestion and distillation followed by nesslerization, titration, or electrode; automated digestion automated phenolate.	175 165 182	437 ----	---- ----	122 ----	[3](612) ----
METALS						
24. Aluminum—Total, milligrams per liter.	Digestion [15] followed by atomic absorption [16] or by colorimetric (Eriochrome Cyanine R).	92 ----	152 171	---- ----	[11] (19) ----	---- ----
25. Aluminum—Dissolved, milligrams per liter.	0.45 micron filtration [17] followed by referenced methods for total aluminum.	----	----	----	----	----
26. Antimony—Total, milligrams per liter.	Digestion [15] followed by atomic absorption.[16]	94	----	----	----	----
27. Antimony—Dissolved, milligrams per liter.	0.45 micron filtration [17] followed by referenced method for total antimony.	----	----	----	----	----
28. Arsenic—Total, milligrams per liter.	Digestion followed by silver diethyldithiocarbamate; or atomic absorption.[16 18]	---- 9 95	285 283 159	---- ---- ----	---- [11] (31) [11] (37)	---- ---- ----
29. Arsenic—Dissolved, milligrams per liter.	0.45 micron filtration [17] followed by referenced method for total arsenic.	----	----	----	----	----
30. Barium—Total, milligrams per liter.	Digestion [15] followed by atomic absorption.[16]	97	152	----	[52	----
31. Barium—Dissolved, milligrams per liter.	0.45 micron filtration [17] followed by referenced method for total barium.	----	----	----	----	----
32. Beryllium—Total, milligrams per liter.	Digestion [15] followed by atomic absorption [16] or by colorimetric (Aluminon).	99 ----	152 177	---- ----	53 ----	---- ----
33. Beryllium—Dissolved, milligrams per liter.	0.45 micron filtration [17] followed by referenced method for total beryllium.	----	----	----	----	----
34. Boron—Total, milligrams per liter.	Colorimetric (Curcumin)	13	287	----	----	----
35. Boron—Dissolved, milligrams per liter.	0.45 micron filtration [17] followed by referenced method for total boron.	----	----	----	----	----
36. Cadmium—Total, milligrams per liter.	Digestion [15] followed by atomic absorption [16] or by colorimetric (Dithizone).	101 ----	148 182	345 ----	62 ----	[3] (619) [10] (37) ----
37. Cadmium—Dissolved, milligrams per liter.	0.45 micron filtration [17] followed by referenced method for total cadmium.	----	----	----	----	----

See footnotes at end of table.

TABLE I.—*List of approved test procedures*[1]—Continued

Parameter and units	Method	References (page nos.) 1974 EPA methods	14th ed. standard methods	Pt. 31 1975 ASTM	USGS methods [2]	Other approved methods
METALS—Continued						
38. Calcium—Total, milligrams per liter.	Digestion [15] followed by atomic absorption; or EDTA titration.	103	148	345	66	
			189			
39. Calcium—Dissolved, milligrams per liter.	0.45 micron filtration [17] followed by referenced method for total calcium.					
40. Chromium VI, milligrams per liter.	Extraction and atomic absorption; colorimetric (Diphenylcarbazide).	89, 105			76	
			192		75	
41. Chromium VI—Dissolved, milligrams per liter.	0.45 micron filtration [17] followed by referenced method for chromium VI.					
42. Chromium—Total, milligrams per liter.	Digestion [15] followed by atomic absorption [16] or by colorimetric (Diphenylcarbazide).	105	148	345	78	[3] (619)
			192	286	77	
43. Chromium—Dissolved, milligrams per liter.	0.45 micron filtration [17] followed by referenced method for total chromium.					
44. Cobalt—Total, milligrams per liter.	Digestion [15] followed by atomic absorption.[16]	107	148	345	80	[10] (37)
45. Cobalt—Dissolved, milligrams per liter.	0.45 micron filtration [17] followed by referenced method for total cobalt.					
46. Copper—Total, milligrams per liter.	Digestion [15] followed by atomic absorption [16] or by colorimetric (Neocuproine).	108	148	345	83	[3] (619) [10] (37)
			196	293		
47. Copper—Dissolved, milligrams per liter.	0.45 micron filtration [17] followed by referenced method for total copper.					
48. Gold—Total, milligrams per liter.	Digestion [15] followed by atomic absorption.[19]					
49. Iridium—Total, milligrams per liter.	Digestion [15] followed by atomic absorption.[19]					
50. Iron—Total, milligrams per liter.	Digestion [15] followed by atomic absorption [16] or by colorimetric (Phenanthroline).	110	148	345	102	[3] (619)
			208	326		
51. Iron—Dissolved, milligrams per liter.	0.45 micron filtration [17] followed by referenced method for total iron.					
52. Lead—Total, milligrams per liter.	Digestion [15] followed by atomic absorption [16] or by colorimetric (Dithizone).	112	148	345	105	[3] (619)
			215			
53. Lead—Dissolved, milligrams per liter.	0.45 micron filtration [17] followed by referenced method for total lead.					
54. Magnesium—Total, milligrams per liter.	Digestion [15] followed by atomic absorption; or gravimetric.	114	148	345	109	[3] (619)
			221			
55. Magnesium—Dissolved milligrams per liter.	0.45 micron filtration [17] dollowed by referenced method for total magnesium.					
56. Manganese—Total milligrams per liter.	Digestion [15] followed by atomic absorption [16] or by colorimetric (Persulfate or periodate).	116	148	345	111	[3] (619)
			225, 227			
57. Manganese—Dissolved milligrams per liter.	0.45 micron filtration [17] followed by referenced method for total manganese.					
58. Mercury—Total, milligrams per liter.	Flameless atomic absorption.	118	156	338	[11] (51)	
59. Mercury—Dissolved, milligrams per liter.	0.45 micron filtration [17] followed by referenced method for total mercury.					

See footnotes at end of table.

TABLE I.—*List of approved test procedures* [1]—Continued

Parameter and units	Method	1974 EPA methods	14th ed. standard methods	References (page nos.) Pt. 31 1975 ASTM	USGS methods [2]	Other approved methods
METALS—Continued						
60. Molybdenum—Total, milligrams per liter.	Digestion [15] followed by atomic absorption.[16]	139		350		
61. Molybdenum—Dissolved, milligrams per liter.	0.45 micron filtration [17] followed by referenced method for total molybdenum.					
62. Nickel—Total, milligrams per liter.	Digestion [15] followed by atomic absorption [16] or by colorimetric (Heptoxime).	141	148	345	115	
		223				
63. Nickel—Dissolved, milligrams per liter.	0.45 micron filtration [17] followed by referenced method for total nickel.					
64. Osmium—Total, milligrams per liter.	Digestion [15] followed by atomic absorption.[19]					
65. Palladium—Total, milligrams per liter.	Digestion [15] followed by atomic absorption.[19]					
66. Platinum—Total, milligrams per liter.	Digestion [15] followed by atomic absorption.[19]					
67. Potassium—Total, milligrams per liter.	Digestion [15] followed by atomic absorption, colorimetric (Cobaltinitrite), or by flame photometric.	143			134	[3] (620)
			235			
			234	403		
68. Potassium—Dissolved, milligrams per liter.	0.45 micron filtration [17] followed by referenced method for total potassium.					
69. Rhodium—Total, milligrams per liter.	Digestion [15] followed by atomic absorption.[19]					
70. Ruthenium—Total, milligrams per liter.	Digestion [15] followed by atomic absorption.[19]					
71. Selenium—Total, milligrams per liter.	Digestion [15] followed by atomic absorption.[18 19]	145	159			
72. Selenium—Dissolved, milligrams per liter.	0.45 micron filtration [17] followed by referenced method for total selenium.					
73. Silica—Dissolved, milligrams per liter.	0.45 micron filtration [17] followed by colorimetric (Molybdosilicate).	274	487	398	139	
74. Silver—Total,[20] milligrams per liter.	Digestion [15] followed by atomic absorption [16] or by colorimetric (Dithizone).	146	148		142	[3] (619) [10] (37)
			243			
75. Silver—Dissolved,[20] milligrams per liter.	0.45 micron filtration [17] followed by referenced method for total sliver.					
76. Sodium—Total, milligrams per liter.	Digestion [15] followed by atomic absorption or by flame photometric.	147			143	[3] (621)
			250	403		
77. Sodium—Dissolved, milligrams per liter.	0.45 micron filtration [17] followed by referenced method for total sodium.					
78. Thallium—Total, milligrams per liter.	Digestion [15] followed by atomic absorption.[16]	149				
79. Thallium—Dissolved, milligrams per liter.	0.45 micron filtration [17] followed by referenced method for total thallium.					
80. Tin—Total, milligrams per liter.	Digestion [15] followed by atomic absorption.[16]	150			[11] (65)	
81. Tin—Dissolved, milligrams per liter.	0.45 micron filtration [17] followed by referenced method for total tin.					
82. Titanium—Total, milligrams per liter.	Digestion [15] followed by atomic absorption.[16]	151				
83. Titanium—Dissolved, milligrams per liter.	0.45 micron filtration [17] followed by referenced method for total titanium.					
84. Vanadium—Total, milligrams per liter.	Digestion [15] followed by atomic absorption [16] or by colorimetric (Gallic acid).	153	152			
			260	441	[11] (67)	

See footnotes at end of table.

TABLE I.—*List of approved test procedures* [1]—Continued

Parameter and units	Method	References (page nos.) 1974 EPA methods	14th ed. standard methods	Pt. 31 1975 ASTM	USGS methods [2]	Other approved methods
METALS—Continued						
85. Vanadium—Dissolved, milligrams per liter.	0.45 micron filtration [17] followed by referenced method for total vanadium.					
86. Zinc—Total, milligrams per liter.	Digestion [15] followed by atomic absorption [16] or by colorimetric (Dithizone).	155	148 265	345	159	[3](619) [10](37)
87. Zinc—Dissolved, milligrams per liter.	0.45 micron filtration [17] followed by referenced method for total zinc.					
88. Nitrate (as N), milligrams per liter.	Cadmium reduction; brucine sulfate; automated cadmium or hydrazine reduction.[21]	201 197 207	423 427 620	358	119	[3](614) [10](28)
89. Nitrite (as N), milligrams per liter.	Manual or automated colorimetric (Diazotization).	215	434		121	
90. Oil and grease, milligrams per liter.	Liquid-liquid extraction with trichloro-trifluoroethane-gravimetric.	229	515			
91. Organic carbon; total (TOC), milligrams per liter.	Combustion—Infrared method.[22]	236	532	467	[23] (4)	
92. Organic nitrogen (as N), milligrams per liter.	Kjeldahl nitrogen minus ammonia nitrogen.	175, 159	437		122	[3] (612, 614)
93. Orthophosphate (as P), milligrams per liter.	Manual or automated ascorbic acid reduction.	249 256	481 624	384	131	[3] (621)
94. Pentachlorophenol, milligrams per liter.	Gas chromatography [12]					
95. Pesticides, milligrams per liter.	....do.[12]		555	529	[23] (24)	
96. Phenols, milligrams per liter	Distillation followed by Colorimetric. (4AAP)	241	574	545		
97. Phosphorus (elemental), milligrams per liter.	Gas chromatography [24]					
98. Phosphorus; total (as P), milligrams per liter.	Persulfate digestion followed by manual or automated ascorbic acid reduction.	249 256	476, 481 624	384	133	[3] (621)
RADIOLOGICAL						
99. Alpha—Total, pCi per liter	Proportional or scintillation counter.		648	591	[11 25](75+78)	
100. Alpha—Counting error, pCi per liter.	....do		648	594	[11] (79)	
101. Beta—Total, pCi per liter	Proportional counter		648	601	[11 25](75+78)	
102. Beta—Counting error, pCi per liter.	....do		648	606	[11] (79)	
103. (a) Radium—Total, pCi per liter.	....do		661	661		
(b) ^{226}Ra, pCi per liter	Scintillation counter		667		[11] (81)	
RESIDUE						
104. Total, milligrams per liter	Gravimetric, 103 to 105° C.	270	91			
105. Total dissolved (filterable), milligrams per liter.	Glass fiber filtration, 180° C.	266	92			
106. Total suspended (nonfilterable), milligrams per liter.	Glass fiber filtration, 103 to 105° C.	268	94			
107. Settleable, milliliters per liter or milligrams per liter.	Volumetric or gravimetric		95			
108. Total volatile, milligrams per liter.	Gravimetric, 550° C	272	95			
109. Specific conductance, micromhos per centimeter at 25° C.	Wheatstone bridge conductimetry.	275	71	120	148	[3] (606)
110. Sulfate (as SO_4), milligrams per liter.	Gravimetric; turbidimetric; or automated colorimetric (barium chloranilate).	277 279	493 496	424 425		[3] (624) [3] (623)

See footnotes at end of table.

TABLE I.—*List of approved test procedures* [1]—Continued

Parameter and units	Method	1974 EPA methods	14th ed. standard methods	References (page nos.) Pt. 31 1975 ASTM	References (page nos.) USGS methods [2]	Other approved methods
RESIDUE—Continued						
111. Sulfide (as S), milligrams per liter.	Titrimetric—Iodine for levels greater than 1 mg per liter; Methylene blue photometric.	284	505 503		154	
112. Sulfite (as SO_3), milligrams per liter.	Titrimetric, iodine-iodate	285	508	435		
113. Surfactants, milligrams per liter.	Colorimetric (Methylene blue).	157	600	494	[23] (11)	
114. Temperature, degrees C	Calibrated glass or electrometric thermometer.	286	125		[26] (31)	
115. Turbidity, NTU	Nephelometric	295	132	223	156	

[1] Recommendations for sampling and preservation of samples according to parameter measured may be found in "Methods for Chemical Analysis of Water and Wastes, 1974" U.S. Environmental Protection Agency, table 2, pp. viii–xii.

[2] All page references for USGS methods, unless otherwise noted, are to Brown, E., Skougstad, M. W., and Fishman, M. J., "Methods for Collection and Analysis of Water Samples for Dissolved Minerals and Gases," U.S. Geological Survey Techniques of Water-Resources Inv., book 5, ch. A1, (1970).

[3] EPA comparable method may be found on indicated page of "Official Methods of Analysis of the Association of Official Analytical Chemists" methods manual, 12th ed. (1975).

[4] Manual distillation is not required if comparability data on representative effluent samples are on company file to show that this preliminary distillation step is not necessary; however, manual distillation will be required to resolve any controversies.

[5] The method used must be specified.

[6] The 5 tube MPN is used.

[7] Slack, K. V. and others, "Methods for Collection and Analysis of Aquatic Biological and Mircobiological Samples: U.S. Geological Survey Techniques of Water-Resources Inv. book 5, ch. A4 (1973)."

[8] Since the membrane filter technique usually yields low and variable recovery from chlorinated wastewaters, the MPN method will be required to resolve any controversies.

[9] Adequately tested methods for benzidine are not available. Until approved methods are available, the following interim method can be used for the estimation of benzidine: (1) "Method for Benzidine and Its Salts in Wastewaters," available from Environmental Monitoring and Support Laboratory, U.S. Environmental Protcetion Agency, Cincinnati, Ohio 45268.

[10] American National Standard on Photographic Processing Effluents, Apr. 2, 1975. Available from ANSI, 1430 Broadway, New York, N.Y. 10018.

[11] Fishman, M. J. and Brown, Eugene, "Selected Methods of the U.S. Geological Survey for Analysis of Wastewaters," (1976) open-file report 76–177.

[12] Procedures for pentachlorophenol, chlorinated organic compounds ,and pesticides can be obtained from the Environmental Monitoring and Support Lbaoratory, U.S. Environmental Protection Agency, Cincinnati, Ohio 45268.

[13] Color method (ADMI procedure) available from Environmental Monitoring and Support Lbaoratory, U.S. Environmental Protection Agency, Cincinnati, Ohio 45268.

[14] For samples suspected of having thiocyanate interference, magnesium chloride is used as the digestion catalyst. In the approved test procedure for cyanides, the recommended catalysts are replaced with 20 ml of a solution of 510 g/l magnesium chloride ($MgCl_2 \cdot 6H_2O$). This substitution will eliminate thiocyanate interference for both total cyanide and cyanide amendable to chlorination measurements.

[15] For the determination of total metals the sample is not filtered before processing. Because vigorous digestion procedures may result in a loss of certain metals through preciptation, a less vigorous treatment is recommended as given on p. 83 (4.1.4) of "Methods for Chemical Analysis of Water and Wastes" (1974). In those instances where a more vigorous digestion is desired the procedure on p. 82 (4.1.3) should be followed. For the measurement of the noble metal series (gold, iridium, osmium, palladium, platimum, rhodium and ruthenium), an aqua regia digestion is to be substituted as follows: Transfer a representitive aliquot of the well-mixed sample to a Griffin beaker and add 3 ml of concentrated redistilled HNO_3. Place the beaker on a steam bath and evaporate to dryness. Cool the beaker and cautiously add a 5 ml portion of aqua regia. (Aqua regia is prepared immediately before use by carefully adding 3 volumes of concentrated HCl to one volume of concentrated HNO_3.) Cover the beaker with a watch glass and return to the steam bath. Continue heating the covered beaker for 50 min. Remove cover and evaporate to dryness. Cool and take up the residue in a small quantity of 1:1 HCl. Wash down the beaker walls and watch glass with distilled water and filter the sample to remove silicates and other insoluble material that could clog the atomizer. Adjust the volm e to some predetermined value based on the expected metal concentration. The sample is now ready for analysis.

[16] As the various furnace devices (flameless AA) are essentially atomic absorption techniques, they are considered to be approved test methods. Methods of standard addition are to be followed as noted in p. 78 of "Methods for Chemical Analysis of Water and Wastes," 1974.

[17] Dissolved metals are defined as those constitutents which will pass though a 0.45 μm membrane filter. A prefiltration is permissible to free the sample from larger suspended solids. Filter the sample as soon as practical after collection using the first 50 to 100 ml to rinse the filter flask. (Glass or plastic filtering apparatus are recommended to avoid possible contamination.) Discard the portion used to rinse the flask and collect the required volume of filtrate. Acidify the filtrate with 1:1 redistilled HNO_3 to a pH of 2. Normally, 3 ml of (1:1) acid per liter should be sufficient to preserve the samples.

[18] See "Atomic Absorption Newsletter," vol. 13, 75 (1974). Available from Perkin-Elmer Corp., Main Ave., Norwalk, Conn. 06852.
[19] Method available from Environmental Monitoring and Support Laboratory, U.S. Environmental Protection Agency, Cincinnati, Ohio 45268.
[20] Recommended methods for the analysis of silver in industrial wastewaters at concentrations of 1 mg/1 and above are inadequate where silver exists as an inorganic halide. Silver halides such as the bromide and chloride are relatively insoluble in reagents such as nitric acid but are readily soluble in an aqueous buffer of sodium thiosulfate and sodium hydroxide to a pH of 12. Therefore, for levels of silver above 1 mg/1 20 ml of sample should be diluted to 100 ml by adding 40 ml each of 2M $Na_2S_2O_3$ and 2M NaOH. Standards should be prepared in the same manner. For levels of silver below 1 mg/1 the recommended method is satisfactory.
[21] An automated hydrazine reduction method is available from the Environmental Monitoring and Support Laboratory, U.S. Environmental Protection Agency, Cincinnati, Ohio 45268.
[22] A number of such systems manufactured by various companies are considered to be comparable in their performance. In addition, another technique, based on combustion-methane detection is also acceptable.
[23] Goerlitz, D., Brown, E., "Methods for Analysis of Organic Substances in Water": U.S. Geological Survey Techniques of Water-Resources Inv., book 5, ch. A3 (1972).
[24] R. F. Addison and R. G. Ackman, "Direct Determination of Elemental Phosphorus by Gas-Liquid Chromatography," "Journal of Chromatography," vol. 47, No. 3, pp. 421-426, 1970.
[25] The method found on p. 75 measures only the dissolved portion while the method on p. 78 measures only suspended. Therefore, the 2 results must be added together to obtain "total."
[26] Stevens, H. H., Ficke, J. F., and Smoot, G. F., "Water Temperature—Influential Factors, Field Measurement and Data Presentation: U.S. Geological Survey Techniques of Water Resources Inv., book 1 (1975)."

[38 FR 28758, Oct. 16, 1973, as amended at 41 FR 52781, Dec. 1, 1976; 42 FR 3306, Jan. 18, 1977]

§ 136.4 Application for alternate test procedures.

(a) Any person may apply to the Regional Administrator in the Region where the discharge occurs for approval of an alternative test procedure.

(b) When the discharge for which an alternative test procedure is proposed occurs within a State having a permit program approved pursuant to section 402 of the Act, the applicant shall submit his application to the Regional Administrator through the Director of the State agency having responsibility for issuance of NPDES permits within such State.

(c) Unless and until printed application forms are made available, an application for an alternate test procedure may be made by letter in triplicate. Any application for an alternate test procedure under this paragraph (c) shall:

(1) Provide the name and address of the responsible person or firm making the discharge (if not the applicant) and the applicable ID number of the existing or pending permit, issuing agency, and type of permit for which the alternate test procedure is requested, and the discharge serial number.

(2) Identify the pollutant or parameter for which approval of an alternate testing procedure is being requested.

(3) Provide justification for using testing procedures other than those specified in Table I.

(4) Provide a detailed description of the proposed alternate test procedure, together with references to published studies of the applicability of the alternate test procedure to the effluents in question.

(d) An application for approval of an alternate test procedure for nationwide use may be made by letter in triplicate to the Director, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268. Any application for an alternate test procedure under this paragraph (d) shall:

(1) Provide the name and address of the responsible person or firm making the application.

(2) Identify the pollutant(s) or parameter(s) for which nationwide approval of an alternate testing procedure is being requested.

(3) Provide a detailed description of the proposed alternate procedure, together with references to published or other studies confirming the general applicability of the alternate test procedure to the pollutant(s) or parameter(s) in waste water discharges from representative and specified industrial or other categories.

(4) Provide comparability data for the performance of the proposed alternate test procedure compared to the performance of the approved test procedures.

[38 FR 28760, Oct. 16, 1973, as amended at 41 FR 52785, Dec. 1, 1976]

§ 136.5 Approval of alternate test procedures.

(a) The Regional Administrator of the region in which the discharge will

occur has final responsibility for approval of any alternate test procedure proposed by the responsible person or firm making the discharge.

(b) Within thirty days of receipt of an application, the Director will forward such application proposed by the responsible person or firm making the discharge, together with his recommendations, to the Regional Administrator. Where the Director recommends rejection of the application for scientific and technical reasons which he provides, the Regional Administrator shall deny the application, and shall forward a copy of the rejected application and his decision to the Director of the State Permit Program and to the Director of the Environmental Monitoring and Support Laboratory, Cincinnati.

(c) Before approving any application for an alternate test procedure proposed by the responsible person or firm making the discharge, the Regional Administrator shall forward a copy of the application to the Director of the Environmental Monitoring and Support Laboratory, Cincinnati.

(d) Within ninety days of receipt by the Regional Administrator of an application for an alternate test procedure, proposed by the responsible person or firm making the discharge, the Regional Administrator shall notify the applicant and the appropriate State agency of approval or rejection, or shall specify the additional information which is required to determine whether to approve the proposed test procedure. Prior to the expiration of such ninety day period, a recommendation providing the scientific and other technical basis for acceptance or rejection will be forwarded to the Regional Administrator by the Director of the Environmental Monitoring and Support Laboratory, Cincinnati. A copy of all approval and rejection notifications will be forwarded to the Director, Environmental Monitoring and Support Laboratory, Cincinnati, for the purposes of national coordination.

(e) Within ninety days of the receipt by the Director of the Environmental Monitoring and Support Laboratory, Cincinnati of an application for an alternate test procedure for nationwide use, the Director of the Environmental Monitoring and Support Laboratory, Cincinnati shall notify the applicant of his recommendation to the Administrator to approve or reject the application, or shall specify additional information which is required to determine whether to approve the proposed test procedure. After such notification, an alternate method determined by the Administrator to satisfy the applicable requirements of this part shall be approved for nationwide use to satisfy the requirements of this subchapter; alternate test procedures determined by the Administrator not to meet the applicable requirements of this part shall be rejected. Notice of these determinations shall be submitted for publication in the FEDERAL REGISTER not later than 15 days after such notification and determination is made.

[38 FR 28760, Oct. 16, 1973, as amended at 41 FR 52785, Dec. 1, 1976]

APPENDIX C

Drinking Water Regulations for Conventional and Radioactive Pollutants (Reproduced from Code of Federal Regulations 40 CFT 141).

PART 141—NATIONAL INTERIM PRIMARY DRINKING WATER REGULATIONS

Subpart A—General

Subpart B—Maximum Contaminant Levels

Subpart C—Monitoring and Analytical Requirements

Subpart D—Reporting, Public Notification and Record Keeping

Subpart E—Special Monitoring Regulations for Organic Chemicals

AUTHORITY: Secs. 1412, 1414, 1445, and 1450 of the Public Health Service Act, 88 Stat. 1660 (42 U.S.C. 300g–1, 300g–3, 300j–4, and 300j–9).

SOURCE: 40 FR 59570, Dec. 24, 1975, unless otherwise noted.

Subpart A—General

§ 141.1 Applicability.

This part establishes primary drinking water regulations pursuant to section 1412 of the Public Health Service Act, as amended by the Safe Drinking Water Act (Pub. L. 93–523); and related regulations applicable to public water systems.

§ 141.2 Definitions.

As used in this part, the term:

(a) "Act" means the Public Health Service Act, as amended by the Safe Drinking Water Act, Pub. L. 93–523.

(b) "Contaminant" means any physical, chemical, biological, or radiological substance or matter in water.

(c) "Maximum contaminant level" means the maximum permissible level of a contaminant in water which is delivered to the free flowing outlet of the ultimate user of a public water system, except in the case of turbidity where the maximum permissible level is measured at the point of entry to the distribution system. Contaminants added to the water under circumstances controlled by the user, except those resulting from corrosion of piping and plumbing caused by water quality, are excluded from this definition.

(d) "Person" means an individual, corporation, company, association, partnership, State, municipality, or Federal agency.

(e) "Public water system" means a system for the provision to the public of piped water for human consumption, if such system has at least fifteen service connections or regularly serves an average of at least twenty-five individuals daily at least 60 days out of the year. Such term includes (1) any collection, treatment, storage, and distribution facilities under control of the operator of

such system and used primarily in connection with such system, and (2) any collection or pretreatment storage facilities not under such control which are used primarily in connection with such system. A public water system is either a "community water system" or a "non-community water system."

(i) "Community water system" means a public water system which serves at least 15 service connections used by year-round residents or regularly serves at least 25 year-round residents.

(ii) "Non-community water system" means a public water system that is not a community water system.

(f) "Sanitary survey" means an on-site review of the water source, facilities, equipment, operation and maintenance of a public water system for the purpose of evaluating the adequacy of such source, facilities, equipment, operation and maintenance for producing and distributing safe drinking water.

(g) "Standard sample" means the aliquot of finished drinking water that is examined for the presence of coliform bacteria.

(h) "State" means the agency of the State government which has jurisdiction over public water systems. During any period when a State does not have primary enforcement responsibility pursuant to Section 1413 of the Act, the term "State" means the Regional Administrator, U.S. Environmental Protection Agency.

(i) "Supplier of water" means any person who owns or operates a public water system.

(j) "Dose equivalent" means the product of the absorbed dose from ionizing radiation and such factors as account for differences in biological effectiveness due to the type of radiation and its distribution in the body as specified by the International Commission on Radiological Units and Measurements (ICRU).

(k) "Rem" means the unit of dose equivalent from ionizing radiation to the total body or any internal organ or organ system. A "millirem (mrem)" is 1/1000 of a rem.

(l) "Picocurie (pCi)" means the quantity of radioactive material producing 2.22 nuclear transformations per minute.

(m) "Gross alpha particle activity" means the total radioactivity due to alpha particle emission as inferred from measurements on a dry sample.

(n) "Man-made beta particle and photon emitters" means all radionuclides emitting beta particles and/or photons listed in Maximum Permissible Body Burdens and Maximum Permissible Concentration of Radionuclides in Air or Water for Occupational Exposure, NBS Handbook 69, except the daughter products of thorium–232, uranium–235 and uranium–238.

(o) "Gross beta particle activity" means the total radioactivity due to beta particle emission as inferred from measurements on a dry sample.

[40 FR 59570, Dec. 24, 1975, as amended at 41 FR 28403, July 9, 1976]

§ 141.3 Coverage.

This part shall apply to each public water system, unless the public water system meets all of the following conditions:

(a) Consists only of distribution and storage facilities (and does not have any collection and treatment facilities);

(b) Obtains all of its water from, but is not owned or operated by, a public water system to which such regulations apply:

(c) Does not sell water to any person; and

(d) Is not a carrier which conveys passengers in interstate commerce.

§ 141.4 Variances and exemptions.

Variances or exemptions from certain provisions of these regulations may be granted pursuant to Sections 1415 and 1416 of the Act by the entity with primary enforcement responsibility. Provisions under Part 142, *National Interim Primary Drinking Water Regulations Implementation*—Subpart E (Variances) and Subpart F (Exemptions)—apply where EPA has primary enforcement responsibility.

§ 141.5 Siting requirements.

Before a person may enter into a financial commitment for or initiate construction of a new public water system or increase the capacity of an existing public water system, he shall notify the

State and, to the extent practicable, avoid locating part or all of the new or expanded facility at a site which:

(a) Is subject to a significant risk from earthquakes, floods, fires or other disasters which could cause a breakdown of the public water system or a portion thereof; or

(b) Except for intake structures, is within the floodplain of a 100-year flood or is lower than any recorded high tide where appropriate records exist.

The U.S. Environmental Protection Agency will not seek to override land use decisions affecting public water systems siting which are made at the State or local government levels.

§ 141.6 Effective date.

The regulations set forth in this part shall take effect 18 months after the date of promulgation.

Subpart B—Maximum Contaminant Levels

§ 141.11 Maximum contaminant levels for inorganic chemicals.

(a) The maximum contaminant level for nitrate is applicable to both community water systems and non-community water systems. The levels for the other inorganic chemicals apply only to community water systems. Compliance with maximum contaminant levels for inorganic chemicals is calculated pursuant to § 141.23.

(b) The following are the maximum contaminant levels for inorganic chemicals other than fluoride:

Contaminant	*Level, milligrams per liter*
Arsenic	0.05
Barium	1.
Cadmium	0.010
Chromium	0.05
Lead	0.05
Mercury	0.002
Nitrate (as N)	10.
Selenium	0.01
Silver	0.05

(c) When the annual average of the maximum daily air temperatures for the location in which the community water system is situated is the following, the maximum contaminant levels for fluoride are:

Temperature Degrees Fahrenheit	Degrees Celsius	Level, milligrams per liter
53.7 and below	12.0 and below	2.4
53.8 to 58.3	12.1 to 14.6	2.2
58.4 to 63.8	14.7 to 17.6	2.0
63.9 to 70.6	17.7 to 21.4	1.8
70.7 to 79.2	21.5 to 26.2	1.6
79.3 to 90.5	26.3 to 32.5	1.4

§ 141.12 Maximum contaminant levels for organic chemicals.

The following are the maximum contaminant levels for organic chemicals. They apply only to community water systems. Compliance with maximum contaminant levels for organic chemicals is calculated pursuant to § 141.24.

	Level, milligrams per liter
(a) Chlorinated hydrocarbons:	
Endrin (1,2,3,4,10, 10-hexachloro-6,7-epoxy-1,4, 4a,5,6,7,8,8a-octahydro-1,4-endo, endo-5,8 - dimethano naphthalene).	0.0002
Lindane (1,2,3,4,5,6-hexachlorocyclohexane, gamma isomer).	0.004
Methoxychlor (1,1,1-Trichloro-2, 2 - bis [p-methoxyphenyl] ethane).	0.1
Toxaphene ($C_{10}H_{10}Cl_8$-Technical chlorinated camphene, 67–69 percent chlorine).	0.005
(b) Chlorophenoxys:	
2,4 - D, (2,4-Dichlorophenoxyacetic acid).	0.1
2,4,5-TP Silvex (2,4,5-Trichlorophenoxypropionic acid).	0.01

§ 141.13 Maximum contaminant levels for turbidity.

The maximum contaminant levels for turbidity are applicable to both community water systems and non-community water systems using surface water sources in whole or in part. The maximum contaminant levels for turbidity in drinking water, measured at a representative entry point(s) to the distribution system, are:

(a) One turbidity unit (TU), as determined by a monthly average pursuant to § 141.22, except that five or fewer turbidity units may be allowed if the supplier of water can demonstrate to the State that the higher turbidity does not do any of the following:

(1) Interfere with disinfection;
(2) Prevent maintenance of an effective disinfectant agent throughout the distribution system; or
(3) Interfere with microbiological determinations.
(b) Five turbidity units based on an average for two consecutive days pursuant to § 141.22.

§ 141.14 Maximum microbiological contaminant levels.

The maximum contaminant levels for coliform bacteria, applicable to community water systems and non-community water systems, are as follows:
(a) When the membrane filter technique pursuant to § 141.21(a) is used, the number of coliform bacteria shall not exceed any of the following:
(1) One per 100 milliliters as the arithmetic mean of all samples examined per month pursuant to § 141.21 (b) or (c);
(2) Four per 100 milliliters in more than one sample when less than 20 are examined per month; or
(3) Four per 100 milliliters in more than five percent of the samples when 20 or more are examined per month.
(b)(1) When the fermentation tube method and 10 milliliter standard portions pursuant to § 141.21(a) are used, coliform bacteria shall not be present in any of the following:
(i) More than 10 percent of the portions in any month pursuant to § 141.21 (b) or (c);
(ii) Three or more portions in more than one sample when less than 20 samples are examined per month; or
(iii) Three or more portions in more than five percent of the samples when 20 or more samples are examined per month.
(2) When the fermentation tube method and 100 milliliter standard portions pursuant to § 141.21(a) are used, coliform bacteria shall not be present in any of the following:
(i) More than 60 percent of the portions in any month pursuant to § 141.21 (b) or (c);
(ii) Five portions in more than one sample when less than five samples are examined per month; or
(iii) Five portions in more than 20 percent of the samples when five or more samples are examined per month.
(c) For community or non-community systems that are required to sample at a rate of less than 4 per month, compliance with paragraphs (a), (b)(1), or (b)(2) of this section shall be based upon sampling during a 3 month period, except that, at the discretion of the State, compliance may be based upon sampling during a one-month period.

§ 141.15 Maximum contaminant levels for radium-226, radium-228, and gross alpha particle radioactivity in community water systems.

The following are the maximum contaminant levels for radium-226, radium-228, and gross alpha particle radioactivity:
(a) Combined radium-226 and radium-228—5 pCi/1.
(b) Gross alpha particle activity (including radium-226 but excluding radon and uranium)—15 pCi/1.
[41 FR 28404, July 9, 1976]

§ 141.16 Maximum contaminant levels for beta particle and photon radioactivity from man-made radionuclides in community water systems.

(a) The average annual concentration of beta particle and photon radioactivity from man-made radionuclides in drinking water shall not produce an annual dose equivalent to the total body or any internal organ greater than 4 millirem/year.
(b) Except for the radionuclides listed in Table A, the concentration of man-made radionuclides causing 4 mrem total body or organ dose equivalents shall be calculated on the basis of a 2 liter per day drinking water intake using the 168 hour data listed in *"Maximum Permissible Body Burdens and Maximum Permissible Concentration of Radionuclides in Air or Water for Occupational Exposure,"* NBS Handbook 69 as amended August 1963, U.S. Department of Commerce. If two or more radionuclides are present, the sum of their annual dose equivalent to the total body or to any organ shall not exceed 4 millirem/year.

TABLE A.—*Average annual concentrations assumed to produce a total body or organ dose of 4 mrem/yr*

Radionuclide	Critical organ	pCi per liter
Tritium	Total body	20,000
Strontium-90	Bone marrow	8

[41 FR 28404, July 9, 1976]

Subpart C—Monitoring and Analytical Requirements

§ 141.21 Microbiological contaminant sampling and analytical requirements.

(a) Suppliers of water for community water systems and non-community water systems shall analyze for coliform bacteria for the purpose of determining compliance with § 141.14. Analyses shall be conducted in accordance with the analytical recommendations set forth in "Standard Methods for the Examination of Water and Wastewater," American Public Health Association, 13th Edition, pp. 662–688, except that a standard sample size shall be employed. The standard sample used in the membrane filter procedure shall be 100 milliliters. The standard sample used in the 5 tube most probable number (MPN) procedure (fermentation tube method) shall be 5 times the standard portion. The standard portion is either 10 milliliters or 100 milliliters as described in § 141.14 (b) and (c). The samples shall be taken at points which are representative of the conditions within the distribution system.

(b) The supplier of water for a community water system shall take coliform density samples at regular time intervals, and in number proportionate to the population served by the system. In no event shall the frequency be less than as set forth below:

Population served:	*Minimum number of samples per month*
25 to 1,000	1
1,001 to 2,500	2
2,501 to 3,300	3
3,301 to 4,100	4
4,101 to 4,900	5
4,901 to 5,800	6
5,801 to 6,700	7
6,701 to 7,600	8
7,601 to 8,500	9
8,501 to 9,400	10
9,401 to 10,300	11
10,301 to 11,100	12
11,101 to 12,000	13
12,001 to 12,900	14
12,901 to 13,700	15
13,701 to 14,600	16
14,601 to 15,500	17
15,501 to 16,300	18
16,301 to 17,200	19
17,201 to 18,100	20
18,101 to 18,900	21
18,901 to 19,800	22
19,801 to 20,700	23
20,701 to 21,500	24
21,501 to 22,300	25
22,301 to 23,200	26
23,201 to 24,000	27
24,001 to 24,900	28
24,901 to 25,000	29
25,001 to 28,000	30
28,001 to 33,000	35
33,001 to 37,000	40
37,001 to 41,000	45
41,001 to 46,000	50
46,001 to 50,000	55
50,001 to 54,000	60
54,001 to 59,000	65
59,001 to 64,000	70
64,001 to 70,000	75
70,001 to 76,000	80
76,001 to 83,000	85
83,001 to 90,000	90
90,001 to 96,000	95
96,001 to 111,000	100
111,001 to 130,000	110
130,001 to 160,000	120
160,001 to 190,000	130
190,001 to 220,000	140
220,001 to 250,000	150
250,001 to 290,000	160
290,001 to 320,000	170
320,001 to 360,000	180
360,001 to 410,000	190
410,001 to 450,000	200
450,001 to 500,000	210
500,001 to 550,000	220
550,001 to 600,000	230
600,001 to 660,000	240
660,001 to 720,000	250
720,001 to 780,000	260
780,001 to 840,000	270
840,001 to 910,000	280
910,001 to 970,000	290
970,001 to 1,050,000	300
1,050,001 to 1,140,000	310
1,140,001 to 1,230,000	320
1,230,001 to 1,320,000	330
1,320,001 to 1,420,000	340
1,420,001 to 1,520,000	350
1,520,001 to 1,630,000	360
1,630,001 to 1,730,000	370
1,730,001 to 1,850,000	380

Population served:	*Minimum number of samples per month*
1,850,001 to 1,970,000	390
1,970,001 to 2,060,000	400
2,060,001 to 2,270,000	410
2,270,001 to 2,510,000	420
2,510,001 to 2,750,000	430
2,750,001 to 3,020,000	440
3,020,001 to 3,320,000	450
3,320,001 to 3,620,000	460
3,620,001 to 3,960,000	470
3,960,001 to 4,310,000	480
4,310,001 to 4,690,000	490
4,690,001 or more	500

Based on a history of no coliform bacterial contamination and on a sanitary survey by the State showing the water system to be supplied solely by a protected ground water source and free of sanitary defects, a community water system serving 25 to 1,000 persons, with written permission from the State, may reduce this sampling frequency except that in no case shall it be reduced to less than one per quarter.

(c) The supplier of water for a non-community water system shall sample for coliform bacteria in each calendar quarter during which the system provides water to the public. Such sampling shall begin within two years after the effective date of this part. If the State, on the basis of a sanitary survey, determines that some other frequency is more appropriate, that frequency shall be the frequency required under these regulations. Such frequency shall be confirmed or changed on the basis of subsequent surveys.

(d) (1) When the coliform bacteria in a single sample exceed four per 100 milliliters (§ 141.14(a)), at least two consecutive daily check samples shall be collected and examined from the same sampling point. Additional check samples shall be collected daily, or at a frequency established by the State, until the results obtained from at least two consecutive check samples show less than one coliform bacterium per 100 milliliters.

(2) When coliform bacteria occur in three or more 10 ml portions of a single sample (§ 141.14(b)(1)), at least two consecutive daily check samples shall be collected and examined from the same sampling point. Additional check samples shall be collected daily, or at a frequency established by the State, until the results obtained from at least two consecutive check samples show no positive tubes.

(3) When coliform bacteria occur in all five of the 100 ml portions of a single sample (§ 141.14(b)(2)), at least two daily check samples shall be collected and examined from the same sampling point. Additional check samples shall be collected daily, or at a frequency established by the State, until the results obtained from at least two consecutive check samples show no positive tubes.

(4) The location at which the check samples were taken pursuant to paragraphs (d) (1), (2), or (3) of this section shall not be eliminated from future sampling without approval of the State. The results from all coliform bacterial analyses performed pursuant to this subpart, except those obtained from check samples and special purpose samples, shall be used to determine compliance with the maximum contaminant level for coliform bacteria as established in § 141.14. Check samples shall not be included in calculating the total number of samples taken each month to determine compliance with § 141.21 (b) or (c).

(e) When the presence of coliform bacteria in water taken from a particular sampling point has been confirmed by any check samples examined as directed in paragraphs (d) (1), (2), or (3) of this section, the supplier of water shall report to the State within 48 hours.

(f) When a maximum contaminant level set forth in paragraphs (a), (b) or (c) of § 141.14 is exceeded, the supplier of water shall report to the State and notify the public as prescribed in § 141.31 and § 141.32.

(g) Special purpose samples, such as those taken to determine whether disinfection practices following pipe placement, replacement, or repair have been sufficient, shall not be used to determine compliance with § 141.14 or § 141.21 (b) or (c).

(h) A supplier of water of a community water system or a non-community water system may, with the approval of the State and based upon a sanitary survey, substitute the use of chlorine residual monitoring for not more than 75 percent of the samples required to be taken by paragraph (b) of this

section, *Provided,* That the supplier of water takes chlorine residual samples at points which are representative of the conditions within the distribution system at the frequency of at least four for each substituted microbiological sample. There shall be at least daily determinations of chlorine residual. When the supplier of water exercises the option provided in this paragraph (h) of this section, he shall maintain no less than 0.2 mg/1 free chlorine throughout the public water distribution system. When a particular sampling point has been shown to have a free chlorine residual less than 0.2 mg/l, the water at that location shall be retested as soon as practicable and in any event within one hour. If the original analysis is confirmed, this fact shall be reported to the State within 48 hours. Also, if the analysis is confirmed, a sample for coliform bacterial analysis must be collected from that sampling point as soon as practicable and preferably within one hour, and the results of such analysis reported to the State within 48 hours after the results are known to the supplier of water. Analyses for residual chlorine shall be made in accordance with "Standard Methods for the Examination of Water and Wastewater," 13th Ed., pp. 129–132. Compliance with the maximum contaminant levels for coliform bacteria shall be determined on the monthly mean or quarterly mean basis specified in § 141.14, including those samples taken as a result of failure to maintain the required chlorine residual level. The State may withdraw its approval of the use of chlorine residual substitution at any time.

§ 141.22 Turbidity sampling and analytical requirements.

(a) Samples shall be taken by suppliers of water for both community water systems and non-community water systems at a representative entry point(s) to the water distribution system at least once per day, for the purpose of making turbidity measurements to determine compliance with § 141.13. The measurement shall be made by the Nephelometric Method in accordance with the recommendations set forth in "Standard Methods for the Examination of Water and Wastewater," American Public Health Association, 13th Edition, pp. 350–353, or "Methods for Chemical Analysis of Water and Wastes," pp. 295–298, Environmental Protection Agency, Office of Technology Transfer, Washington, D.C. 20460, 1974.

(b) If the result of a turbidity analysis indicates that the maximum allowable limit has been exceeded, the sampling and measurement shall be confirmed by resampling as soon as practicable and preferably within one hour. If the repeat sample confirms that the maximum allowable limit has been exceeded, the supplier of water shall report to the State within 48 hours. The repeat sample shall be the sample used for the purpose of calculating the monthly average. If the monthly average of the daily samples exceeds the maximum allowable limit, or if the average of two samples taken on consecutive days exceeds 5 TU, the supplier of water shall report to the State and notify the public as directed in §§ 141.31 and 141.32.

(c) Sampling for non-community water systems shall begin within two years after the effective date of this part.

(d) The requirements of this § 141.22 shall apply only to public water systems which use water obtained in whole or in part from surface sources

§ 141.23 Inorganic chemical sampling and analytical requirements.

(a) Analyses for the purpose of determining compliance with § 141.11 are required as follows:

(1) Analyses for all community water systems utilizing surface water sources shall be completed within one year following the effective date of this part. These analyses shall be repeated at yearly intervals.

(2) Analyses for all community water systems utilizing only ground water sources shall be completed within two years following the effective date of this part. These analyses shall be repeated at three-year intervals.

(3) For non-community water systems, whether supplied by surface or ground water sources, analyses for nitrate shall be completed within two years following the effective date of this part. These analyses shall be repeated at intervals determined by the State.

(b) If the result of an analysis made pursuant to paragraph (a) of this section indicates that the level of any contaminant listed in § 141.11 exceeds the maximum contaminant level, the supplier of water shall report to the State within 7 days and initiate three additional analyses at the same sampling point within one month.

(c) When the average of four analyses made pursuant to paragraph (b) of this section, rounded to the same number of significant figures as the maximum contaminant level for the substance in question, exceeds the maximum contaminant level, the supplier of water shall notify the State pursuant to § 141.31 and give notice to the public pursuant to § 141.32. Monitoring after public notification shall be at a frequency designated by the State and shall continue until the maximum contaminant level has not been exceeded in two successive samples or until a monitoring schedule as a condition to a variance, exemption or enforcement action shall become effective.

(d) The provisions of paragraphs (b) and (c) of this section notwithstanding, compliance with the maximum contaminant level for nitrate shall be determined on the basis of the mean of two analyses. When a level exceeding the maximum contaminant level for nitrate is found, a second analysis shall be initiated within 24 hours, and if the mean of the two analyses exceeds the maximum contaminant level, the supplier of water shall report his findings to the State pursuant to § 141.31 and shall notify the public pursuant to § 141.32.

(e) For the initial analyses required by paragraph (a)(1), (2) or (3) of this section, data for surface waters acquired within one year prior to the effective date and data for ground waters acquired within 3 years prior to the effective date of this part may be substituted at the discretion of the State.

(f) Analyses conducted to determine compliance with § 141.11 shall be made in accordance with the following methods:

(1) Arsenic—Atomic Absorption Method, "Methods for Chemical Analysis of Water and Wastes," pp. 95–96, Environmental Protection Agency, Office of Technology Transfer, Washington, D.C. 20460, 1974.

(2) Barium—Atomic Absorption Method, "Standard Methods for the Examination of Water and Wastewater," 13th Edition, pp. 210–215, or "Methods for Chemical Analysis of Water and Wastes," pp. 97–98, Environmental Protection Agency, Office of Technology Transfer, Washington, D.C. 20460, 1974.

(3) Cadmium—Atomic Absorption Method, "Standard Methods for the Examination of Water and Wastewater," 13th Edition, pp. 210–215, or "Methods for Chemical Analysis of Water and Wastes," pp. 101–103, Environmental Protection Agency, Office of Technology Transfer, Washington, D.C. 20460, 1974.

(4) Chromium—Atomic Absorption Method, "Standard Methods for the Examination of Water and Wastewater," 13th Edition, pp. 210–215, or "Methods for Chemical Analysis of Water and Wastes," pp. 105–106, Environmental Protection Agency, Office of Technology Transfer, Washington, D.C. 20460, 1974.

(5) Lead—Atomic Absorption Method, "Standard Methods for the Examination of Water and Wastewater," 13th Edition, pp. 210–215, or "Methods for Chemical Analysis of Water and Wastes," pp. 112–113, Environmental Protection Agency, Office of Technology Transfer, Washington, D.C. 20460, 1974.

(6) Mercury—Flameless Atomic Absorption Method, "Methods for Chemical Analysis of Water and Wastes," pp. 118–126, Environmental Protection Agency, Office of Technology Transfer, Washington, D.C. 20460, 1974.

(7) Nitrate—Brucine Colorimetric Method, "Standard Methods for the Examination of Water and Wastewater," 13th Edition, pp. 461–464, or Cadmium Reduction Method, "Methods for Chemical Analysis of Water and Wastes," pp. 201–206, Environmental Protection Agency, Office of Technology Transfer, Washington, D.C. 20460, 1974.

(8) Selenium—Atomic Absorption Method, "Methods for Chemical Analysis of Water and Wastes," p. 145, Environmental Protection Agency, Office of Technology Transfer, Washington, D.C. 20460, 1974.

(9) Silver—Atomic Absorption Method, "Standard Methods for the Examination of Water and Wastewater", 13th Edition, pp. 210–215, or "Methods for Chemical Analysis of Water and Wastes", p. 146, Environmental Protec-

tion Agency, Office of Technology Transfer, Washington, D.C. 20460, 1974.

(10) Fluoride—Electrode Method, "Standard Methods for the Examination of Water and Wastewater", 13th Edition, pp. 172–174, or "Methods for Chemical Analysis of Water and Wastes," pp. 65–67, Environmental Protection Agency, Office of Technology Transfer, Washington, D.C. 20460, 1974, or Colorimetric Method with Preliminary Distillation, "Standard Methods for the Examination of Water and Wastewater," 13th Edition, pp. 171–172 and 174–176, or "Methods for Chemical Analysis of Water and Wastes," pp. 59–60, Environmental Protection Agency, Office of Technology Transfer, Washington, D.C. 20460, 1974.

§ 141.24 Organic chemical sampling and analytical requirements.

(a) An analysis of substances for the purpose of determining compliance with § 141.12 shall be made as follows:

(1) For all community water systems utilizing surface water sources, analyses shall be completed within one year following the effective date of this part. Samples analyzed shall be collected during the period of the year designated by the State as the period when contamination by pesticides is most likely to occur. These analyses shall be repeated at intervals specified by the State but in no event less frequently than at three year intervals.

(2) For community water systems utilizing only ground water sources, analyses shall be completed by those systems specified by the State.

(b) If the result of an analysis made pursuant to paragraph (a) of this section indicates that the level of any contaminant listed in § 141.12 exceeds the maximum contaminant level, the supplier of water shall report to the State within 7 days and initiate three additional analyses within one month.

(c) When the average of four analyses made pursuant to paragraph (b) of this section, rounded to the same number of significant figures as the maximum contaminant level for the substance in question, exceeds the maximum contaminant level, the supplier of water shall report to the State pursuant to § 141.31 and give notice to the public pursuant to § 141.32. Monitoring after public notification shall be at a frequency designated by the State and shall continue until the maximum contaminant level has not been exceeded in two successive samples or until a monitoring schedule as a condition to a variance, exemption or enforcement action shall become effective.

(d) For the initial analysis required by paragraph (a) (1) and (2) of this section, data for surface water acquired within one year prior to the effective date of this part and data for ground water acquired within three years prior to the effective date of this part may be substituted at the discretion of the State.

(e) Analyses made to determine compliance with § 141.12(a) shall be made in accordance with "Method for Organochlorine Pesticides in Industrial Effluents," MDQARL, Environmental Protection Agency, Cincinnati, Ohio, November 28, 1973.

(f) Analyses made to determine compliance with § 141.12(b) shall be conducted in accordance with "Methods for Chlorinated Phenoxy Acid Herbicides in Industrial Effluents," MDQARL, Environmental Protection Agency, Cincinnati, Ohio, November 28, 1973.

§ 141.25 Analytical Methods for Radioactivity.

(a) The methods specified in *Interim Radiochemical Methodology for Drinking Water,* Environmental Monitoring and Support Laboratory, EPA–600/4–75–008, USEPA, Cincinnati, Ohio 45268, or those listed below, are to be used to determine compliance with §§ 141.15 and 141.16 (radioactivity) except in cases where alternative methods have been approved in accordance with § 141.27.

(1) Gross Alpha and Beta—Method 302 "Gross Alpha and Beta Radioactivity in Water" *Standard Methods for the Examination of Water and Wastewater,* 13th Edition, American Public Health Association, New York, N.Y., 1971.

(2) Total Radium—Method 304 "Radium in Water by Precipitation" Ibid.

(3) Radium-226—Method 305 "Radium-226 by Radon in Water" Ibid.

(4) Strontium-89,90 — Method 303 "Total Strontium and Strontium-90 in Water" Ibid.

(5) Tritium—Method 306 "Tritium in Water" Ibid.

(6) Cesium-134 — ASTM D–2459 "Gamma Spectrometry in Water," *1975 Annual Book of ASTM Standards, Water and Atmospheric Analysis,* Part 31, American Society for Testing and Materials, Philadelphia, PA. (1975).

(7) Uranium—ASTM D–2907 "Microquantities of Uranium in Water by Fluorometry," Ibid.

(b) When the identification and measurement of radionuclides other than those listed in paragraph (a) is required, the following references are to be used, except in cases where alternative methods have been approved in accordance with § 141.27.

(1) *Procedures for Radiochemical Analysis of Nuclear Reactor Aqueous Solutions,* H. L. Krieger and S. Gold, EPA–R4–73–014. USEPA, Cincinnati, Ohio, May 1973.

(2) *HASL Procedure Manual,* Edited by John H. Harley. HASL 300, ERDA Health and Safety Laboratory, New York, N.Y., 1973.

(c) For the purpose of monitoring radioactivity concentrations in drinking water, the required sensitivity of the radioanalysis is defined in terms of a detection limit. The detection limit shall be that concentration which can be counted with a precision of plus or minus 100 percent at the 95 percent confidence level (1.96σ where σ is the standard deviation of the net counting rate of the sample).

(1) To determine compliance with § 141.15 (a) the detection limit shall not exceed 1 pCi/l. To determine compliance with § 141.15(b) the detection limit shall not exceed 3 pCi/l.

(2) To determine compliance with § 141.16 the detection limits shall not exceed the concentrations listed in Table B.

TABLE B.—DETECTION LIMITS FOR MAN-MADE BETA PARTICLE AND PHOTON EMITTERS

Radionuclide	*Detection limit*
Tritium	1,000 pCi/l.
Strontium-89	10 pCi/l.
Strontium-90	2 pCi/l.
Iodine-131	1 pCi/l.
Cesium-134	10 pCi/l.
Gross beta	4 pCi/l.
Other radionuclides	1/10 of the applicable limit.

(d) To judge compliance with the maximum contaminant levels listed in sections 141.15 and 141.16, averages of data shall be used and shall be rounded to the same number of significant figures as the maximum contaminant level for the substance in question.

[41 FR 28404, July 9, 1976]

§ 141.26 Monitoring Frequency for Radioactivity in Community Water Systems.

(a) Monitoring requirements for gross alpha particle activity, radium-226 and radium-228.

(1) Initial sampling to determine compliance with § 141.15 shall begin within two years of the effective date of these regulations and the analysis shall be completed within three years of the effective date of these regulations. Compliance shall be based on the analysis of an annual composite of four consecutive quarterly samples or the average of the analyses of four samples obtained at quarterly intervals.

(i) A gross alpha particle activity measurement may be substituted for the required radium-226 and radium-228 analysis *Provided,* That the measured gross alpha particle activity does not exceed 5 pCi/1 at a confidence level of 95 percent (1.65σ where σ is the standard deviation of the net counting rate of the sample). In localities where radium–228 may be present in drinking water, it is recommended that the State require radium–226 and/or radium–228 analyses when the gross alpha particle activity exceeds 2 pCi/1.

(ii) When the gross alpha particle activity exceeds 5 pCi/1, the same or an equivalent sample shall be analyzed for radium–226. If the concentration of radium–226 exceeds 3 pCi/1 the same or an equivalent sample shall be analyzed for radium–228.

(2) For the initial analysis required by paragraph (a) (1), data acquired within one year prior to the effective date of this part may be substituted at the discretion of the State.

(3) Suppliers of water shall monitor at least once every four years following the procedure required by paragraph (a) (1). At the discretion of the State, when an annual record taken in conformance with paragraph (a) (1) has established that the average annual concentration is less than half the maximum contaminant levels established by § 141.15, analysis of

a single sample may be substituted for the quarterly sampling procedure required by paragraph (a)(1).

(i) More frequent monitoring shall be conducted when ordered by the State in the vicinity of mining or other operations which may contribute alpha particle radioactivity to either surface or ground water sources of drinking water.

(ii) A supplier of water shall monitor in conformance with paragraph (a)(1) within one year of the introduction of a new water source for a community water system. More frequent monitoring shall be conducted when ordered by the State in the event of possible contamination or when changes in the distribution system or treatment processing occur which may increase the concentration of radioactivity in finished water.

(iii) A community water system using two or more sources having different concentrations of radioactivity shall monitor source water, in addition to water from a free-flowing tap, when ordered by the State.

(iv) Monitoring for compliance with § 141.15 after the initial period need not include radium–228 *except when* required by the State, *Provided,* That the average annual concentration of radium–228 has been assayed at least once using the quarterly sampling procedure required by paragraph (a)(1).

(v) Suppliers of water shall conduct annual monitoring of any community water system in which the radium-226 concentration exceeds 3 pCi/1, when ordered by the State.

(4) If the average annual maximum contaminant level for gross alpha particle activity or total radium as set forth in § 141.15 is exceeded, the supplier of a community water system shall give notice to the State pursuant to § 141.31 and notify the public as required by § 141.32. Monitoring at quarterly intervals shall be continued until the annual average concentration no longer exceeds the maximum contaminant level or until a monitoring schedule as a condition to a variance, exemption or enforcement action shall become effective.

(b) Monitoring requirements for man-made radioactivity in community water systems.

(1) Within two years of the effective date of this part, systems using surface water sources and serving more than 100,000 persons and such other community water systems as are designated by the State shall be monitored for compliance with § 141.16 by analysis of a composite of four consecutive quarterly samples or analysis of four quarterly samples. Compliance with § 141.16 may be assumed without further analysis if the average annual concentration of gross beta particle activity is less than 50 pCi/1 and if the average annual concentrations of tritium and strontium-90 are less than those listed in Table A, *Provided,* That if both radionuclides are present the sum of their annual dose equivalents to bone marrow shall not exceed 4 millirem/year.

(i) If the gross beta particle activity exceeds 50 pCi/1, an analysis of the sample must be performed to identify the major radioactive constituents present and the appropriate organ and total body doses shall be calculated to determine compliance with § 141.16.

(ii) Suppliers of water shall conduct additional monitoring, as ordered by the State, to determine the concentration of man-made radioactivity in principal watersheds designated by the State.

(iii) At the discretion of the State, suppliers of water utilizing only ground waters may be required to monitor for man-made radioactivity.

(2) For the initial analysis required by paragraph (b)(1) of this section data acquired within one year prior to the effective date of this part may be substituted at the discretion of the State.

(3) After the initial analysis required by paragraph (b)(1) of this section suppliers of water shall monitor at least every four years following the procedure given in paragraph (b)(1) of this section.

(4) Within two years of the effective date of these regulations the supplier of any community water system designated by the State as utilizing waters contaminated by effluents from nuclear facilities shall initiate quarterly monitoring for gross beta particle and iodine-131 radioactivity and annual monitoring for strontium-90 and tritium.

(i) Quarterly monitoring for gross beta particle activity shall be based on the analysis of monthly samples or the analysis of a composite of three monthly samples. The former is recommended. If the gross beta particle activity in a sample exceeds 15 pCi/1, the same or an

equivalent sample shall be analyzed for strontium-89 and cesium-134. If the gross beta particle activity exceeds 50 pCi/1, an analysis of the sample must be performed to identify the major radioactive constituents present and the appropriate organ and total body doses shall be calculated to determine compliance with § 141.16.

(ii) For iodine-131, a composite of five consecutive daily samples shall be analyzed once each quarter. As ordered by the State, more frequent monitoring shall be conducted when iodine-131 is identified in the finished water.

(iii) Annual monitoring for strontium-90 and tritium shall be conducted by means of the analysis of a composite of four consecutive quarterly samples or analysis of four quarterly samples. The latter procedure is recommended.

(iv) The State may allow the substitution of environmental surveillance data taken in conjunction with a nuclear facility for direct monitoring of man-made radioactivity by the supplier of water where the State determines such data is applicable to a particular community water system.

(5) If the average annual maximum contaminant level for man-made radioactivity set forth in § 141.16 is exceeded, the operator of a community water system shall give notice to the State pursuant to § 141.31 and to the public as required by § 141.32. Monitoring at monthly intervals shall be continued until the concentration no longer exceeds the maximum contaminant level or until a monitoring schedule as a condition to a variance, exemption or enforcement action shall become effective.

[41 FR 28404, July 9, 1976]

§ 141.27 Alternative analytical techniques.

With the written permission of the State, concurred in by the Administrator of the U.S. Environmental Protection Agency, an alternative analytical technique may be employed. An alternative technique shall be acceptable only if it is substantially equivalent to the prescribed test in both precision and accuracy as it relates to the determination of compliance with any maximum contaminant level. The use of the alternative analytical technique shall not decrease the frequency of monitoring required by this part.

§ 141.28 Approved laboratories.

For the purpose of determining compliance with § 141.21 through § 141.27, samples may be considered only if they have been analyzed by a laboratory approved by the State except that measurements for turbidity and free chlorine residual may be performed by any person acceptable to the State.

§ 141.29 Monitoring of consecutive public water systems.

When a public water system supplies water to one or more other public water systems, the State may modify the monitoring requirements imposed by this part to the extent that the interconnection of the sysems jusifies treating them as a single system for monitoring purposes. Any modified monitoring shall be conducted pursuant to a schedule specified by the State and concurred in by the Administrator of the U.S. Environmental Protection Agency.

Subpart D—Reporting, Public Notification and Record Keeping

§ 141.31 Reporting requirements.

(a) Except where a shorter reporting period is specified in this part, the supplier of water shall report to the State within 40 days following a test, measurement or analysis required to be made by this part, the results of that test, measurement or analysis.

(b) The supplier of water shall report to the State within 48 hours the failure to comply with any primary drinking water regulation (including failure to comply with monitoring requirements) set forth in this part.

(c) The supplier of water is not required to report analytical results to the State in cases where a State laboratory performs the analysis and reports the results to the State office which would normally receive such notification from the supplier.

§ 141.32 Public notification.

(a) If a community water system fails to comply with an applicable maximum contaminant level established in Subpart B, fails to comply with an applicable testing procedure established in Subpart C of this part, is granted a variance or an exemption from an applicable maximum contaminant level, fails to comply with the requirements of any schedule

prescribed pursuant to a variance or exemption, or fails to perform any monitoring required pursuant to Section 1445 (a) of the Act, the supplier of water shall notify persons served by the system of the failure or grant by inclusion of a notice in the first set of water bills of the system issued after the failure or grant and in any event by written notice within three months. Such notice shall be repeated at least once every three months so long as the system's failure continues or the variance or exemption remains in effect. If the system issues water bills less frequently than quarterly, or does not issue water bills, the notice shall be made by or supplemented by another form of direct mail.

(b) If a community water system has failed to comply with an applicable maximum contaminant level, the supplier of water shall notify the public of such failure, in addition to the notification required by paragraph (a) of this section, as follows:

(1) By publication on not less than three consecutive days in a newspaper or newspapers of general circulation in the area served by the system. Such notice shall be completed within fourteen days after the supplier of water learns of the failure.

(2) By furnishing a copy of the notice to the radio and television stations serving the area served by the system. Such notice shall be furnished within seven days after the supplier of water learns of the failure.

(c) If the area served by a community water system is not served by a daily newspaper of general circulation, notification by newspaper required by paragraph (b) of this section shall instead be given by publication on three consecutive weeks in a weekly newspaper of general circulation serving the area. If no weekly or daily newspaper of general circulation serves the area, notice shall be given by posting the notice in post offices within the area served by the system.

(d) If a non-community water system fails to comply with an applicable maximum contaminant level established in Subpart B of this part, fails to comply with an applicable testing procedure established in Subpart C of this part, is granted a variance or an exemption from an applicable maximum contaminant level, fails to comply with the requirement of any schedule prescribed pursuant to a variance or exemption or fails to perform any monitoring required pursuant to Section 1445(a) of the Act, the supplier of water shall given notice of such failure or grant to the persons served by the system. The form and manner of such notice shall be prescribed by the State, and shall insure that the public using the system is adequately informed of the failure or grant.

(e) Notices given pursuant to this section shall be written in a manner reasonably designed to inform fully the users of the system. The notice shall be conspicuous and shall not use unduly technical language, unduly small print or other methods which would frustrate the purpose of the notice. The notice shall disclose all material facts regarding the subject including the nature of the problem and, when appropriate, a clear statement that a primary drinking water regulation has been violated and any preventive measures that should be taken by the public. Where appropriate, or where designated by the State, bilingual notice shall be given. Notices may include a balanced explanation of the significance or seriousness to the public health of the subject of the notice, a fair explanation of steps taken by the system to correct any problem and the results of any additional sampling.

(f) Notice to the public required by this section may be given by the State on behalf of the supplier of water.

(g) In any instance in which notification by mail is required by paragraph (a) of this section but notification by newspaper or to radio or television stations is not required by paragraph (b) of this section, the State may order the supplier of water to provide notification by newspaper and to radio and television stations when circumstances make more immediate or broader notice appropriate to protect the public health.

§ 141.33 Record maintenance.

Any owner or operator of a public water system subject to the provisions of this part shall retain on its premises or at a convenient location near its premises the following records:

(a) Records of bacteriological analyses made pursuant to this part shall be kept for not less than 5 years. Records of chemical analyses made pursuant to this

part shall be kept for not less than 10 years. Actual laboratory reports may be kept, or data may be transferred to tabular summaries, provided that the following information is included:

(1) The date, place, and time of sampling, and the name of the person who collected the sample;

(2) Identification of the sample as to whether it was a routine distribution system sample, check sample, raw or process water sample or other special purpose sample;

(3) Date of analysis;

(4) Laboratory and person responsible for performing analysis;

(5) The analytical technique/method used; and

(6) The results of the analysis.

(b) Records of action taken by the system to correct violations of primary drinking water regulations shall be kept for a period not less than 3 years after the last action taken with respect to the particular violation involved.

(c) Copies of any written reports, summaries or communications relating to sanitary surveys of the system conducted by the system itself, by a private consultant, or by any local, State or Federal agency, shall be kept for a period not less than 10 years after completion of the sanitary survey involved.

(d) Records concerning a variance or exemption granted to the system shall be kept for a period ending not less than 5 years following the expiration of such variance or exemption.

Subpart E—Special Monitoring Regulations for Organic Chemicals

§ 141.40 Special monitoring for organic chemicals.

(a) The Administrator may designate, by publication in the FEDERAL REGISTER, public water systems which are required to take water samples, provide information, and in appropriate cases analyze water samples for the purpose of providing information on contamination of drinking water sources and of treated water by organic chemicals.[1]

(b) The Administrator shall provide to each public system designated pursuant to paragraph (a) of this section a written schedule for the sampling of source water or treated water by the system, with written instructions for the sampling methods and for handling of samples. The schedule may designate the locations or types of locations to be sampled.

(c) In cases where the public water system has a laboratory capable of analyzing samples for constituents specified by the Administrator, the Administrator may require analyses to be made by the public water system for submission to EPA. If the Administrator requires the analyses to be made by the public water system, he shall provide the system with written instructions as to the analytical procedures to be followed, or with references to technical documents describing the analytical procedures.

(d) Public water systems designated by the Administrator pursuant to paragraph (a) of this section shall provide to the Administrator, upon request, information to be used in the evaluation of analytical results, including records of previous monitoring and analyses, information on possible sources of contamination and treatment techniques used by the system.

[40 FR 59588, Dec. 24, 1975]

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[1] A list of designated public water systems was published at 41 FR 5281, Jan. 5, 1976.

APPENDIX D

ALLOWED DISCHARGES FOR POINT SOURCE CATEGORIES

This Appendix lists the Point Source Categories and subcategories listed in Title 40, Code of Federal Regulations, in parts 400 to 459. The table shows which of the effluent guidelines and standards had been promulgated by the EPA as of Oct. 1, 1978 and which pollutants may be discharged or parameters changed in the Best Practicable Control Technology Currently Available (BPTCA) and Best Available Technology Economically Achievable (BATEA) Guidelines.

APPENDIX D

Point Source Category	Part	Subpart	BPTCA[a]	BATEA[b]	ExSPrS[c]	NSPS[d]	NSPrS[e]	BCT[f]	Pollutants or Parameters Discharged[g] BPTCA(BATEA)
Cooling water intake structures	402		•[h]						Development document issued contains guidelines for minimizing adverse impact
	Revisions: 43 FR 37134 (8-21-78), proposed deletion								
Dairy products processing	405	A Receiving stations	•	•	•	•	•	*	BOD5[i], TSS, pH(proposed: BCT = BATEA, BATEA reserved)
		B Fluid products	•	•	•	•	•	*	do
		C Cultured products	•	•	•	•	•	*	do
		D Butter	•	•	•	•	•	*	do
		E Cottage cheese and cultured cream	•	•	•	•	•	*	do
		F Natural and processed cheese	•	•	•	•	•	*	do
		G Fluid mix for ice cream and other frozen desserts	•	•	•	•	•	*	do
		H Ice cream, frozen desserts, novelties and other dairy desserts	•	•	•	•	•	*	do
		I Condensed milk	•	•	•	•	•	*	do
		J Dry milk	•	•	•	•	•	*	do
		K Condensed whey	•	•	•	•	•	*	do
		L Dry whey	•	•	•	•	•	*	do
	Revisions: 43 FR 37570 (8-23-78), proposed BCT guidelines								
Grain Mills	406	A Corn wet milling	•	•	•	•	•	*	BOD5, TSS, pH(proposed: BCT = current BATEA; BATEA reserved)
		B Corn dry milling	•	•	•	•	•	*	do
		C Normal wheat flour milling	•	•	•	•	•	*	BOD5, TSS, pH(no discharge; proposed: BCT-no discharge)
		D Bulgar wheat flour milling	•	•	•	•	•	*	BOD5, TSS, pH(proposed: BCT-pH; BATEA reserved)
		E Normal rice milling	•	•	•	•	•	*	BOD5, TSS, pH(no discharge; proposed: BCT-no discharge)
		F Parboiled rice processing	•	•	•	•	•	*	BOD5, TSS, pH(proposed: BCT = current BATEA, BATEA - reserved)
		G Animal feed	•	•		•	•	*	BOD5, TSS, pH(no discharge; proposed: BCT-no discharge)
		H Hot cereal	•	•		•	•	*	do
		I Ready to eat cereal	•	•		•	•	*	BOD5, TSS, pH(proposed: BCT = current BATEA, BATEA reserved)

*Proposed BCT Guidelines

Point Source Category	Part	Subpart	BPTCA[a]	BATEA[b]	EXSPrS[c]	NSPS[d]	NSPrS[e]	BCT[f]	Pollutants or Parameters Discharged[g] BPTCA(BATEA)
Grain Mills	406 (cont'd)	J Wheat starch and gluten	•	•		•	•	*	do
		Revisions: 43 FR 37570 (8-23-78), proposed BCT guidelines							
Canned and Preserved Fruits and Vegetables Processing	407	A Apple juice	•	•	•	•	•	*	BOD5, TSS, pH(proposed: BCT = current BATEA; BATEA reserved)
		B Apple products	•	•	•	•	•	*	do
		C Citrus products	•	•	•	•	•	*	do
		D Frozen potato product	•	•	•	•	•	*	do
		E Dehydrated potato products	•	•	•	•	•	*	do
		F Canned and preserved fruits	•	•	•	•	•	*	BOD5, TSS, pH(proposed: BATEA, withdrawn, reserved; BCT- BOD5, TSS, pH for mushrooms and tomatoes, all others reserved)
		G Canned and preserved vegetables	•	•	•	•	•	*	do
		H Canned and miscellaneous specialities	•	•	•	•	•	*	BOD5, TSS, pH(proposed: BATEA, withdrawn, reserved; BCT-pH, all others reserved)
		Revisions: 43 FR 37570 (8-23-78), proposed BCT guidelines							
Canned and preserved seafood processing	408	A Farm-raised catfish	•	•	•	•	•	*	TSS, oil and grease, pH (proposed: BATEA reserved; BCT-pH)
		B Conventional blue crab processing	•	•	•	•	•	*	do
		C Mechanized blue crab processing	•	•	•	•	•	*	do
		D Non-remote Alaskan crab meat proc.	•	•	•	•	•	*	do
		E Remote Alaskan crab meat proc.	•	•	•	•	•	*	None larger than 0.5" (TSS, oil and grease, pH; proposed: BATEA reserved, BCT-pH)
		F Non-remote Alaskan whole crab and crab section Proc.	•	•	•	•	•	*	TSS, oil and grease, pH (BOD5, TSS, oil and grease, pH; proposed: BATEA reserved; BCT-pH)

*Proposed BCT Guidelines

Point Source Category	Part	Subpart	BPTCA[a]	BATEA[b]	ExSPrS[c]	NSPS[d]	NSAS[e]	BCT[f]	Pollutants or Parameters Discharged[g] BPTCA(BATEA)
Canned and preserved seafood processing (cont'd)	408	G Remote Alaskan crab and crab section proc.	●	●	●	●	●	*	None larger than 0.5" (TSS, oil and grease, pH; proposed: BATEA reserved, BCT-pH)
		H Dungeness and Tanner crab proc.	●	●	●	●	●	*	TSS, oil and grease, pH (BOD5, TSS, oil and grease, pH; proposed: BATEA reserved; BCT-pH)
		I Non-remote Alaskan shrimp proc.	●	●	●	●	●	*	do
		J Remote Alaskan shrimp proc.	●	●	●	●	●	*	None larger than 0.5"; (TSS, oil and grease, pH; proposed: BATEA reserved; BCT-pH)
		K Northern shrimp proc. in the contiuous states	●	●	●	●	●	*	TSS, oil and grease, pH (TSS, oil and grease, pH, BOD5; proposed: BATEA reserved; BCT-pH)
		L Southern non-breaded shrimp proc. in the contiguous states	●	●	●	●	●	*	do
		M Breaded shrimp proc. in the contiguous states	●	●	●	●	●	*	do
		N Tuna processing	●	●	●	●	●	*	TSS, oil and grease, pH (TSS, oil and grease, pH, BOD5 proposed: BATEA reserved; BCT-pH)
		O Fish meal	●	●	●	●	●	*	TSS, oil and grease, pH (BOD5, TSS, pH, oil and grease; proposed: BCT = current BATEA; current BATEA-reserved)
		P Alaskan hand-butchered salmon processing	●		●	●	●		TSS, oil and grease, pH
		Q Alaskan mechanized salmon proc.	●		●	●	●		do
		R West Coast hand-butchered salmon processing	●	●	●	●	●	*	TSS, oil and grease, pH (BOD5, TSS, oil and grease, current BATEA; current BATEA reserved)
		S West Coast mechanized salmon proc.	●	●	●	●	●	*	do
		T Alaskan bottom fish processing	●		●	●	●		TSS, oil and grease, pH

*Proposed BCT Guidelines

Point Source Category	Part		Subpart	BPTCA[a]	BATEA[b]	ExSPrS[c]	NSPS[d]	NSPrS[e]	BCT[f]	Pollutants or Parameters Discharged[g] BPTCA(BATEA)
Canned and preserved seafood processing (cont'd)	408	U	Non-Alaskan conventional bottom fish processing	●	●	●	●	●	*	TSS, oil and grease, pH (BOD5, TSS, oil and grease, pH; proposed: BCT = current BATEA; current BATEA reserved)
		V	Non-Alaskan mechanized bottom fish processing	●	●	●	●	●	*	do
		W	Hand-shucked clam processing	●	●	●	●	●	*	TSS, oil and grease, pH (proposed: BCT = current BATEA; current BATEA reserved)
		Y	Pacific Coast hand-shucked oyster processing	●	●	●	●	●	*	TSS, oil and grease, pH (proposed: BCT = current BATEA; current BATEA reserved)
		Z	Atlantic and Gulf Coast hand-shucked oyster processing	●	●	●	●	●	*	TSS, oil and grease, pH (BOD5, TSS, oil and grease, pH; proposed: BCT = current BATEA; current BATEA reserved)
		AA	Steamed and canned oyster processing	●	●	●	●	●	*	do
		AB	Sardine processing	●	●	●	●	●	*	TSS, oil and grease, pH (proposed: BCT = current BATEA; current BATEA reserved)
		AC	Alaskan scallop	●		●	●	●		TSS, oil and grease, pH
		AD	Non-Alaskan scallop processing	●	●	●	●	●	*	TSS, oil and grease, pH (proposed: BCT = current BATEA; current BATEA, reserved)
		AE	Alaskan herring fillet processing	●		●	●	●		TSS, oil and grease, pH
		AF	Non-Alaskan Herring fillet processing	●	●	●	●	●	*	TSS, oil and grease, pH (BOD5, TSS, oil and grease, proposed BCT = current BATEA; current BATEA reserved

*Proposed BCT Guidelines

Point Source Category	Part	Subpart	BPTCA[a]	BATEA[b]	ExSPrS[c]	NSPS[d]	NSPrS[e]	BCT[f]	Pollutants or Parameters Discharged[g] BPTCA(BATEA)
Canned and preserved seafood proc. (cont'd)	408 AG	Abalone processing	●	●	●	●	●	*	TSS, oil and grease, pH (proposed: BCT = current BATEA; current BATEA reserved)
	Revisions: 43 FR 37570 (8-23-78), proposed BCT guidelines								
Sugar Processing	409 A	Beet sugar proc.	●	●	●	●	●	*	BOD5, pH, temperature, TSS, fecal coliform, (proposed BCT = current BATEA; current BATEA reserved)
	B	Crystalline cane sugar refining	●	●	●	●	●	*	BOD5, TSS, pH (proposed: BATEA, reserved; BCT = BOD5, TSS, pH)
	C	Liquid cane sugar refining	●	●	●	●	●	*	BOD5, TSS, pH (proposed: BCT = current BATEA; current BATEA reserved)
	D	Louisiana raw cane sugar processing	●						BOD5, TSS, pH
	E	Florida and Texas raw cane sugar processing	●						No discharge[j]
	F	Hilo-Hamakua Coast of the Island of Hawaii raw cane sugar processing	●						BOD5, TSS, pH
	G	Hawaiian raw cane sugar processing	●						BOD5, TSS, pH
	H	Puerto Rican raw cane sugar proc.	●						BOD5, TSS, pH
	Revisions: 43 FR 37570 (8-23-78), proposed BCT guidelines								
Textile industry	410 A	Wool scouring	●	●	●	●	●		BOD5, TSS, COD, oil and grease, Cr, phenol, $S^{=}$, pH (fecal coliform, color in addition to BPTCA)
	B	Wool finishing	●	●	●	●	●		BOD5, TSS, COD, Cr, phenol, $S^{=}$, pH (fecal coliform, color in addition to BPTCA)
	C	Dry processing	●	●	●	●	●		BOD5, TSS, COD, fecal coliform, pH
	D	Woven fabric finishing	●	●	●	●	●		BOD5, TSS, COD, Cr, phenol, $S^{=}$, pH (fecal coliform, color in addition to BPTCA)
	E	Knit fabric finishing	●	●	●	●	●		do

*Proposed BCT Guidelines

Point Source Category	Part	Subpart	BPTCA[a]	BATEA[b]	ExSPrS[c]	NSPS[d]	NSPrS[e]	BCT[f]	Pollutants or Parameters Discharged[g] BPTCA(BATEA)
Textile industry (cont'd)	410	F Carpet Mill	●	●	●	●	●		do
		G Stock and yarn dyeing	●	●	●	●	●		do
Cement Manufacturer	411	A Non-leaching	●	●	●	●	●	*	TSS, temperature, pH (proposed: BCT-TSS, pH; BATEA-temperature)
		B Leaching	●	●	●	●	●	*	TSS, temperature, pH (proposed: BATEA-temperature; BCT-pH)
		C Materials storage runoff	●	●	●	●	●		TSS, pH
	Revision: 43 FR 37570 (8-23-78), proposed BCT guidelines								
Feedlots	412	A All subcategories, except ducks	●	●	●	●	●	*	No discharge (proposed: BCT-no discharge)
		B Ducks	●	●	●	●	●	*	BOD5, fecal coliform (no discharge; proposed: BCT-no discharge)
	Revision: 43 FR 37570 (8-23-78), proposed BCT guidelines								
Electroplating	413	A Electroplating of common metals	●		●	§			Cu,Ni,Cr,Cr(VI),Zn,CN,CN(A), F^-,Cd,Pb,Fe,Sn,P,TSS,pH
		B Electroplating of precious metals	●		●	§			Ag,Au,CN,CN(A),Cr,Cr(VI), Ir,Os,Pd,Pt,Rh,Ru,P,TSS,pH
		C Electroplating of specialty metals							Reserved
		D Anodizing	●		●	§			Cu,Ni,Cr,Cr(VI),Zn,CN,CN(A), F^-,Cd,Fe,Sn,P,TSS,pH,flow
		E Coatings	●		●	§			do
		F Chemical etching and milling	●		●	§			do
		G Electrodeless plating			●	§			
		H Printed circuit board			●	§			
	Revisions: 41 FR 19311 (5-12-76), all enacted BPTCA guidelines were suspended. 42 FR 35834 (7-1-77, interim final regulation, establishes subparts G and H, and promulgates ExPrS for subparts, A,B,D,E,F,G and H. 43 FR 6560 (2-14-78), proposed standard(§)								
Organic Chemicals Proc.	414	A (Reserved)							

*Proposed BCT Guidelines

Point Source Category	Part	Subpart	BPTCA[a]	BATEA[b]	ExSPrS[c]	NSPS[d]	NSPrS[e]	BCT[f]	Pollutants or Parameters Discharged[g] BPTCA(BATEA)
Organic Chemicals	414 (cont'd)	B Processes with process water contact only as steam diluent, quench or vent gas absorbent	•	•		•	•		BOD5, TSS, pH (COD in addition to BPTCA)
		C (Reserved)							
		D (Reserved)							
Inorganic Chemicals Manufacturer	415	A Aluminum chloride production	•	•	•	•	•		No discharge
		B Aluminum sulfate production	•	•	•	•	•		No discharge† TSS, pH
		C Calcium carbide production	•	•		•	•		No discharge
		D Calcium chloride production	•	•		•	•		No discharge† TSS, pH (no discharge)
		E Calcium oxide and calcium hydroxide production	•	•		•	•		No discharge† TSS, pH
		F Chlorine and sodium or potassium nydroxide	•			•	•		TSS, Hg, pH or TSS, Pb, pH
		G Hydrochloric acid production							
		H Hydrofluoric acid production							
		I Hydrogen peroxide production	•						TSS, TOC, pH or TSS, CN(A) pH
		J Nitric acid production							
		K Potassium metal production	•	•		•	•		No discharge
		L Potassium dichromate production	•	•	•	•	•		No discharge
		M Potassium sulfate production	•	•		•	•		No discharge† pH, TSS
		N Sodium bicarbonate production	•	•		•	•		No discharge
		O Sodium carbonate production							
		P Sodium chloride production	•	•		•	•		No discharge or TSS, pH (no discharge)

Point Source Category	Part	Subpart	BPTCA[a]	BATEA[b]	ExSPrS[c]	NSPS[d]	NSPrS[e]	BCT[f]	Pollutants or Parameters Discharged[g] BPTCA(BATEA)
Inorganic Chemicals Manufacturer (cont'd)	415	Q Sodium dichromate production and sodium sulfate production	●			●	●		TSS, Cr(VI), Cr, pH
		R Sodium metal production							
		S Sodium silicate production							
		T Sodium sulfite production	●	●		●	●		TSS, COD, pH (no discharge†)
		U Sulfuric acid production							
		V Titanium dioxide production							
		W Aluminum fluoride production							
		X Ammonium chloride production	●						No discharge or $NH_3(N)$, pH
		Y Ammonium hydroxide production							
		Z Barium crbonate production							
		AA Borax production	●						No discharge (may return brine to source)
		AB Boric acid production	●						No discharge (may return brine to source) or As, TSS, pH
		AC Bromine production	●						No discharge (may return brine to source)
		AD Calcium carbonate production	●						TSS, pH
		AE Calcium hydroxide production	●						No discharge
		AF Carbon dioxide							
		AG Carbon monoxide and hydrogen by-product production	●						COD, TSS, pH
		AH Chrome pigments production							
		AI Chromic acid production	●						No discharge
		AJ Copper sulfate	●		●				Cu,pH or TSS,Cu,Ni,Se, pH
		AK Cuprous oxide production							
		AL Ferric chloride	●		●				No discharge
		AM Ferrous sulfate production							
		AN Fluorine production	●						No discharge
		AO Hydrogen production	●						No discharge† except as in Part 419

Point Source Category	Part	Subpart	BPTCA[a]	BATEA[b]	ExSPrS[c]	NSPS[d]	NSPrS[e]	BCT[f]	Pollutants or Parameters Discharged[g] BPTCA(BATEA)
Inorganic Chemicals Manufacturer (cont'd)	415	AP Hydrogen cyanide production							
		AQ Iodine production	•						No discharge
		AR Lead monoxide production	•		•				No discharge
		AS Lithium carbonate production	•						No discharge (brine may be returned to source) or TSS, pH
		AT Manganese sulfate production							
		AU Nickel sulfate production	•		•				No discharge or Ni, TSS, pH
		AV Strong nitric acid production							
		AW Oxygen and nitrogen production	•						Oil and grease, pH
		AX Potassium chloride production	•						No discharge (brine may be returned to source)
		AY Potassium iodide production	•						TSS, $S^{=}$, Fe, Ba, pH
		AZ Potassium permanganate production							
		BA Silver nitrate production	•		•				Ag, TSS, pH
		BB Sodium bisulfate production							
		BC Sodium fluoride production							No discharge
		BD Sodium hydrosulfide production							
		BE Sodium hydrosulfite production							
		BF Sodium silicofluoride production							
		BG Sodium thiosulfate production							
		BH Stannic oxide production	•						No discharge
		BI Sulfur dioxide production							
		BJ Zinc oxide production							
		BK Zinc sulfate production	•						No discharge

Revisions: 42 FR 37294 (7-20-78), addition of several pretreatment standards for exiting sources, subparts A, B, L, AJ, AL, AR, AU, BA and BC

Point Source Category	Part		Subpart	BPTCA[a]	BATEA[b]	ExSPrS[c]	NSPS[d]	NSPrS[e]	BCT[f]	Pollutants or Parameters Discharged[g] BPTCA(BATEA)
Plastics and Synthetics	416	A	Polyvinyl chloride	●	●		●			pH
		B	Polyvinyl acetate	●	●		●			do
		C	Polystyrene	●	●		●			do
		D	Polypropylene	●	●		●			do
		E	Polyethylene	●	●		●			do
		F	Cellophane	●	●		●			do
		G	Rayon	●	●		●			do
		H	Acrylonitrile-butadiene-styrene (ABS) and styrene-acrylonitrile (SAN) resin copolymers	●	●		●			do
		I	Polyester	●	●		●			do
		J	Nylon 66	●	●		●			do
		K	Nylon 6	●	●		●			do
		L	Cellulose acetate	●	●		●			do
		M	Acrylics							do
		N	Ethylene-vinyl acetate copolymers	●	●		●			do
		O	Polytetra-fluoroethylene	●	●		●			do
		P	Polypropylene fiber	●	●		●			do
		Q	Alkyds and unsaturated polyester resins	●	●		●			do
		R	Cellulose nitrate	●	●		●			do
		S	Polyamide (Nylon 6/12)	●	●		●			do
		T	Polyester resins (thermoplastic)	●	●		●			do
		U	Silicones	●	●		●			do

Revisions: 41 FR 32587 (8-4-76), all limitations and standards of performance for all parameters, but pH were revoked, the limitations and standards for pH were suspended and NSPrS were revoked.
40 FR 21731 (5-19-75), subpart M suspended.

Soap Mfg.	417	A	Soap mfg. by batch kettle	●	●	●	●	●		BOD5, COD, TSS, oil and grease, pH
		B	Fatty acid by fat splitting	●	●	●	●	●		do
		C	Soap mfg. by fatty acid	●	●	●	●	●		do
		D	Glycerine concentration	●	●	●	●	●		do
		E	Glycerine distillation	●	●	●	●	●		do
		F	Manufacture of soap flakes and powders	●	●	●	●	●		do
		G	Manufacture of bar soaps	●	●	●	●	●		do
		H	Manufacture of liquid soaps	●	●	●	●	●		do
		I	Oleum sulfonation and sulfation	●	●	●	●	●		BOD5, COD, TSS, surfactants, oil and grease, pH

Point Source Category	Part		Subpart	BPTCA[a]	BATEA[b]	ExSPrS[c]	NSPS[d]	NSPrS[e]	BCT[f]	Pollutants or Parameters Discharged[g] BPTCA(BATEA)
Soap Mfg.	417 (cont'd)	J	Air-SO3 sulfation and sulfonation	•	•	•	•	•		do
		K	SO3 solvent and vacuum sulfonation	•	•	•	•	•		do
		L	Sulfamic acid sulfation	•	•	•	•	•		do
		M	Chlorosulfonic acid sulfation	•	•	•	•	•		do
		N	Neutralization of sulfuric acid esters and sulfonic acids	•	•	•	•	•		do
		O	Mfg. of spray dried detergents	•	•		•	•		do
		P	Mfg. of liquid detergents	•	•		•	•		do
		Q	Mfg. of drain dried detergents	•	•		•	•		do
		R	Mfg. of drain dried detergents	•	•		•	•		do
		S	Mfg. of detergent bars and cakes	•	•	•	•	•		do
Fertilizer Manufacturing	418	A	Phosphate	•	•		•	•	*	No discharge† P, F^-, TSS (proposed: BAT = no discharge† F^-; BCT = no discharge† P, TSS, or P)
		B	Ammonia	•	•		•	•	*	$NH_3(N)$ pH (proposed: BATEA-$NH_3(N)$, BCT-pH)
		C	Urea	•	•		•	•	•	$NH_3(N)$, Org.N(N), pH
		D	Ammonium nitrate	•	•		•	•	•	$NH_3(N)$, $NO_3(N)$, pH
		E	Nitric acid	•	•		•	•		$NH_3(N)$, $NO_3(N)$
		F	Ammonium sulfate	•	•		•	•	*	No discharge (proposed: BCT-no discharge
		G	Mixed and blend fertilizer	•	•		•	•	*	No discharge (proposed: BCT-no discharge)
Petroleum Refining	419	A	Topping	•	•	•	•	•		BOD5, TSS, COD, oil and grease, phenolics, $NH_3(N)$, $S^=$, Cr, Cr(VI), pH
		B	Cracking	•	•	•	•	•		do
		C	Petrochemical	•	•	•	•	•		do

Revisions: 40 FR 26275 (6-23-75), subpart D suspended
43 FR 17821 (4-26-78), subpart D reissued values changed, but no changes were made concerning which water quality characteristics or pollutants could be discharged. An adjustment was made for conventional pollutants; BATEA regulations for subpart C and D concern only $NH_3(N)$ and $NO_3(N)$ and BCT regulates pH.
43 FR 37570 (8-23-78), proposed BCT guidelines

*Proposed BCT Guidelines

Point Source Category	Part		Subpart	BPTCA[a]	BATEA[b]	ExSPrS[c]	NSPS[d]	NSPrS[e]	BCT[f]	Pollutants or Parameters Discharged[g] BPTCA(BATEA)
Petroleum Refining (cont'd)	419	D	Lube	•	•	•	•	•		do
		E	Integrated	•	•	•	•	•		do
Iron and Steel Mfg.	420	A	By-product coke	•	•		•	•		NH_3, CN, oil and grease phenol, TSS, pH
		B	Beehive coke	•	•		•	•		No discharge
		C	Sintering coke	•	•		•	•		TSS, oil and grease, pH (Oil and grease, $S^=$, F^-, TSS, pH)
		D	Blast furnace(iron)	•	•		•	•		TSS, CN, phenol, NH_3, pH, (TSS, CN(A), phenol, NH_3, $S^=$, F^-, pH)
		E	Blast furnace (ferro-manganese)	•	•		•	•		TSS, CN, phenol, NH_3, pH (TSS, CN(A), phenol, NH_3, $S^=$, Mn, pH)
		F	Basic oxygen furnace (semiwet air pollution control methods)	•	•		•	•		No discharge
		G	Basic oxygen furnace (wet air pollution control methods)	•	•		•	•		TSS, pH, (TSS, F^-, pH)
		H	Open hearth furnace	•	•		•	•		TSS, pH, (TSS, F^-, NO_3, Mn, pH)
		I	Electric arc furnace (semiwet air pollution control methods)	•	•		•	•		No discharge
		J	Electric arc furnace (wet air pollution control methods)	•	•		•	•		TSS, pH, (TSS, F^-, Zn, pH)
		K	Vacuum degassing	•	•		•	•		TSS, pH, (TSS, Zn, Mn, Pb, NO_3, pH)
		L	Continuous casting, pressure and slab molding	•	•		•	•		TSS, oil and grease, pH
		M	Hot forming-primary	•						do
		N	Hot forming-section	•						do
		O	Hot forming-flat	•						do
		P	Pipe and tube	•						do
		Q	Pickling-sulfuric acid-batch and continuous	•						Fe (dissolved), TSS, oil and grease, pH
		R	Pickling-hydrochloric acid-batch batch and continuous	•						do
		S	Cold rolling	•						do

Point Source Category	Part	Subpart	BPTCA[a]	BATEA[b]	ExSPrS[c]	NSPS[d]	NSPrS[e]	BCT[f]	Pollutants or Parameters Discharged[g] BPTCA(BATEA)
Iron and Steel Mfg. (cont'd)	420	T Hot coatings-galvanizing	•						Zn, Cr, Cr(VI), TSS, oil and grease, pH
		U Hot coatings-terne	•						Oil and grease, TSS, Pb, Sn, pH
		V Miscellaneous runoffs-storage piles, casting and slagging	•						No limit or no discharge
		W Combination acid pickling (batch and continuous)	•						TSS, oil and grease, Cr(diss), Fe(diss), Ni(diss), F^-, pH
		X Scale removal hydride)	•						TSS, Cr(VI), Cr(diss), Fe(diss), CN^-, pH
		Y Wire pickling and coating	•						TSS, oil and grease, Cr(diss), Fe(diss), Ni(diss), Cu(diss), CN^-, pH, F^-
		Z Continuous alkaline cleaning	•						TSS, Cr(diss), Fe(diss), Ni(diss), pH
Non-Ferrous Metals Mfg.	421	A Bauxite refining	•	•		•	•		No discharge†§
		B Primary aluminum smelting	•	•		•	•		F^-, TSS, pH
		C Secondary aluminum smelting	•	•	•	•	•		No discharge†(§)
		D Primary copper smelting	•	•					No discharge†(§)
		E Primary copper ref.	•	•					No discharge†(§)
		F Secondary copper	•	•	•				No discharge†(§)
		G Primary lead	•	•					No discharge†(§)
		H Primary zinc	•	•					TSS, As, Cd, Se, Zn, pH
Phosphate Mfg.	422	A Phosphorous product	•	•		•	•		TSS, P, F^-, P(O) pH (no discharge)
		B Phosphorous consuming	•	•		•	•		No discharge or TSS, P, P(O), As, pH (no discharge)
		C Phosphate	•	•		•	•		No discharge or TSS, P, pH (no discharge)

†(§)In case of a 10 year, 24 hr rainfall event, the following pollutants may be discharged:

C. TSS, COD, pH or TSS, F^-, $NH_3(N)$, Al, Cu, COD, pH
D. TSS, As, Cu, Pb, Cd, Se, Zn, pH
E. TSS, Cu, Zn, oil and grease, pH
F. TSS, Cu, Zn, oil and grease, pH
G. TSS, Cd, Pb, Zn

Point Source Category	Part		Subpart	BPTCA[a]	BATEA[b]	ExSPrS[c]	NSPS[d]	NSPrS[e]	BCT[f]	Pollutants or Parameters Discharged[g] BPTCA(BATEA)
Phosphate Mfg.	422 (cont'd)	D	Defluorinated	•	•		•	•	*	No discharge[†] P, F⁻, TSS, pH (proposed: BATEA-no discharge; F⁻ BCT-no discharge[†]TSS, P, pH)
		E	Defluorinated phosphoric acid	•	•		•		*	do
		F	Sodium phosphates	•	•		•		*	TSS, P, F⁻, pH (proposed: BATEA-F⁻; BCT-TSS, P, pH)
	Revision: 43 FR 37570 (8-23-78), proposed BCT quidelines									
Steam Electric Power Generating	423	A	Generating unit	•	•	•	•	•		pH, PCB, TSS, oil and grease, Cu, Fe, Cl (free. avail.), Cl (tot., resid.) (Zn, Cr, P, heat, in addition to BPTCA's)
		B	Small unit	•	•	•	•	•		pH, PCB , TSS, oil and grease, Cu, Fe, Cl(free avail.) Cl(tot. resid.)
		C	Old unit	•	•	•				do
		D	Area runoff	•	•	•	•	•		TSS, pH
	Revision: 43 FR 8812 (3-5-78), proposed ammendment, not involving changes in which water quality characteristics may be changed or pollutants discharged									
Ferroalloy Mfg.	424	A	Open electrical furnaces with wet air pollution control devices	•	•		•	•	*	TSS, Cr, Cr(VI), Mn, pH (proposed: BATEA-Cr, Cr(VI), Mn; BCT-TSS, pH)
		B	Covered electric furnaces and other smelting devices with wet air pollution control devices	•	•		•	•	*	TSS, Cr, Cr(VI), Mn, CN phenols, pH (proposed: BATEA, Cr, Cr(VI) Mn, phenols, CN(total);BCT-pH, TSS
		C	Slag processing	•	•		•	•	*	TSS, Cr, Mn, pH (proposed: BATEA-Cr, Cr(VI), Mn; BCT-TSS, pH)
		D	Covered calcium carbide furnaces with wet air pollution control devices	•	•		•		*	TSS, CN, pH (proposed: BATEA-CN⁻; BCT-pH)
		E	Other calcium carbide furnaces	•	•		•		*	No discharge (proposed: BCT-no discharge)

*Proposed BCT Guidelines

Point Source Category	Part	Subpart	BPTCA[a]	BATEA[b]	ExSPrS[c]	NSPS[d]	NSPrS[e]	BCT[f]	Pollutants or Parameters Discharged[g] BPTCA(BATEA)
Ferroalloy Mfg.	424 (cont'd)	F Electrolytic manganese	•	•				*	TSS, Mn, $NH_3(N)$, pH (prposed: BATEA-Mn, Cr, $NH_3(N)$; BCT-pH)
		G Electrolytic chromium	•	•				*	TSS, Mn, Cr, $NH_3(N)$, pH (proposed: BATEA-Mn, Cr, $NH_3(N)$; BCT-pH)
	Revision: 43 FR 37570 (8-23-78), proposed BCT quidelines								
Leather Tanning and Finishing	425	A Hair pulp unhairing with chrome tanning and finishing	•	•	•	•	•		BOD5, TSS, chrome, oil and grease, pH ($S^=$, TKN, fecal coliform in addition to BPTCA's)
		B Hair save unhairing with chrome tanning, and finishing	•	•	•	•	•		do
		C Unhairing with vegetable or Alum tanning and finishing	•	•	•	•	•		do
		D Finishing of tanned hides	•	•	•	•	•		do
		E Vegetable or chrome tanning of unhaired hides	•	•	•	•	•		do
		F Unhair with chrome tanning and no finishing	•	•	•	•	•		do
		G (Reserved)							
Glass Mfg.	426	A Insulation fiberglass mfg.	•	•		•	•	*	No discharge or phenol, COD, BOD5, TSS, pH (no discharge; proposed: BCT-no discharge
		B Sheet glass mfg.	•	•	•	•	•	*	No discharge (proposed: BCT-no discharge)
		C Rolled glass mfg.	•	•	•	•	•	*	do
		D Plate glass mfg.	•	•	•	•	•	*	TSS, pH (proposed: BCT=current BATEA; current BATEA reserved)
		E Float glass mfg.	•	•		•	•	*	TSS, oil, P, pH (proposed: BCT-pH; BATEA reserved)
		F Automotive glass tempering	•	•	•	•	•	*	TSS, oil, pH (proposed: BCT-pH; BATEA reserved)

*Proposed BCT Guidelines

Point Source Category	Part	Subpart	BPTCA[a]	BATEA[b]	ExSPrS[c]	NSPS[d]	NSPrS[e]	BCT[f]	Pollutants or Parameters Discharged[g] BPTCA(BATEA)
Glass Mfg.	426 (cont'd)	G Automotive glass laminating	•	•		•	•	*	TSS, oil, P, pH (proposed, BCT-pH; BATEA reserved
		H Glass container	•	•		•	•	*	TSS, oil, pH (proposed: BCT-pH; BATEA reserved)
		I Machine and blown glass							reserved
		J Glass tubing mfg. (Danner)	•	•		•	•	*	TSS, pH (proposed: BCT-pH; BATEA reserved)
		K Television picture tube envelope mfg.	•	•		•	•	*	TSS, oil, F^-, Pb, pH (proposed: BCT-pH; BATEA-Pb, F^-)
		L Incandescent lamp envelope mfg.	•	•		•	•	*	Oil, TSS, pH, F^-, NH_3 (proposed: BCT-pH; BATEA-F^-, NH_3)
		M Hand pressed and blown glass mfg.	•	•		•	•	*	Pb, F^-, TSS, pH (Proposed: BCT-pH; BATEA-F^- or F^-, Pb)
	Revisions: 43 FR 37570 (8-23-78), proposed BCT quidelines								
Asbestos Mfg.	427	A Asbestos-cement pipe	•	•	•	•	•		TSS, pH (no discharge)
		B Asbestos-cement sheet	•	•	•	•	•		do
		C Asbestos paper (starch binder)	•	•	•	•	•		do
		D Asbestos paper (elastomeric binder)	•	•	•	•	•		do
		E Asbestos millboard	•	•	•	•	•		No discharge
		F Asbestos roofing	•	•	•	•	•		COD, TSS, pH (no discharge)
		G Asbestos floor tile	•	•	•	•	•		do
		H Coating or finishing of asbestos textiles	•	•		•	•		No discharge
		I Solvent recovery	•	•		•	•	*	COD, TSS, pH (proposed: BATEA-COD, TSS; BCT-pH)
		J Vapor absorption	•	•		•	•		No discharge
		K Wet dust collection	•	•		•	•		TSS, pH (no discharge
	Revisions: 43 FR 37570 (8-23-78), proposed BCT's except for part E, H, I and J, BCT analysis was not required, so no action was taken								

*Proposed BCT Guidelines

Point Source Category	Part	Subpart	BPTCA[a]	BATEA[b]	ExSPrS[c]	NSPS[d]	NSPrS[e]	BCT[f]	Pollutants or Parameters Discharged[g] BPTCA(BATEA)
Rubber Mfg.	428	A Tire and inner tube plants	•	•		•	•		TSS, oil and grease, pH
		B Emulsion crumb rubber	•	•		•			COD, BOD5, TSS, oil and grease, pH
		C Solution crumb rubber	•	•		•			do
		D Latex Rubber	•	•		•	•		do
		E Small-sized general molded, extruded and fabricated rubber plant	•	•		•	•		Oil and grease, TSS, pH, Pb
		F Medium-sized general molded, extruded and fabricated rubber plants	•	•		•	•		do
		G Large-sized general molded, extruced and fabricated rubber plants	•	•		•	•		do
		H Wet digesting reclaimed rubber	•	•		•	•		COD, oil and grease, TSS, pH
		I Pan, dry digestion and mechanical reclaimed rubber	•	•		•	•		Oil and grease, TSS, pH
		J Latex-dipped latex-extruded and latex-molded rubber	•	•		•	•		BOD5, oil and grease, TSS, pH, Cr
		K Latex foam	•	•		•	•		Zn, BOD5, TSS, pH
	Revisions: 43 FR 6230, NSPrS revoked for subparts B, C.								
Timber Products Processing	429	A Barking	•	•	•	•	•		BOD5, TSS, pH (no discharge)
		B Veneer	•	•	•	•	•		No discharge or BOD5, pH (no discharge)
		C Plywood	•	•	•	•	•		No discharge
		D Hard board dry process	•	•	•	•	•		do
		E Hard board wet process			•		•		BOD5, TSS, pH
		F Wood preserving	•	•	•	•	•		No discharge
		G Wood preserving-steam	•	•	•	•	•		COD, phenols, oil and grease, pH
		H Wood preserving boltinizing	•	•	•	•	•		No discharge

Point Source Category	Part		Subpart	BPTCA[a]	BATEA[b]	ExSPrS[c]	NSPS[d]	NSPrS[e]	BCT[f]	Pollutants or Parameters Discharged[g] BPTCA(BATEA)
Timber Products Processing	429 (cont'd)	I	Wet storage	•	•	•	•	•		Debris, pH
		J	Log washing	•	•	•	•	•		TSS, pH (no discharge)
		K	Sawmills and plaining mills	•	•	•	•	•		No discharge
		L	Finishing	•	•	•	•	•		do
		M	Particle board mfg.	•	•	•	•	•		do
		N	(Reserved)							
		O	(Reserved)							
		P	(Reserved)							
		Q	Wood furniture and fixture production without water	•	•	•	•	•		No discharge
		R	Wash spray booth(s) or laundry facilities							
		S	Wood furniture and fixture prod. with water wash spray booth(s) or with laundry facilities	•	•	•	•	•		Settleable solids, pH
	Revision: 42 FR 49812 (9-28-77), revocation BPTCA, BATEA and NSPS for subpart E									
Pulp, paper and paperboard	430	A	Unbleached Kraft	•	•	•	•	•		BOD5, TSS, pH (BOD5, TSS, pH, color)
		B	Sodium-based neutral sulfite semi-chemical	•	•	•	•	•		do
		C	Ammonia base natural sulfite semi-chemical	•	•	•	•	•		do
		D	Unbleached kraft-neutral sulfite semi-chemical (cross recovery)	•	•	•	•	•		do
		E	Paperboard from waste paper	•	•	•	•	•		BOD5, TSS, pH
		F	Dissolving Kraft	•						do
		G	Market bleached kraft	•						do
		H	BCT bleached Kraft	•						do
		I	Fire bleached Kraft	•						do
		J	Papergrade sulfite (blow pit wash)	•						do
		K	Dissolving sulfite pulp	•						do
		L	Groundwood-chemi-mechanical	•						do
		M	Groundwood-thermo-mechanical	•						do

Point Source Category	Part		Subpart	BPTCA[a]	BATEA[b]	ExSPrS[c]	NSPS[d]	NSPrS[e]	BCT[f]	Pollutants or Parameters Discharged[g] BPTCA(BATEA)
Pulp, paper and paperboard	430 (cont'd)	N	Groundwood-CMN paper	•						do
		O	Groundwood-fine papers	•						do
		P	Soda	•						do
		Q	Deink	•						do
		R	NI fine papers	•						do
		S	NI tissue papers	•						do
		T	NI tissue (FWP)	•						do
		U	Papergrade sulfite (drum wash)	•						do
		V	Papergrade sulfite market pulp	•						do
Builders' Paper and Roofing Felt Segment of the Builders Paper and Board Mills	431	A	Builders paper and roofing felt	•	•		•	•		BOD5, TSS, settleable solid, pH
Meat Products	432	A	Sample slaughter-house	•	•		•	•	*	BOD5, TSS, oil and grease fecal coliform, pH (BPTCA and NH_3; proposed: BATEA-suspended; BCT-fecal coliform, pH)
		B	Complex slaughter-house	•	•		•	•	*	BOD5, TSS, oil and grease fecal coliform, pH (BOD5, TSS, NH_3, oil and grease, fecal coliform, pH; proposed: BATEA-suspended; BCT-fecal coliform, pH
		C	Low processing packinghouse	•	•		•	•	*	do
		D	High processing packinghouse	•	•		•	•	*	do
		E	Small processor	•	•		•	•	*	BOD5, TSS, oil and grease fecal coliform, pH (proposed: BCT = current BATEA; current BATEA reserved)
		F	Meat cutter	•	•		•	•	*	BOD5, TSS, oil and grease fecal coliform, pH (BOD5, TSS, oil and grease, NH_3, fecal coliform, pH; proposed: BATEA-NH_3; BCT-BOD5, TSS oil and grease, fecal coliform, pH)
		G	Sausage and luncheon meat processor	•	•		•	•	*	do
		H	Ham processor	•	•		•	•	*	do

*Proposed BCT Guidelines

Point Source Category	Part	Subpart	BPTCA[a]	BATEA[b]	ExSPrS[c]	NSPS[d]	NSPrS[e]	BCT[f]	Pollutants or Parameters Discharged[g] BPTCA(BATEA)
Meat Products	432 (cont'd)	I Canned meats processor	●	●		●	●	*	do
		J Renderer	●	●		●	●	*	do
	Revisions: 42 FR 54417, BATEA and NSPS promulgated in Subpart J 43 FR 37570 (8-23-78), proposed BCT guidelines								
Coal Mining	434	A General definitions							
		B Coal preparation plants and associated areas	●						Fe, Mn, TSS, pH
		C Acid ferruginous mine drainage	●						do
		D Alkaline mine drainage	●						Fe, TSS, pH
Offshore Segement of the Oil and Gas Extraction	435	A Near-offstore	●						Oil and grease, residual chlorine
		B Far-offshore	●						do
		C Onshore	●						No discharge
		D Coastal	●						Oil and grease, residual chlorine
		E Beneficial use	●						No discharge or oil and grease
		F Stripper							
Mineral Mining and Processing	436	A Dimension stone							
		B Crushed stone	●						TSS, pH
		C Construction sand and gravel	●						do
		D Industrial sand	●						No discharge, or TSS, F^-, pH
		E Gypsum	●						No discharge†
		F Asphaltic Minerals	●						do
		G Asbestos and Wollastonite	●						do
		H Lightweight Aggregate							
		I Mica and Sericite							
		J Barite	●						No discharge
		K Fluorspar	●						do
		L Salines from brine lakes	●						No discharge† {same source and discharge point

*Proposed BCT Guidelines

Point Source Category	Part		Subpart	BPTCA[a]	BATEA[b]	ExSPrS[c]	NSPS[d]	NSPrS[e]	BCT[f]	Pollutants or Parameters Discharged[g] BPTCA(BATEA)
Mineral Mining and Processing (cont'd)	436	M	Borax	•						No discharge†
		N	Potash	•						do
		O	Sodium sulfate	•						do
		P	Trona							
		Q	Rock salt							
		R	Phosphate rock	•			•			TSS, pH
		S	Frasch sulfur	•						No discharge†
		T	Mineral pigments							
		U	Lithium							
		V	Bentonite	•						No discharge
		W	Magnesite	•						No discharge†
		X	Diatomite	•						do
		Y	Jade	•						do
		Z	Novaculite	•						do
		AA	Fire clay							
		AB	Attapulgite and montmorillonite							
		AC	Kyamite							
		AD	Shale and common clay							
		AE	Aplite							
		AF	Tripoli	•						No discharge
		AG	Kolin							
		AH	Ball clay							
		AI	Feldspar							
		AJ	Talc, steatite, soapstone and pyrophillite							
		AK	Garnet							
		AL	Graphite	•						TSS, Fe, pH
	Revisions: 42 FR 35843 (7-12-77), final BPTCA regulation promulgated for subparts B, C, D and R, changes not involving pollutants which may be discharged 43 FR 9808 (3-10-78), NSPS promulgated in Subpart R.									
Pharmaceutical Mfg.	439	A	Fermentation products	•						BOD5, COD, pH
		B	Extraction products	•						BOD5, COD, TSS, pH
		C	Chemical synthetic products	•						BOD5, COD, pH
		D	Mixing/compounding and formulation	•						do
		E	Research	•						do
Ore Mining and Dressing	440	A	Iron ore	•						TSS, Fe(dissolved), pH
		B	Base and precious metals	•						TSS, Cu, Zn, Pb, Hg, Ph, Cd, CN
		C	Bauxite	•						TSS, Fe, Al, pH

Point Source Category	Part	Subpart	BPTCA[a]	BATEA[b]	ExSPrS[c]	NSPS[d]	NSPrS[e]	BCT[f]	Pollutants or Parameters Discharged[g] BPTCA(BATEA)
Ore Mining and Dressing	440 (cont'd)	D Ferroalloy ores	•						TSS, Cd, Cu, Zn, Pb, As, pH, CN
		E Uranium, radium and vanadium	•						TSS, Cd, Zn, As, Ra226, U, COD, pH
		F Mercury	•						TSS, Hg, Ni, pH
		G Titanium	•						TSS, Fe, pH, Zn, Ni
	Revisions: 43 FR 29775 (7-11-78), allowed discharge pollutant ammendment in subpart A, amended to read Fe (dissolved), not Fe (filterable).								
Paving and Roofing (tars and asphalts)	443	A Asphalt emulsion	•	•		•	•		Oil and grease, pH (TSS, oil and grease, pH)
		B Asphalt concrete	•	•		•	•		No discharge
		C Asphalt roofing	•	•		•	•		TSS, pH
		D Linoleum and printed asphalt felt	•	•		•	•		do
Paint Formulating	446	A Oil-base solvent wash paint	•	•		•	•		No discharge
Ink Formulation	447	A Oil-based solvent wash ink	•	•		•	•		No discharge
Gum and Wood Chemicals Mfg.	454	A Char and charoal briquets	•						No discharge
		B Gum rosin and turpentine	•						BOD5, TSS, pH
		C Wood rosin, turpentine and pine oil	•						do
		D Tall oil rosin, pitch and fatty acids	•						do
		E Essential oils	•						do
		F Rosin based derivatives	•						do
Pesticide Chemicals Mfg.	455	A Halogenated organic pesticides	•						COD, BOD5, TSS, total pesticides, pH
		B Organo-phosphorous pesticides	•						No discharge

Point Source Category	Part	Subpart	BPTCA[a]	BATEA[b]	ExSPrS[c]	NSPS[d]	NSPrS[e]	BCT[f]	Pollutants or Parameters Discharged[g] BPTCA(BATEA)
Pesticide Chemicals Mfg. (cont'd)	455	C Organo-nitrogen pesticides	•						do
		D Metallo-organic pesticides	•						do
		E Pesticide formulators and packagers	•						do
	Revisions: 43 FR 17776 (4-25-78), BPTCA regulations changed in subpart A (no phenols allowed), B (no discharge) and C (no discharge).								
Exposive Mfg.	457	A Manufacture of explosive	•						COD, BOD5, TSS, pH
		B (Reserved)							
		C Explosives load, assemble and pack plants	•						Oil and grease, TSS, pH
Carbon Black Mfg.	458	A Carbon black furnace process		•		•	•		No discharge
		B Carbon black thermal proc.		•		•	•		do
		C Carbon black channel proc.		•		•	•		do
		D Carbon black lamp proc.		•		•	•		do
	Revisions: 43 FR 1343 (1-9-78), final promulgation of BATEA, NSPS and NSPrS for this part. BPTCA regulations were withdrawn.								
Photographic	459	A Photographic processing	•						Ag, CN, pH
Hospital	460	A Hospital	•						BOD5, TSS, pH

FOOTNOTES TO TABLE

a. Best practicable control technology currently available.

b. Best available technology economically achievable.

c. Pretreatment standards for existing sources.

d. Standards of performance for new sources.

e. Pretreatment standards for existing sources.

f. Best conventional pollutant control technology.

g. The pollutants compiled are those which may be discharged. (There is always a disclaimer for plants or bodies of water with unusual circumstances which are considered on a case-by-case basis, in which case the eliminations may be more or less stringent than mentioned in the CRF). The first parameters are those for BPTCA. Those in ( ) are for BATEA, if they differ from BPTCA and if they have been established. If the parameters whose discharge is permitted are the same as those in the succeeding point source category, the term "do" or "ditto" has been used. This does not imply that the quantities concerned are the same.

   Sometimes within a subcategory, there are further subdivisions, and each subdivision may have different allowed discharges. In this table, no attempt has been made to differentiate between subdivisions. The reader wishing to know more specifics about each subcategory should refer to the CFR and the associated development document.

h. A ● in the column indicates that the regulation on guideline has been promulgated.

i. Necessarily, many abbreviations were used in compiling this table. Their meaning is compiled below in alphabetical order.

   Ag - Silver*
   APCD - Air pollution control device
   As - Arsenic
   Au - Gold
   Ba - Barium
   BOD_5 - 5 day biochemical oxygen demand
   Cd - Cadmium
   Cl - Chlorine
   CN - Cyanide
   CN(A) - Cyanide amenable to chlorination
   COD - Chemical oxygen demand
   Cr(VI) - Chromium in the +6 oxidation state
   Cu - Copper
   Diss - Dissolved
   do - Ditto
   F^- - Fluoride
   Fe - Iron
   Hg - Mercury
   Ir - Irridium
   Mn - Manganese
   $NH_3(N)$ - Ammonia determined as its nitrogen content
   Ni - Nickel
   $NO_3^-(N)$ - Nitrate determined as its nitrogen content
   organic N(N) - Organic nitrogen compounds determined as their nitrogen content
   Os - Osmium
   P - Phosphorous
   Pb - Lead
   PCB - Polychlorinated biphenyls
   Pd - Palladium

*Just the symbol "M" implies the total constituent unless otherwise specified.

pH - log hydrogen ion concentration
Pt - Platinum
Ra^{226} - Radium 226
Rh - Phodium
Ru - Ruthenium
$S^{=}$ - Sulfide
Se - Selenium
Sn - Tin
TKN - Total Kjeldahl nitrogen
TOC - Total organic carbon
TSS - Total suspended solids
U - Uranium
Zn - Zinc

j. No discharge. The term "no discharge" frequently appears, often with various qualifying statements. Their presentation in the table is explained below.

- No discharge - the guideline reads "There shall be no discharge of process wastewater to navigable waters".
- No discharge†, implies "There shall be no discharge... (as above), but if there is a substantial rainfall usually a 10 year (or 25 years), 24 hour event process water effluents may be discharged.
- No discharge†x,y, implies as above "There shall be no...", but that a discharge is permitted in case of precipitation greater than a 24 hour, 10 year event or in some cases a 25 year event, and that process waste water in an impoundment may be released equal to the amount of rainfall adjusted for evaporation, and in that water, the parameters or pollutants following the dagger may appear.

APPENDIX E

Completed List of Point Source Categories and Standard Industrial Classifications Affected by the Consent Decree (8 ERC 2120, D.D.C. 1976)

POINT SOURCE CATEGORIES

1. TIMBER PRODUCTS PROCESSING

SIC 2411 - Logging Camps and Logging Contractors (Camps Only)
SIC 2421 - Saw Mills and Planing Mills, General
SIC 2426 - Hardwood Dimension and Flooring Mills
SIC 2429 - Special Purpose Sawmills, Not Elsewhere Classified
SIC 2431 - Millwork
SIC 2434 - Wood Kitchen Cabinets
SIC 2435 - Hardwood Veneer and Plywood
SIC 2436 - Softwood Veneer and Plywood
SIC 2439 - Structural Wood Members, Not Elsewhere Classified
SIC 2491 - Wood Preserving
SIC 2499 - Wood Products, Not Elsewhere Classified (Furniture Mills)
SIC 2661 - Building Paper and Building Board Mills (Hardboard Only)

2. STEAM ELECTRIC POWER PLANTS

SIC 4911 - Electric Services (Limited to Steam-Electric Power Plants)

3. LEATHER TANNING AND FINISHING

SIC 31 - Leather and Leather Products

4. IRON AND STEEL MANUFACTURING

SIC 3312 - Blast Furnaces (Including Coke Ovens), Steel Works and Rolling Mills
SIC 3313 - Electrometallurgical Products
SIC 3315 - Steel Wire Drawing and Steel Nails and Spikes
SIC 3316 - Cold Rolled Steel Sheet, Strip and Bars
SIC 3317 - Steel Pipe and Tubes

5. PETROLEUM REFINING

SIC 2911 - Petroleum Refining (Including 1) Topping Plant; 2) Topping and Cracking Plants; 3) Topping, Cracking and Petro-chemical Plants; 4) Integrated Plants; and 5) Integrated and Petro-chemical Plants)

6. INORGANIC CHEMICALS MANUFACTURING

SIC 2812 - Alkalies and Chlorine
SIC 2813 - Industrial Gasses
SIC 2816 - Inorganic Pigments
SIC 2819 - Industrial Inorganic Chemicals, Not Elsewhere Classified

7. TEXTILE MILLS

SIC 22 - Textile Mill Products
SIC 23 - Apparel and Other Finished Products Made from Fabrics and Similar Materials

8. ORGANIC CHEMICALS MANUFACTURING

SIC 2865 - Cylic (Coal Tar) Crudes, and Cylic Intermediates, Dyes, and Organic Pigments (Lakes and Tonners)
SIC 2869 - Industrial Organic Chemicals, Not Elsewhere Classified

9. NONFERROUS METALS MANUFACTURING

SIC 2819 - Industrial Inorganic Chemicals, Not Elsewhere Classified (Bauxite Refining Only)
SIC 3331 - Primary Smelting and Refining of Copper
SIC 3332 - Primary Smelting and Refining of Lead
SIC 3333 - Primary Smelting and Refining of Zinc
SIC 3334 - Primary Production of Aluminum
SIC 3341 - Secondary Smelting and Refining of Nonferrous Metals

10. PAVING AND ROOFING MATERIALS (TARS AND ASPHALT)

SIC 2951 - Paving Mixtures and Blocks
SIC 2952 - Asphalt Felts and Coatings
SIC 3996 - Linoleum, Asphalted-Felt-Base, and Other Hard Surface Floor Coverings, Not Elsewhere Classified

11. PAINT AND INK FORMULATION AND PRINTING

SIC 2711 - Newspapers: Publishing, Publishing and Printing
SIC 2721 - Periodicals: Publishing, Publishing and Printing
SIC 2731 - Books: Publishing, Publishing and Printing
SIC 2732 - Book Printing
SIC 2741 - Miscellaneous Publishing
SIC 2751 - Commercial Printing, Letterpress and Screen
SIC 2752 - Commercial Printing, Letterpress and Lithographic
SIC 2753 - Engraving and Plate Printing
SIC 2754 - Commercial Printing, Gravure
SIC 2761 - Mainfold Business Forms
SIC 2771 - Greeting Card Publishing
SIC 2793 - Photoengraving
SIC 2794 - Electrotyping and Stereotyping

SIC 2795 - Lithographic Platenmaking and Related Services
SIC 2851 - Paints, Varnishes, Lacquers, Enamels, and Allied Products
SIC 2893 - Printing Ink
SIC 3951 - Pens, Mechanical pencils, and Parts and Stamp Pads (Inked Materials Only)
SIC 3952 - Lead Pencils, Crayons, and Artists' Materials
SIC 3955 - Carbon Paper and Inked Ribbons

12. SOAP AND DETERGENT MANUFACTURING

SIC 2841 - Soap and Other Detergents, except Specially Cleaners

13. AUTO AND OTHER LAUNDRIES

SIC 7211 - Power Laundries, Family and Commercial
SIC 7213 - Linen Supply
SIC 7214 - Diaper Service
SIC 7215 - Coin-operated Laundries and Dry Cleaning
SIC 7216 - Dry Cleaning Plants, Except Rug Cleaning
SIC 7217 - Carpet and Upholstery Cleaning
SIC 7218 - Industrial Laundries
SIC 7219 - Laundry and Garment Services, Not Elsewhere Classified
None - Auto Wash Establishments

14. PLASTIC AND SYNTHETIC MATERIALS MANUFACTURING

SIC 282 - Plastic Materials and Synthetic Resins, Synthetic and Other Manmade Fibers, except Glass

15. PULP AND PAPERBOARD MILLS AND CONVERTED PAPER PRODUCTS

SIC 2611 - Pulp Mills
SIC 2621 - Paper Mills, except Building Paper Mills
SIC 2641 - Paper Coating and Glazing
SIC 2642 - Envelopes
SIC 2643 - Bags, Except Textile Bags
SIC 2645 - Die-Cut Paper and Paperboard and Cardboard
SIC 2646 - Pressed and Molded Pulp Goods
SIC 2647 - Sanitary Paper Products
SIC 2648 - Stationery, Tablets, and Related Products
SIC 2649 - Converted Paper and Paperboard Products, Not Elsewhere Classified
SIC 2651 - Folding Paperboard Boxes
SIC 2652 - Set-up Paperboard Boxes
SIC 2653 - Corrugated and Solid Fiber Boxes
SIC 2654 - Sanitary Food Containers
SIC 2655 - Fiber Cans, Tubes, Drums, and Similar Products
SIC 2661 - Building Paper and Building Board Mills
SIC 2782 - Blankbooks, Looseleaf Binders and Devices

16. RUBBER PROCESSING

SIC 2822 - Synthetic Rubber (Vulcanizable Elastomers)
SIC 2891 - Rubber Cement
SIC 3011 - Tires and Inner Tubes
SIC 3021 - Rubber and Plastics Footwear (Rubber Only)
SIC 3031 - Reclaimed Rubber
SIC 3069 - Fabricated Rubber Products, Not Elsewhere Classified
SIC 3293 - Gaskets, Packing, and Sealing Devices (Rubber Packing Only)

17. MISCELLANEOUS CHEMICALS

SIC 2831 - Biological Products
SIC 2833 - Medicinal Chemicals and Botanical Products
SIC 2834 - Pharmaceutical Preparations
SIC 2861 - Gum and Wood Chemicals
SIC 2879 - Pesticides and Agricultural Chemicals, Not Elsewhere Classified
SIC 2891 - Adhesive and Sealants
SIC 2892 - Explosives
SIC 2895 - Carbon Black
SIC 2899 - Chemicals and Chemical Preparation, Not Elsewhere Classified
SIC 3861 - Photographic Equipment and Supplies

18. MACHINERY AND MECHANICAL PRODUCTS MANUFACTURING

SIC 3021 - Rubber and Plastics Footwear (Balance)
SIC 3041 - Rubber and Plastic Hose and Belting (Balance)
SIC 3079 - Miscellaneous Plastics Products
SIC 3293 - Gaskets, Packing, and Sealing Devices (Balance)
SIC 3321 - Malleable Iron Foundries
SIC 3324 - Steel Investment Foundries
SIC 3325 - Steel Foundries, Not Elsewhere Classified
SIC 3351 - Aluminum Sheet, Plate, and Foil
SIC 3354 - Aluminum Extruded Products
SIC 3355 - Aluminum Rolling and Drawing, Not Elsewhere Classified
SIC 3356 - Rolling, Drawing, and Extruding of Nonferrous Metals, except copper and Aluminum
SIC 3357 - Drawing and Insulating of Nonferrous Wire
SIC 3361 - Aluminum Foundries (Castings)
SIC 3362 - Brass, Bronze, Copper, Copper Base Alloy Foundries (Castings)
SIC 3369 - Nonferrous Foundries (Casings), Not Elsewhere Classified
SIC 3398 - Metal Heat Treating
SIC 3399 - Primary Metal Products, Not Elsehwere Classified
SIC 3411 - Metal Cans
SIC 3412 - Metal Shipping Barrels, Drums, Kegs, and Pails
SIC 3421 - Cutlery
SIC 3423 - Hand and Edge Tools, Except Machine Tools and Hand Saws

SIC 3425 - Hand Saws and Saw Blades
SIC 3429 - Hardware, Not Elsewhere Classified
SIC 3421 - Enameled Iron and Metal Sanitary Ware
SIC 3432 - Plumbing Fixture Fittings and Trim (Brass Goods)
SIC 3433 - Heating Equipment, Except Electric and Warm Air Furnaces
SIC 3441 - Fabricated Structural Metal
SIC 3442 - Metal Doors. Sash, Frames, Molding, and Trim
SIC 3443 - Fabricated Platework (Boiler Shops)
SIC 3444 - Sheet Metal Work
SIc 3446 - Architectural and Ornamental Metal Work
SIC 3448 - Prefabricated Metal Buildings and Components
SIC 3449 - Miscellaneous Metal Work
SIC 3451 - Screw Machine Products
SIC 3452 - Bolts, Nuts, Screws, Rivets, and Washers
SIC 3462 - Iron and Steel Forgings
SIC 3463 - Nonferrous Forgings
SIC 3465 - Crowns and Closures
SIC 3469 - Metal Stampings, Not Elsewhere Classifed
SIC 3483 - Ammunition, Except for Small Arms, Not Elsewhere Classified
SIC 3484 - Small Arms
SIC 3489 - Ordnance and Accessories, Not Elsewhere Classified
SIC 3493 - Steel Springs, Except Wire
SIC 3495 - Wire Springs
SIC 3496 - Miscellaneous Fabricated Wire Products
SIC 3497 - Metal Foil and Leaf
SIC 3498 - Fabricated Pipe and Fabricated Pipe Fittings
SIC 3499 - Fabricated Metal Products, Not Elsewhere Classified
SIC 3511 - Steam, Gas, and Hydraulic Turbines and Turbine Generator Set Units
SIC 3519 - Internal Combustion Engines, Not Elsewhere Classified
SIC 3523 - Farm Machinery and Equipment
SIC 3524 - Garden Tractors and Lawn and Garden Equipment
SIC 3531 - Construction Machinery and Equipment
SIC 3532 - Mining Machinery and Equipment, Except Oil Field Machinery and Equipment
SIC 3533 - Oil Field Machinery and Equipment
SIC 3434 - Elevators and Moving Stairways
SIC 3535 - Conveyors and Conveying Equipment
SIC 3536 - Hoists, Industrial Cranes, and Monorail Systems
SIC 3537 - Industrial Trucks, Tractors, Trailers, and Stackers
SIC 3541 - Machine Tools, Metal Cutting Types
SIC 3542 - Machine Tools, Metal Forming Types
SIC 3544 - Special Dies and Tools, Die Sets, Jigs and Fixtures and Industrial Molds
SIC 3545 - Machine Tool Accessories and Measuring Devices
SIC 3546 - Power Driven Hand Tools
SIC 3547 - Rolling Mill Machinery and Equipment
SIC 3549 - Metalworking Machinery, Not Elsewhere Classified
SIC 3551 - Food Products Machinery
SIC 3552 - Textile Machinery
SIC 3553 - Woodworking Machinery
SIC 3554 - Paper industries Machinery
SIC 3555 - Printing Trades Machinery and Equipment
SIC 3561 - Pumps and Pumping Equipment
SIC 3562 - Ball and Roller Bearings
SIC 3563 - Air and Gas Compressors
SIC 3564 - Blowers and Exhaust and Ventilation Fans
SIC 3565 - Industrial Patterns
SIC 3566 - Changers, Industrial High Speed Drives, and Gears
SIC 3567 - Industrial Process Furnaces and Ovens
SIC 3568 - Mechanical Power Transmission Equipment. Not Elsewhere Classified
SIC 3569 - General Industrial Machinery and Equipment. Not Elsewhere Classified
SIC 3572 - Typewriters
SIC 3573 - Electronic Computing Equipment
SIC 3574 - Calculating and Accounting Machines, Except Electronic Computing Equipment
SIC 3576 - Scales and Balances, Except Laboratory
SIC 3579 - Office Machines, Not Elsewhere Classified
SIC 3581 - Automatic Merchandising Machines
SIC 3582 - Air Conditioning and Warm Air Heating Equipment and Commercial and Industrial Refrigeration Equipment
SIC 3585 - Air Conditioning and Warm Air Heating Equipment and Commercial and Industrial Refrigeration Equipment
SIC 3586 - Measuring and Dispensing Pumps
SIC 3589 - Service Industry Machines, Not Elsewhere Classified
SIC 3592 - Carburetors, Piston, Piston Rings, and Valves
SIC 3599 - Machinery, Except Electrical, Not Elsewhere Classified
SIC 3612 - Power, Distribution, and Specialty Transformers
SIC 3613 - Switchgear and Switchboard Apparatus
SIC 3621 - Motors and Generators
SIC 3622 - Industrial Controls
SIC 3623 - Welding Apparatus, Electric
SIC 3624 - Carbon and Graphtie Products
SIC 3629 - Electrical Industrial Apparatus, Not Elsewhere Classified
SIC 3631 - Household Cooking Equipment
SIC 3632 - Household Refrigerators and Home and Farm Freezers
SIC 3623 - Household Laundry Equipment
SIC 3634 - Electric Housewares and Fans
SIC 3635 - Household Vacuum Cleaners

SIC 3639 - Household Appliances, Not Elsewhere Classified
SIC 3641 - Electric Lamps
SIC 3643 - Current-Carrying wiring Devices
SIC 3644 - Noncurent-Carrying Wiring Devices
SIC 3645 - Residential Electric Lighting Fixtures
SIC 3646 - Commercial, Industrial, and Institutional Electric Lighting Fixtures
SIC 3648 - Lighting Equipment, Not Elsewhere Classified
SIC 3651 - Radio and Television Receiving Sets, Except Communication Types
SIC 3652 - Phonograph Records and Pre-corded Magnetic Tape
SIC 3661 - Telephone and Telegraph Apparatus
SIC 3662 -Radio and Television Transmitting. Signaling, and Detection Equipment and Apparatus
SIC 3671 - Radio and Television Receiving Type Electron Tubes, Except Cathode Ray
SIC 3672 - Cathode Ray Television Picture Tubes
SIC 3673 - Transmitting. Industrial, and Special Purpose Electron Tubes
SIC 3674 - Semiconductors and Related Devices
SIC 3675 - Electronic Capacitors
SIC 3676 - Resistors, for Electronic Applications
SIC 3677 - Electronic Coils, Transformers and Other Inductors
SIC 3678 - Connectors, for Electronic Applications
SIC 3679 - Electronic Components, Not Elsewhere Classified
SIC 3691 - Storage Batteries
SIC 3692 - Primary Batteries, Dry and Wet
SIC 3693 - Radiographic X-ray, Fluo-roscopic X-ray, Therapeutic X-ray and Other X-ray Apparatus and Tubes; Electromedical and Electrotherapeutic Apparatus
SIC 3694 - Electrical Equipment for Internal Combustion Engines
SIC 3699 - Electrical Machinery, Equipment, and Supplies, Not Elsewhere Classified
SIC 3711 - Motor Vehicles and Passenger Car Bodies
SIC 3713 - Truck and Buss Bodies
SIC 3714 - Motor Vehicle Parts and Accessories
SIC 3715 - Truck Trailers
SIC 3721 - Aircraft
SIC 3724 - Aircraft Engines and Engine Parts
SIC 3728 - Aircraft Parts and Auxiliary Equipment, Not Elsewhere Classified
SIC 3731 - Ship Building and Reparing
SIC 3732 - Boat Building and Repairing
SIC 3743 - Railroad Equipment
SIC 3751 - Motorcycles, Bicycles, and Parts
SIC 3761 - Guided Missiles and Space Vehicles
SIC 3764 - Guided Missile and Space Vehicle Propulsion Units and Propulsion Unit Parts
SIC 3769 - Guided Missile and Space Vehicle Parts and Auxiliary Equipment, Not Elsewhere Classified
SIC 3792 - Travel Trailers and Campers
SIC 3795 - Tanks and Tank Components
SIC 3799 - Transportation Equipment, Not Elsewhere Classified
SIC 3811 - Engineering, Laboratory, Scientific, and Research Instruments and Associated Equipment
SIC 3822 - Automatic Controls for Regulating Residential and Commercial Environments and Appliances
SIC 3823 - Industrial Instruments for Measurement, Display and Control of Process Variables; and Related Products
SIC 3825 - Instruments for Measuring and Testing of Electricity and Electrical Signals
SIC 3829 - Measuring and Controlling Devices, Not Elsewhere Classified
SIC 3832 - Optical Instruments and Lenses
SIC 3841 - Surgical and Medical Instruments and Apparatus
SIC 3842 - Orthopedic, and Surgical Appliances and Supplies
SIC 3843 - Dental Equipment and Supplies
SIC 3851 - Ophthalmic Goods
SIC 3873 - Watches, Clocks, Clockwork Operated Devices and Parts
SIC 3911 - Jewelry, Precious Metal
SIC 3914 - Silverware, Plated Ware, and Stainless Steel Ware
SIC 3915 - Jewelers' Findings and Materials, and Lapidary Work
SIC 3931 - Musical Instruments
SIC 3942 - Dolls
SIC 3944 - Games, Toys, and Children's Vehicles; Except Dolls and Bicycles
SIC 3949 - Sporting and Athletic Goods, Not Elsewhere Classified
SIC 3951 - Pens, Mechanical Pencils, and Parts (Balance)
SIC 3961 - Costume Jewelry and Costume Novelties, Except Precious Metal
SIC 3991 - Brooms and Brushes
SIC 3993 - Signs and Advertising Displays
SIC 3995 - Burial Caskets

19. ELECTROPLATING

SIC 347 - Coating, Engraving, and Allied Services

20. ORE MINING AND DRESSING

SIC 1011 - Iron Ores
SIC 1021 - Copper Ores
SIC 1031 - Lead and Zinc Ores
SIC 1041 - Gold Ores
SIC 1044 - Silver Ores
SIC 1051 - Bauxite and Other Aluminum Ores
SIC 1061 - Ferroalloy Ores, Except Vanadium
SIC 1092 - Mercury Ores
SIC 1094 - Uranium-Radium-Vanadium Ores
SIC 1099 - Metal Ores, Not Elsewhere Classified

21. COAL MINING

SIC 1111 - Anthracite
SIC 1112 - Anthracite Mining Services
SIC 1211 - Bituminous Coal and Lignite
SIC 1213 - Bituminous Coal and Lignite Mining Services

APPENDIX F

Toxic Pollutant Effluent Standards (Reproduced from Code of Federal Regulations 40 CFR 129).

PART 129—TOXIC POLLUTANT EFFLUENT STANDARDS

Subpart A—Toxic Pollutant Effluent Standards and Prohibitions

AUTHORITY: Sec. 307, 308, 501, Federal Water Pollution Control Act Amendments of 1972 (Pub. L. 92–500, 86 Stat. 816, (33 U.S.C. 1251 et seq.)).

SOURCE: 42 FR 2613, Jan. 12, 1977, unless otherwise noted.

Subpart A—Toxic Pollutant Effluent Standards and Prohibitions

§ 129.1 Scope and Purpose.

(a) The provisions of this Subpart apply to owners or operators of specified facilities discharging into navigable waters.

(b) The effluent standards or prohibitions for toxic pollutants established in this Subpart shall be applicable to the sources and pollutants hereinafter set forth, and may be incorporated in any NPDES permit, modification or renewal thereof, in accordance with the provisions of this Subpart.

(c) The provisions of 40 CFR Parts 124 and 125 shall apply to any NPDES permit proceedings for any point source discharge containing any toxic pollutant for which a standard or prohibition is established under this Part.

§ 129.2 Definitions.

All terms not defined herein shall have the meaning given them in the Act or in 40 CFR Parts 124 or 125. As used in this Part, the term:

(a) "Act" means the Federal Water Pollution Control Act, as amended (Pub. L. 92–500, 86 Stat. 816 et seq., 33 U.S.C. 1251 et seq.). Specific references to sections within the Act will be according to Pub. L. 92–500 notation.

(b) "Administrator" means the Administrator of the Environmental Protection Agency or any employee of the Agency to whom the Administrator may by order delegate the authority to carry out his functions under section 307(a) of the Act, or any person who shall by operation of law be authorized to carry out such functions.

(c) "Effluent standard" means, for purposes of § 307, the equivalent of "effluent limitation" as that term is defined in section 502(11) of the Act with the exception that it does not include a schedule of compliance.

(d) "Prohibited" means that the constituent shall be absent in any discharge subject to these standards, as determined by any analytical method.

(e) "Permit" means a permit for the discharge of pollutants into navigable waters under the National Pollutant Discharge Elimination System established by section 402 of the Act and implemented in regulations in 40 CFR Parts 124 and 125.

(f) "Working day" means the hours during a calendar day in which a facility discharges effluents subject to this Part.

(g) "Ambient water criterion" means that concentration of a toxic pollutant in a navigable water that, based upon available data, will not result in adverse impact on important aquatic life, or on consumers of such aquatic life, after exposure of that aquatic life for periods of time exceeding 96 hours and continuing at least through one reproductive cycle; and will not result in a significant risk of adverse health effects in a

large human population based on available information such as mammalian laboratory toxicity data, epidemiological studies of human occupational exposures, or human exposure data, or any other relevant data.

(h) "New Source" means any source discharging a toxic pollutant, the construction of which is commenced after proposal of an effluent standard or prohibition applicable to such source if such effluent standard or prohibition is thereafter promulgated in accordance with section 307.

(i) "Existing Source" means any source which is not a new source as defined above.

(j) "Source" means any building, structure, facility, or installation from which there is or may be the discharge of toxic pollutants designated as such by the Administration under section 307(a)(1) of the Act.

(k) "Owner or operator" means any person who owns, leases, operates, controls, or supervises a source as defined above.

(l) "Construction" means any placement, assembly, or installation of facilities or equipment (including contractual obligations to purchase such facilities or equipment) at the premises where such equipment will be used, including preparation work at such premises.

(m) "Manufacturer" means any establishment engaged in the mechanical or chemical transformation of materials or substances into new products including but not limited to the blending of materials such as pesticidal products, resins, or liquors.

(n) "Process Wastes" means any designated toxic pollutant, whether in wastewater or otherwise present, which is inherent to or unavoidably resulting from any manufacturing process, including that which comes into direct contact with or results from the production or use of any raw material, intermediate product, finished product, by-product or waste product and is discharged into the navigable waters.

(o) "Air emissions" means the release or discharge of a toxic pollutant by an owner or operator into the ambient air either (1) by means of a stack or (2) as a fugitive dust, mist or vapor as a result inherent to the manufacturing or formulating process.

(p) "Fugitive dust, mist or vapor" means dust, mist or vapor containing a toxic pollutant regulated under this Part which is emitted from any source other than through a stack.

(q) "Stack" means any chimney, flue, conduit, or duct arranged to conduct emissions to the ambient air.

(r) "Ten year 24-hour rainfall event" means the maximum precipitation event with a probable recurrence interval of once in 10 years as defined by the National Weather Service in technical paper No. 40, "Rainfall Frequency Atlas of the United States," May 1961, and subsequent amendments or equivalent regional or State rainfall probability information developed therefrom.

(s) "State Director" means the chief administrative officer of a State or interstate water pollution control agency operating an approved HPDES permit program. In the event responsibility for water pollution control and enforcement is divided among two or more State or interstate agencies, the term "State Director" means the administrative officer authorized to perform the particular procedure to which reference is made.

§ 129.3 Abbreviations.

The abbreviations used in this Part represent the following terms:

lb=pound (or pounds)
g=gram
μg/l=micrograms per liter (1 one-millionth gram/liter)
kg=kilogram(s)
kkg=1000 kilogram(s)

§ 129.4 Toxic pollutants.

The following are the pollutants subject to regulation under the provisions of this subpart:

(a) Aldrin/Dieldrin—"Aldrin" means the compound aldrin as identified by the chemical name, 1,2,3,4,10,10-hexachloro-1,4,4a,5,8,8a - hexahydro - 1,4 - endo - 5,8 - exo - dimethanonaphthalene; "Dieldrin" means the compound dieldrin as identified by the chemical name 1,2,3,4,10,10-hexachloro - 6,7 - epoxy - 1,4,4a,5,6, 7, 8, 8a - octahydro - 1,4-endo - 5,8-exo-dimethanonaphthalene.

(b) DDT—"DDT" means the compounds DDT, DDD, and DDE as identified by the chemical names: (DDT)-1,1,1-trichloro-2,2 - bis(p - chlorophenyl)

ethane and some o,p'-isomers; (DDD) or (TDE) - 1,1 - dichloro - 2,2 - bis(p-chlorophenyl) ethane and some o,p'-isomers; (DDE) - 1,1 - dichloro - 2,2-bis (p-chlorophenyl) ethylene.

(c) Endrin—"Endrin" means the compound endrin as identified by the chemical name 1,2,3,4,10,10-hexachloro-6,7-epoxq - 1,4,4a,5,6,7,8,8a - octahydro - 1,4-endo-5,8-endo-dimethanonaphthalene.

(d) Toxaphene—"Toxaphene" means a material consisting of technical grade chlorinated camphene having the approximate formula of $C_{10}H_{10}Cl_8$ and normally containing 67–69 percent chlorine by weight.

(e) Benzidine—"Benzidine" means the compound benzidine and its salts as identified by the chemical name 4,4'-diaminobiphenyl.

(f) Polychlorinated Biphenyls (PCBs)—polychlorinated biphenyls (PCBs) means a mixture of compounds composed of the biphenyl molecule which has been chlorinated to varying degrees.

[42 FR 2613, Jan. 12, 1977, as amended at 42 FR 2620, Jan. 12, 1977; 42 FR 6555, Feb. 2, 1977]

§ 129.5 Compliance.

(a)(1) Within 60 days from the date of promulgation of any toxic pollutant effluent standard or prohibition each owner or operator with a discharge subject to that standard or prohibition must notify the Regional Administrator (or State Director, if appropriate) of such discharge. Such notification shall include such information and follow such procedures as the Regional Administrator (or State Director, if appropriate) may require.

(2) Any owner or operator who does not have a discharge subject to any toxic pollutant effluent standard at the time of such promulgation but who thereafter commences or intends to commence any activity which would result in such a discharge shall first notify the Regional Administrator (or State Director, if appropriate) in the manner herein provided at least 60 days prior to any such discharge.

(b) Upon receipt of any application for issuance or reissuance of a permit or for a modification of an existing permit for a discharge subject to a toxic pollutant effiuent standard or prohibition the permitting authority shall proceed thereon in accordance with 40 CFR Parts 124 or 125, whichever is applicable.

(c)(1) Every permit which contains limitations based upon a toxic pollutant effluent standard or prohibition under this Part is subject to revision following the completion of any proceeding revising such toxic pollutant effluent standard or prohibition regardless of the duration specified on the permit.

(2) For purposes of this section, all toxic pollutants for which standards are set under this Part are deemed to be injurious to human health within the meaning of section 402(k) of the Act unless otherwise specified in the standard established for any particular pollutant.

(d)(1) Upon the compliance date for any section 307(a) toxic pollutant effluent standard or prohibition, each owner or operator of a discharge subject to such standard or prohibition shall comply with such monitoring, sampling, recording, and reporting conditions as the Regional Administrator (or State Director, if appropriate) may require for that discharge. Notice of such conditions shall be provided in writing to the owner or operator.

(2) In addition to any conditions required pursuant to paragraph (d)(1) and to the extent not required in conditions contained in NPDES permits, within 60 days following the close of each calendar year each owner or operator of a discharge subject to any toxic standard or prohibition shall report to the Regional Administrator (or State Director, if appropriate) concerning the compliance fo such discharges. Such report shall include, as a minimum, information concerning (i) relevant identification of the discharger such as name, location of facility, discharge points, receiving waters, and the industrial process or operation emitting the toxic pollutant; (ii) relevant conditions (pursuant to paragraph (d)(1) or to an NPDES permit) as to flow, section 307 (a) toxic pollutant concentrations, and section 307(a) toxic pollutant mass emission rate; (iii) compliance by the discharger with such conditions.

(3) When samples collected for analysis are composited, such samples shall be composited in proportion to the flow at

time of collection and preserved in compliance with requirements of the Regional Administrator (or State Director, if appropriate), but shall include at least five samples collected at approximately equal intervals throughout the working day.

(e)(1) Nothing in these regulations shall preclude a Regional Administrator from requiring in any permit a more stringent effluent limitation or standard pursuant to section 301(b)(1)(C) of the Act and implemented in 40 CFR 125.11 and other related provisions of 40 CFR Part 125.

(2) Nothing in these regulations shall preclude the Director of a State Water Pollution Control Agency or interstate agency operating a National Pollutant Discharge Elimination System Program which has been approved by the Administrator pursuant to section 402 of the Act from requiring in any permit a more stringent effluent limitation or standard pursuant to section 301(b)(1)(C) of the Act and implemented in 40 CFR 124.42 and other related provisions of 40 CFR Part 124.

(f) Any owner or operator of a facility which discharges a toxic pollutant to the navigable waters and to a publicly owned treatment system shall limit the summation of the mass emissions from both discharges to the less restrictive standard, either the direct discharge standard or the pretreatment standard; but in no case will this Subsection allow a discharge to the navigable waters greater than the toxic pollutant effluent standard established for a direct discharge to the navigable waters.

(g) In any permit hearing or other administrative proceeding relating to the implementation or enforcement of these standards, or any modification thereof, or in any judicial proceeding other than a petition for review of these standards pursuant to section 509(b)(1)(C) of the Act, the parties thereto may not contest the validity of any national standards established in this Part, or the ambient water criterion established herein for any toxic pollutant.

§ 129.6 Adjustment of effluent standard for presence of toxic pollutant in the intake water.

(a) Upon the request of the owner or operator of a facility discharging a pollutant subject to a toxic pollutant effluent standard or prohibition, the Regional Administrator (or State Director, if appropriate) shall give credit, and shall adjust the effluent standard(s) in such permit to reflect credit for the toxic pollutant(s) in the owner's or operator's water supply if (1) the source of the owner's or operator's water supply is the same body of water into which the discharge is made and if (2) it is demonstrated to the Regional Administrator (or State Director, if appropriate) that the toxic pollutant(s) present in the owner's or operator's intake water will not be removed by any wastewater treatment systems whose design capacity and operation were such as to reduce toxic pollutants to the levels required by the applicable toxic pollutant effluent standards in the absence of the toxic pollutant in the intake water.

(b) Effluent limitations established pursuant to this section shall be calculated on the basis of the amount of section 307(a) toxic pollutant(s) present in the water after any water supply treatment steps have been performed by or for the owner or operator.

(c) Any permit which includes toxic pollutant effluent limitations established pursuant to this section shall also contain conditions requiring the permittee to conduct additional monitoring in the manner and locations determined by the Regional Administrator (or State Director, if appropriate) for those toxic pollutants for which the toxic pollutant effluent standards have been adjusted.

§ 129.7 Requirement and procedure for establishing a more stringent effluent limitation.

(a) In exceptional cases (1) where the Regional Administrator (or State Director, if appropriate) determines that the ambient water criterion established in these standards is not being met or will not be met in the receiving water as a result of one or more discharges at levels allowed by these standards, and

(2) where he further determines that this is resulting in or may cause or contribute to significant adverse effects on aquatic or other organisms usually or potentially present, or on human health, he may issue to an owner or operator a permit or a permit modification containing a toxic pollutant effluent limitation at a

more stringent level than that required by the standard set forth in these regulations. Any such action shall be taken pursuant to the procedural provisions of 40 CFR Parts 124 and 125, as appropriate. In any proceeding in connection with such action the burden of proof and of going forward with evidence with regard to such more stringent effluent limitation shall be upon the Regional Administrator (or State Director, if appropriate) as the proponent of such more stringent effluent limitation.

(3) Evidence in such proceeding shall include at a minimum: an analysis using data and other information to demonstrate receiving water concentrations of the specified toxic pollutant, projections of the anticipated effects of the proposed modification on such receiving water concentrations, and the hydrologic and hydrographic characteristics of the receiving waters including the occurrence of dispersion of the effluent. Detailed specifications for presenting relevant information by any interested party may be prescribed in guidance documents published from time to time, whose availability will be announced in the FEDERAL REGISTER.

(b) Any effluent limitation in an NPDES permit which a State proposes to issue which is more stringent than the toxic pollutant effluent standards promulgated by the Administrator is subject to review by the Administrator under section 402(d) of the Act. The Administrator may approve or disapprove such limitation(s) or specify another limitation(s) upon review of any record of any proceedings held in connection with the permit issuance or modification and any other evidence available to him. If he takes no action within ninety days of his receipt of the notification of the action of the permit issuing authority and any record thereof, the action of the State permit issuing authority shall be deemed to be approved.

§ 129.8 Compliance date.

(a) The effluent standards or prohibitions set forth herein shall be complied with not later than one year after promulgation unless an earlier date is established by the Administrator for an industrial subcategory in the promulgation of the standards or prohibitions.

(b) Toxic pollutant effluent standards or prohibitions set forth herein shall become enforceable under sections 307(d) and 309 of the Act on the date established in subsection (a) regardless of proceedings in connection with the issuance of any NPDES permit or application therefor, or modification or renewal thereof.

§§ 129.9–129.99 [Reserved]

§ 129.100 Aldrin/dieldrin.

(a) *Specialized definitions*—(1) "Aldrin/Dieldrin Manufacturer" means a manufacturer, excluding any source which is exclusively an aldrin/dieldrin formulator, who produces, prepares or processes technical aldrin or dieldrin or who uses aldrin or dieldrin as a material in the production, preparation or processing of another synthetic organic substance.

(2) "Aldrin/Dieldrin Formulator" means a person who produces, prepares or processes a formulated product comprising a mixture of either aldrin or dieldrin and inert materials or other diluents, into a product intended for application in any use registered under the Federal Insecticide, Fungicide and Rodenticide Act, as amended (7 U.S.C. 135, et seq.).

(3) The ambient water criterion for aldrin/dieldrin in navigable waters is 0.003 μg/l.

(b) *Aldrin/Dieldrin manufacturer.*—(1) *Applicability.*

(i) These standards or prohibitions apply to:

(A) all discharges of process wastes; and

(B) all discharges from the manufacturing areas, loading and unloading areas, storage areas and other areas which are subject to direct contamination by aldrin/dieldrin as a result of the manufacturing process, including but not limited to:

(*1*) Stormwater and other runoff except as hereinafter provided in subparagraph (ii); and

(2) Water used for routine cleanup or cleanup of spills.

(ii) These standards do not apply to stormwater runoff or other discharges from areas subject to contamination solely by fallout from air emissions of aldrin/dieldrin; or to stormwater runoff

that exceeds that from the ten year 24-hour rainfall event.

(2) *Analytical Method Acceptable.* Environmental Protection Agency method specified in 40 CFR Part 136, except that a 1-liter sample size is required to increase the analytical sensitivity.

(3) *Effluent Standard.*—(i) *Existing Sources.* Aldrin or dieldrin is prohibited in any discharge from any aldrin/dieldrin manufacturer.

(ii) *New Sources.* Aldrin or dieldrin is prohibited in any discharge from any aldrin/dieldrin manufacturer.

(c) *Aldrin/Dieldrin Formulator.*—(1) *Applicability.*

(i) These standards or prohibitions apply to:

(A) All discharges of process wastes; and

(B) All discharges from the formulating areas, loading and unloading areas, storage areas and other areas which are subject to direct contamination by aldrin/dieldrin as a result of the formulating process, including but not limited to:

(*1*) Stormwater and other runoff except as hereinafter provided in subparagraph (ii); and

(*2*) Water used for routine cleanup or cleanup of spills.

(ii) These standards do not apply to stormwater runoff or other discharges from areas subject to contamination solely by fallout from air emissions of aldrin/dieldrin; or to stormwater runoff that exceeds that from the ten year 24-hour rainfall event.

(2) *Analytical Method Acceptable.* Environmental Protection Agency method specified in 40 CFR Part 136, except that a 1-liter sample size is required to increase the analytical sensitivity.

(3) *Effluent Standard.*—(i) *Existing Sources.* Aldrin or dieldrin is prohibited in any discharge from any aldrin/dieldrin formulator.

(ii) *New Sources.* Aldrin or dieldrin is prohibited in any discharge from any aldrin/dieldrin formulator.

§ 129.101 DDT, DDD and DDE.

(a) *Specialized Definitions.* (1) "DDT Manufacturer" means a manufacturer, excluding any source which is exclusively a DDT formulator, who produces, prepares or processes technical DDT, or who uses DDT as a material in the production, preparation or processing of another synthetic organic substance.

(2) "DDT Formulator" means a person who produces, prepares or processes a formulated product comprising a mixture of DDT and inert materials or other diluents into a product intended for application in any use registered under the Federal Insecticide, Fungicide and Rodenticide Act, as amended (7 U.S.C. 135, et seq.).

(3) The ambient water criterion for DDT in navigable waters is 0.001 μg/l.

(b) *DDT Manufacturer.*—(1) *Applicability.*

(i) These standards or prohibitions apply to:

(A) All discharges of process wastes; and

(B) All discharges from the manufacturing areas, loading and unloading areas, storage areas and other areas which are subject to direct contamination by DDT as a result of the manufacturing process, including but not limited to:

(*1*) Stormwater and other runoff except as hereinafter provided in subparagraph (ii); and

(*2*) Water used for routine cleanup or cleanup of spills.

(ii) These standards do not apply to stormwater runoff or other discharges from areas subject to contamination solely by fallout from air emissions of DDT; or to stormwater runoff that exceeds that from the ten year 24-hour rainfall event.

(2) *Analytical Method Acceptable.*—Environmental Protection Agency method specified in 40 CFR Part 136, except that a 1-liter sample size is required to increase the analytical sensitivity.

(3) *Effluent Standard.*—(i) *Existing Sources.* DDT is prohibited in any discharge from any DDT manufacturer.

(ii) *New Sources.* DDT is prohibited in any discharge from any DDT manufacturer.

(c) *DDT Formulator.*—(1) *Applicability.* (i) These standards or prohibitions apply to:

(A) All discharges of process wastes; and

(B) All discharges from the formulating areas, loading and unloading

areas, storage areas and other areas which are subject to direct contamination by DDT as a result of the formulating process, including but not limited to:

(1) Stormwater and other runoff except as hereinafter provided in subparagraph (ii); and

(2) Water used for routine cleanup or cleanup of spills.

(ii) These standards do not apply to stormwater runoff or other discharges from areas subject to contamination solely by fallout from air emissions of DDT; or to stormwater runoff that exceeds that from the ten year 24-hour rainfall event.

(2) *Analytical Method Acceptable.* Environmental Protection Agency method specified in 40 CFR Part 136, except that a 1-liter sample size is required to increase the analytical sensitivity.

(3) *Effluent Standard.*—(i) *Existing Sources.* DDT is prohibited in any discharge from any DDT formulator.

(ii) *New Sources.* DDT is prohibited in any discharge from any DDT formulator.

§ 129.102 Endrin.

(a) *Specialized definitions.* (1) "Endrin Manufacturer" means a manufacturer, excluding any source which is exclusively an endrin formulator, who produces, prepares or processes technical endrin or who uses endrin as a material in the production, preparation or processing of another synthetic organic substance.

(2) "Endrin Formulator" means a person who produces, prepares or processes a formulated product comprising a mixture of endrin and inert materials or other diluents into a product intended for application in any use registered under the Federal Insecticide, Fungicide and Rodenticide Act, as amended (7 U.S.C. 135, et seq.).

(3) The ambient water criterion for endrin in navigable waters is 0.004 μg/l.

(b) *Endrin manufacturer*—(1) *Applicability.* (i) These standards or prohibitions apply to:

(A) All discharges of process wastes; and

(B) All discharges from the manufacturing areas, loading and unloading areas, storage areas and other areas which are subject to direct contamination by endrin as a result of the manufacturing process, including but not limited to: (1) Stormwater and other runoff except as hereinafter provided in subparagraph (ii); and (2) Water used for routine cleanup or cleanup of spills.

(ii) These standards do not apply to stormwater runoff or other discharges from areas subject to contamination solely by fallout from air emissions of endrin; or to stormwater runoff that exceeds that from the ten year 24-hour rainfall event.

(2) *Analytical Method Acceptable*—Environmental Protection Agency method specified in 40 CFR Part 136.

(3) *Effluent Standard*—(i) *Existing Sources*—Discharges from an endrin manufacturer shall not contain endrin concentrations exceeding an average per working day of 1.5 μg/l calculated over any calendar month; and shall not exceed a monthly average daily loading of 0.0006 kg/kkg of endrin produced; and shall not exceed 7.5 μg/l in a sample(s) representing any working day.

(ii) *New Sources*—Discharges from an endrin manufacturer shall not contain endrin concentrations exceeding an average per working day of 0.1 μg/l calculated over any calendar month; and shall not exceed a monthly average daily loading of 0.00004 kg/kkg of endrin produced; and shall not exceed 0.5 μg/l in a sample(s) representing any working day.

(iii) *Mass Emission Standard During Shutdown of Production*—In computing the allowable monthly average daily loading figure required under the preceding subparagraphs (i) and (ii), for any calendar month for which there is no endrin being manufactured at any plant or facility which normally contributes to the discharge which is subject to these standards, the applicable production value shall be deemed to be the average monthly production level for the most recent preceding 360 days of actual operation of the plant or facility.

(c) *Endrin Formulator*—(1) *Applicability.* (i) These standards or prohibitions apply to:

(A) All discharges of process wastes; and

(B) All discharges from the formulating areas, loading and unloading areas, storage areas and other areas which are subject to direct contamination by endrin

as a result of the formulating process, including but not limited to: (*1*) Stormwater and other runoff except as hereinafter provided in subparagraph (ii); and (2) Water used for routine cleanup or cleanup of spills.

(ii) These standards do not apply to stormwater runoff or other discharges from areas subject to contamination solely by fallout from air emissions of endrin; or to storm-water runoff that exceeds that from the ten year 24-hour rainfall event.

(2) *Analytical Method Acceptable*—Environmental Protection Agency method specified in 40 CFR Part 136, except that a 1-liter sample size is required to increase the analytical sensitivity.

(3) *Effluent Standard*—(i) *Existing Sources*—Endrin is prohibited in any discharge from any endrin formulator.

(ii) New Sources—Endrin is prohibited in any discharge from any endrin formulator.

(d) The standards set forth in this Section shall apply to the tctal combined weight or concentration of endrin, excluding any associated element or compound.

§ 129.103 Toxaphene.

(a) *Specialized definitions.* (1) "Toxaphene Manufacturer" means a manufacturer, excluding any source which is exclusively a toxaphene formulator, who produces, prepares or processes toxaphene or who uses toxaphene as a material in the production, preparation or processing of another synthetic organic substance.

(2) "Toxaphene Formulator" means a person who produces, prepares or processes a formulated product comprising a mixture of toxaphene and inert materials or other diluents into a product intended for application in any use registered under the Federal Insecticide, Fungicide and Rodenticide Act, as amended (7 U.S.C. 135, *et seq.*).

(3) The ambient water criterion for toxaphene in navigable waters is 0.005 μg/l.

(b) *Toxaphene manufacturer*—(1) *Applicability.* (i) These standards or prohibitions apply to:

(A) All discharges of process wastes; and

(B) All discharges from the manufacturing areas, loading and unloading areas, storage areas and other areas which are subject to direct contamination by toxaphene as a result of the manufacturing process, including but not limited to: (*1*) Stormwater and other runoff except as hereinafter provided in subparagraph (ii); and (2) Water used for routine cleanup or cleanup of spills.

(ii) These standards do not apply to stormwater runoff or other discharges from areas subject to contamination solely by fallout from air emissions of toxaphene; or to stormwater runoff that exceeds that from the ten year 24-hour rainfall event.

(2) *Analytical Method Acceptable*—Environmental Protection Agency method specified in 40 CFR Part 136.

(3) *Effluent Standard*—(i) *Existing Sources*—Discharges from a toxaphene manufacturer shall not contain toxaphene concentrations exceeding an average per working day of 1.5 μg/l calculated over any calendar month; and shall not exceed a monthly average daily loading of 0.00003 kg/kkg of toxaphene produced, and shall not exceed 7.5 μg/l in a sample(s) representing any working day.

(ii) *New Sources*—Discharges from a toxaphene manufacturer shall not contain toxaphene concentrations exceeding an average per working day of 0.1 μg/l calculated over any calendar month; and shall not exceed a monthly average daily loading of 0.000002 kg/kkg of toxaphene produced, and shall not exceed 0.5 μ/l in a sample(s) representing any working day.

(iii) *Mass Emission During Shutdown of Production*—In computing the allowable monthly average daily loading figure required under the preceding subparagraphs (i) and (ii), for any calendar month for which there is no toxaphene being manufactured at any plant or facility which normally contributes to the discharge which is subject to these standards, the applicable production value shall be deemed to be the average monthly production level for the most recent preceding 360 days of actual operation of the plant or facility.

(c) *Toxaphene Formulator*—(1) *Applicability.* (i) These standards or prohibitions apply to:

(A) All discharges of process wastes; and

(B) All discharges from the formulating areas, loading and unloading areas, storage areas and other areas which are subject to direct contamination by toxaphene as a result of the formulating process, including but not limited to: (*1*) Stormwater and other runoff except as hereinafter provided in subparagraph (ii); and (2) Water used for routine cleanup or cleanup of spills.

(ii) These standards do not apply to stormwater runoff or other discharges from areas subject to contamination solely by fallout from air emissions of toxaphene; or to stormwater runoff that exceeds that from the ten year 24-hour rainfall event.

(2) *Analytical Method Acceptable*—Environmental Protection Agency method specified in 40 CFR Part 136, except that a 1-liter sample size is required to increase the analytical sensitivity.

(3) *Effluent Standards*—(i) *Existing Sources*—Toxaphene is prohibited in any discharge from any toxaphene formulator.

(ii) *New Sources*—Toxaphene is prohibited in any discharge from any toxaphene formulator.

(d) The standards set forth in this Section shall apply to the total combined weight or concentration of toxaphene, excluding any associated element or compound.

§ 129.104 Benzidine.

(a) *Specialized definitions.* (1) "Benzidine Manufacturer" means a manufacturer who produces benzidine or who produces benzidine as an intermediate product in the manufacture of dyes commonly used for textile, leather and paper dyeing.

(2) "Benzidine-Based Dye Applicator" means an owner or operator who uses benzidine-based dyes in the dyeing of textiles, leather or paper.

(3) The ambient water criterion for benzidine in navigable waters is 0.1 μg/1.

(b) *Benzidine manufacturer*—(1) *Applicability.* (i) These standards apply to:

(A) All discharges into the navigable waters of process wastes, and

(B) All discharges into the navigable waters of wastes containing benzidine from the manufacturing areas, loading and unloading areas, storage areas, and other areas subject to direct contamination by benzidine or benzidine-containing product as a result of the manufacturing process, including but not limited to:

(*1*) Stormwater and other runoff except as hereinafter provided in paragraph (b)(1)(ii) of this section and

(2) Water used for routine cleanup or cleanup of spills.

(ii) These standards do not apply to stormwater runoff or other discharges from areas subject to contamination solely by fallout from air emissions of benzidine; or to stormwater runoff that exceeds that from the ten year 24-hour rainfall event.

(2) *Analytical method acceptable*—Environmental Protection Agency method specified in 40 CFR Part 136.

(3) *Effluent standards*—(i) *Existing sources*—Discharges from a benzidine manufacturer shall not contain benzidine concentrations exceeding an average per working day of 10 μg/l calculated over any calendar month, and shall not exceed a monthly average daily loading of 0.130 kg/kkg of benzidine produced, and shall not exceed 50 μg/l in a sample(s) representing any working day.

(ii) *New sources*—Discharges from a benzidine manufacturer shall not contain benzidine concentrations exceeding an average per working day of 10 μg/l calculated over any calendar month, and shall not exceed a monthly average daily loading of 0.130 kg/kkg of benzidine produced, and shall not exceed 50 μg/l in a sample(s) representing any working day.

(4) The standards set forth in this paragraph (b) shall apply to the total combined weight or concentration of benzidine, excluding any associated element or compound.

(c) *Benzidine-based Dye Applicators*—(1) *Applicability.* (i) These standards apply to:

(A) All discharges into the navigable waters of process wastes, and

(B) All discharges into the navigable waters of wastes containing benzidine

from the manufacturing areas, loading and unloading areas, storage areas, and other areas subject to direct contamination by benzidine or benzidine-containing product as a result of the manufacturing process, including but not limited to:

(*1*) Stormwater and other runoff except as hereinafter provided in paragraph (c) (1) (ii) of this section and

(2) Water used for routine cleanup or cleanup of spills.

(ii) These standards do not apply to stormwater runoff or other discharges from areas subject to contamination solely by fallout from air emissions of benzidine; or to stormwater that exceeds that from the ten year 24-hour rainfall event.

(2) *Analytical method acceptable.* (i) Environmental Protection Agency method specified in 40 CFR Part 136; or

(ii) Mass balance monitoring approach which requires the calculation of the benzidine concentration by dividing the total benzidine contained in dyes used during a working day (as certified in writing by the manufacturer) by the total quantity of water discharged during the working day.

(COMMENT: The Regional Administrator (or State Director, if appropriate) shall rely entirely upon the method specified in 40 CFR 136 in analyses performed by him for enforcement purposes.)

(3) *Effluent standards*—(i) *Existing sources*—Discharges from benzidine-based dye applicators shall not contain benzidine concentrations exceeding an average per working day of 10 μg/l calculated over any calendar month; and shall not exceed 25 μg/l in a sample(s) or calculation(s) representing any working day.

(ii) *New sources*—Discharges from benzidine-based dye applicators shall not contain benzidine concentrations exceeding an average per working day of 10 μg/l calculated over any calendar month; and shall not exceed 25 μg/l in a sample(s) or calculation(s) representing any working day.

(4) The standards set forth in this paragraph (c) shall apply to the total combined concentrations of benzidine, excluding any associated element or compound.

[42 FR 2620, Jan. 12, 1977]

§ 129.105 Polychlorinated Biphenyls (PCBs).

(a) *Specialized definitions.* (1) "PCB Manufacturer" means a manufacturer who produces polychlorinated biphenyls.

(2) "Electrical capacitor manufacturer" means a manufacturer who produces or assembles electrical capacitors in which PCB or PCB-containing compounds are part of the dielectric.

(3) "Electrical transformer manufacturer" means a manufacturer who produces or assembles electrical transformers in which PCB or PCB-containing compounds are part of the dielectric.

(4) The ambient water criterion for PCBs in navigable waters is 0.001 μg/l.

(b) *PCB Manufacturer*—(1) *Applicability.* (i) These standards or prohibitions apply to:

(A) All discharges of process wastes;

(B) All discharges from the manufacturing or incinerator areas, loading and unloading areas, storage areas, and other areas which are subject to direct contamination by PCBs as a result of the manufacturing process, including but not limited to:

(*1*) Stormwater and other runoff except as hereinafter provided in subparagraph (ii); and

(2) Water used for routine cleanup or cleanup of spills.

(ii) These standards do not apply to stormwater runoff or other discharges from areas subject to contamination solely by fallout from air emissions of PCBs; or to stormwater runoff that exceeds that from the ten-year 24-hour rainfall event.

(2) Analytical Method Acceptable—Environmental Protection Agency method specified in 40 CFR Part 136 except that a 1-liter sample size is required to increase analytical sensitivity.

(3) Effluent Standards: (i) *Existing Sources.* PCBs are prohibited in any discharge from any PCB manufacturer; (ii) *New Sources.* PCBs are prohibited in any discharge from any PCB manufacturer.

(c) *Electrical Capacitor Manufacturer*—(1) *Applicability.* (i) These standards or prohibitions apply to:

(A) All discharges of process wastes; and

(B) All discharges from the manufacturing or incineration areas, loading and unloading areas, storage areas and other areas which are subject to direct contamination by PCBs as a result of the manufacturing process, including but not limited to:

(*1*) Stormwater and other runoff except as hereinafter provided in subparagraph (ii); and

(2) Water used for routine cleanup or cleanup of spills.

(ii) These standards do not apply to stormwater runoff or other discharges from areas subject to contamination solely by fallout from air emissions of PCBs; or to stormwater runoff that exceeds that from the ten-year 24-hour rainfall event.

(2) *Analytical Method Acceptable.* Environmental Protection Agency method specified in 40 CFR Part 136, except that a 1-liter sample size is required to increase analytical sensitivity.

(3) *Effluent Standards*—(i) Existing *Sources.* PCBs are prohibited in any discharge from any electrical capacitor manufacturer; (ii) *New Sources.* PCBs are prohibited in any discharge from any electrical capacitor manufacturer.

(d) *Electrical Transformer Manufacturer*—(1) *Applicability.* (i) These standards or prohibitions apply to:

(A) All discharges of process wastes; and

(B) All discharges from the manufacturing or incineration areas, loading and unloading areas, storage areas, and other areas which are subject to direct contamination by PCBs as a result of the manufacturing process, including but not limited to: (*1*) Stormwater and other runoff except as hereinafter provided in subparagraph (ii); and (2) Water used for routine cleanup or cleanup of spills.

(ii) These standards do not apply to stormwater runoff or other discharges from areas subject to contamination solely by fallout from air emissions of PCBs; or to stormwater runoff that exceeds that from the ten-year 24-hour rainfall event.

(2) *Analytical Method Acceptable.* Environmental Protection Agency method specified in 40 CFR Part 136, except that a 1-liter sample size is required to increase analytical sensitivity.

(3) *Effluent Standards*—(i) *Existing Sources.* PCBs are prohibited in any discharge from any electrical transformer manufacturer; (ii) *New Sources.* PCBs are prohibited in any discharge from any electrical transformer manufacturer.

(e) *Adjustment of effluent standard for presence of PCBs in intake water.* Whenever a facility which is subject to these standards has PCBs in its effluent which result from the presence of PCBs in its intake waters, the owner may apply to the Regional Administrator (or State Director, if appropriate), for a credit pursuant to the provisions of § 129.6, where the source of the water supply is the same body of water into which the discharge is made. The requirement of subparagraph (1) of § 129.-6(a), relating to the source of the water supply, shall be waived, and such facility shall be eligible to apply for a credit under § 129.6, upon a showing by the owner or operator of such facility to the Regional Administrator (or State Director, if appropriate) that the concentration of PCBs in the intake water supply of such facility does not exceed the concentration of PCBs in the receiving water body to which the plant discharges its effluent.

[42 FR 6555, Feb. 2, 1977]

CALIBRATION OF WATER MONITORING INSTRUMENTATION

Contents

A. INTRODUCTION

1. Purpose of Calibration

The increasing recognition after the Second World War that the water resources of the United States were finite and were being degraded to an unacceptable degree by man's activities, resulted in an unprecedented attempt to reverse the deterioration of these resources. These efforts have now become more searching as evidence accumulates of the possible health effects of low levels of certain inorganic and organic constituents of water. The investigation of long term effects must, in the short term, depend on existing or current data, and there are great pressures to expand these data as soon as possible so that their relationship, if any, to current biostatistical information can be assessed. The consequence for water and wastewater laboratories is mandatory analysis of many more samples, on which many more tests are made. The most efficient way to handle this greatly increased workload is by analytical instrumentation, particularly when the instrumentation is automated as much as possible.

In discussing analytical instrumentation, the term "calibration" as used herein, refers to the entire analytical procedure in which the instrumentation is used, including those steps taken to obtain the desired precision and accuracy. A characteristic feature of most physical and physico-chemical techniques for trace analysis is the necessity for finding empirically the value of an output (digital, scale reading, graphic display) corresponding to the concentration of the constituent of interest. All of these methods require the use of standards containing known amounts of the constituent, in suitable matrices, which serve as bases of comparison in the measurements. Thus calibration is an integral part of quantitative trace analysis.

The use of standard samples performs another important function in the analysis. The goal of quantitative analysis is accuracy, i.e., the ability to approach the "true" value. Errors affecting the results may be classified as either systematic or random. The former, often referred to as determinate errors, are due to causes over which the analyst has a degree of control, and their effect may be subject to reduction, elimination, or a correction factor. On the other hand random errors are not subject to control and are present even in the absence of systematic errors. Although the magnitude of random errors can be reduced by keeping all operations as identical as possible, they are never eliminated completely. The precision of results therefore depends on random errors, including those resulting from systematic errors not completely eliminated. In this situation the distinction between precision and accuracy becomes less apparent, i.e., the precision defines the accuracy that can be achieved in the absence of systematic errors. Detailed discussion of the sources of errors is given later.

While calibration procedures must be applied to the entire analytical system, calibration of individual portions (e.g., sampling, pretreatment, transducer) is helpful for diagnostic purposes. By way of illustration, gradual drift of a zero or 100% span setting can be differentiated from faulty operation, for example a clogged line by calibration of the readout device.

2. Calibration Statistics

If a normally operating analog instrument is used to make a number of measurements on a sample, the resultant readings will not be identical to one another. The closer they are together the more precise the instrument. This idea can be put on a more quantative basis. Let us assume that we make n measurements on the unknown, obtaining the reading R_i where i goes from 1 to n. The average of arithmetic mean of the reading is:

$$\bar{R} = \frac{1}{n} \Sigma R_i .$$

The variance of the readings will be given by:

$$V = \frac{\Sigma(R_i - \bar{R})^2}{n}$$

and the standard deviation of the reading is

$$s = \sqrt{V} .$$

The standard deviation of the instrument is an inverse measure of the precision of the instrument. The smaller the standard deviation the more precise the instrument. If the instrument is well behaved and its error is made up of a number of small internal inaccuracies, then a graph of a large number of readings R_i plotted against the number of times a value occurs will be a Gaussian curve. In this case, it can be shown that there is a 50% chance that any given reading lies within 0.6915 x s where s is the standard deviation. Indeed e = 0.6915s is known as the most probable error. On the other hand the probability that a reading falls outside 3s is only 0.0013. If, in testing an instrument, a reading is found to fall say at 4s or 5s, then it is probably because the operator misread the device. However, such a value of R_i should alert the user to the possibility that there is an intermittent loose connection or similar defect in the device.

If a sample whose characteristic being measured is known very exactly, the accuracy of the instrument determines how close an individual R_i is to C_i, the known characteristic. If these differences are small the instrument can be said to be accurate.

Calibration is the procedure used to ensure instrument accuracy. If the instrument is of low or poor precision, the calibration cannot improve its precision, but it can make $\overline{R}$ as close as desired to C_i. The calibration may take one of two forms. There may be an adjustment that can be made on the instrument permitting R_i or $\overline{R}$ to be brought closer to C_i as measurements are made on one or more C_i's or standard samples. Alternatively the calibration may be in the form of a curve giving the functional relationship between R_i and C_i. Methods and means for carrying out calibration procedures is the subject of this section.

If the functional relation between R_i and C_i is linear or can be linearized it greatly simplifies plotting an accurate calibration curve. Assume that $R_i = a + bC_i$ then the problem reduces to one of evaluating "a" and "b." The first step is to make n readings using n values of C_i where i = 1 to n. From this "a" and "b" can be calculated as follows:

$$a = \frac{n\Sigma R_i C_i - \Sigma C_1 \Sigma R_1}{n\Sigma R_i^2 - (\Sigma R_i)^2}$$

$$b = \frac{\Sigma R_i^2 \Sigma C_i - \Sigma R_i \Sigma R_i C_i}{n\Sigma R_i^2 - (\Sigma R_1)^2} .$$

This is known as the method of least squares and the resulting calibration curve is free from subjective judgment and makes nearly maximum use of the measurements made.

In most quantitative analytical methods the foregoing is complicated by many sources of error, both determinate and indeterminate. They include sampling errors (which may not be apparent until the analytical results are obtained), errors due to handling (chemical operations, extractions, storage) and errors due to sample presentation to the instrument. The statistical treatment is the same as for calibration errors, but it is important to recognize that these additional factors will cause variations in the results of a method which cannot properly be ascribed to the instrumentation.

For trace determinations, reliable standard samples may not be available for the desired low concentrations, but only for relatively high ones. In these cases, one is forced to extrapolate the calibration function into the desired low range, sometimes through several orders of magnitude. This task requires a high degree of critical judgment because small deviations at the start may cause grave systematic errors in the low range.

In order to make extended extrapolation practicable, two basic requirements should be fulfilled:

(a) *The calibration function must be linear.* If not, it must be 'linearized' by a suitable transformation as discussed earlier, or to suitably arrange the standardization function such that it is graphically linear. This can be accomplished by, for example, a semi-logarithmic or a logarithmic representation.

(b) The calibration function must be established for the net measure only; *the blank portion of the measure must be eliminated.*

(c) A program to assure traceability to a common reference standard, referred to as a primary standard, must also be included.

Accuracy, as discussed, normally refers to the difference (error or bias) between the set of results measured and the value which is accepted as the true or correct value for the quantity measured. Precision refers to the extent to which a given set of measurements agrees with the mean of the measurements. Figure 1 illustrates examples of accuracy and precision in target shooting.

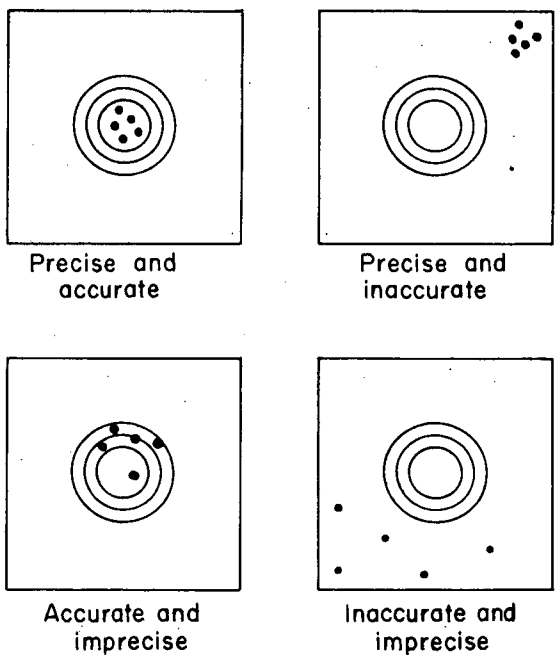

Fig. 1. Random and systematic errors.

There are two broad classes of error which should be recognized: (1) determinate or bias (systematic) errors and (2) indeterminate or random errors. Bias errors are due generally to poor procedures and may be caused by equipment and/or personnel. Systematic human errors are reduced by using standard procedures. Systematic equipment errors may be accounted by proper calibrating techniques which result in the generation of calibration curves of the

type shown in Fig. 2. Bias errors are often constant for each case and of a unidirectional nature (positive or negative). Thus, if the magnitude and direction of the errors are known, their effect can be taken into account and the following expression applies

$$x_c = x_0 \pm e_0$$

where

x_0 is the observed value

e_0 is the absolute error (bias) at the condition at which the observation is made.

Instrumentation bias is not necessarily a limiting factor if it can be evaluated by calibration.

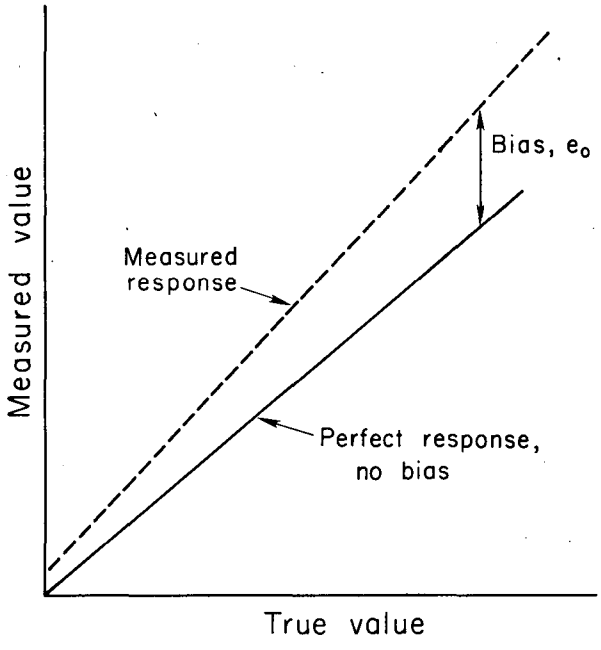

Fig. 2. Typical calibration curve.

Random errors are as likely to be positive as negative and their specific magnitude and direction cannot be predicted for each measurement. They occur because in each test there are a number of experimental variables, each of which causes a small uncontrolled error. Random errors are described by laws of probability and statistics and are usually normally distributed. Information on standardization statistics may be obtained from Standard Methods, (14th edition (Ref. 2), The Book of ASTM Standards, Part 31 (Ref. 3), Chemical Analysis (Ref. 4), and the draft Manual on Analysis for Water Pollution Control (Ref. 5).

Calibration techniques depend in a large part upon an understanding of the operation of the instrument and the manner in which the instrument is to be used. Usually, standardization involves a determination of instrument response of at least 3 points on a calibration curve. Knowledge of whether the response is linear or exponential is important, particularly if extrapolations of the standard curve are necessary. Before the response of the instrument can be calibrated, the matrix in which the constituent(s) of interest occurs must be known. The matrix may be definable at the time of sample collection, or more often by a properly sequenced quantitative analysis. When the matrix is shown to contain interferences, several techniques are available, including standard addition, and preparing standards which contain the interferences as they occur in the sample.

The accuracy of any instrument calibration depends upon many factors, but it must be remembered that indeterminate errors are not necessarily random. The most probable cumulative error can then be determined according to the following equation:

$$E_c = \sqrt{E_1^2 + E_2^2 + E_3^2 + \cdots} \quad .$$

As mentioned above, other factors in sampling and handling are often of much greater variability than the response of the instrument.

The sensitivity and range of an instrument's response are prime considerations in the calibration of an instrument.

3. Sources of Error in Water Calibration

Errors in water quality measurements are classified as either determinate or indeterminate (Fig. 1). Calibration is aimed at increasing the accuracy of the analysis by eliminating determinate errors, and minimizing indeterminate errors.

a. Bias Error

Bias errors are those errors over which the analyst exercises some degree of control, for example by maintaining clean glassware. They are said to be present when the analytical result is either higher or lower than the true value, and the mean of repeated measurements on portions of the same sample does not approach the true value as the number of measurements increases.

When bias errors occur, the results are biased; the term bias has been used synonymously with the term systematic error (Ref. 5).

Instrument drift is an example of a bias error which is avoidable by calibration of the

instrument zero and 100% span settings. Modern instrumentation generally has low electronic drift rates. For example, a typical manufacturer's specification lists electronic drift rate as follows:

± 0.5% of full scale per 4 weeks; ± 1 digit or ± 0.3% per 24 hours; ± 0.001 absorbance units per hour.

The overall stability of automated instruments during unattended operation is particularly important in the generation of reliable data. The automated equipment should be evaluated for its performance during extended operation. For example, see Table (1) which lists drift data obtained from a TOC/TC automated analyzer. For this test, drift was defined as the net change in instrument output with time at a constant TOC concentration with unadjusted continuous operation. No measurable change was observed for zero drift, while the span drift ranged from zero to maximum of 0.8% full scale per day (Ref. 6).

In summary, bias errors are assumed present when results are greater or smaller than the true or calibrated value. Bias errors are minimized by good laboratory practice: e.g., checks for drift, cleanliness of sample transport lines, and use of reliable standards for calibration.

b. Random Errors

Random or indeterminate errors may be intrinsic to the instrumental analytical system; they are not controllable by the analyst. Examples of sources of errors in water analysis systems are the following: (1) nature of sample (e.g., fresh water, waste water), (2) sample chemical pretreatment (e.g., oxidation, precipitation), and (3) instrumental sensitivity. In many water analysis systems, the nature of the sample or the sample pretreatment cannot be changed. However, the type of instrumental method used for the measurement may be optional. In this case, the analyst should select a method with high sensitivity in order to increase the precision, reduce the error, and therefore decrease the number of replicate measurements required to arrive at the true value. This is because the precision of the result depends on random errors, and the precision defines the accuracy that can be achieved in the absence of systematic errors. Tables (2) and (3) list sensitivities for a number of important instrumental methods.

The magnitude of random errors is indicated by the scatter about the mean value of results of repeated measurements on portions of the same sample. Both the sign and magnitude of the error show a random scatter, and frequently cannot be predicted beforehand with exactness. The degree of scatter of the results defines the precision of the measurement which decreases as the random errors increase. Some random error is always present by the very nature of the physical world.

In summary, the *precision* of an instrument is its reproducibility; the *accuracy* is how close its reading is to the true value. A systematic error causes a loss of accuracy, and it may or may not affect the precision depending upon whether the error is constant or variable. Random errors cause a lowering of reproducibility, but by making sufficient observations it may be possible to compensate for the scatter so that the accuracy is not necessarily affected. Statistical treatment, can be properly applied only to random errors, but it is not known in advance whether the errors will be truly random. However, the laws of probability can be applied to determine whether nonrandomness (e.g., trends, discontinuities, clustering) is a factor. If such is the case, an effort should be made to locate and correct the systematic causes. (Ref. 4).

4. Interlaboratory Comparisons

Interlaboratory comparison is accomplished by the comparison of results obtained among a number of cooperating laboratories on the same water standard. Such a standard may be a synthetic solution prepared by dissolving pure (99.9+%) metal in the minimum amount of acid and diluting to volume with the highest grade reagent water. Another type of standard is prepared by adding a solution of a single metal to a sample of fresh (natural) water. These are made up to simulate actual field conditions to the greatest extent possible, with matrices being comparable. Each participating laboratory is then sent a representative sample from the bulk standard for analysis by the method under evaluation. The analyses provided by each participating laboratory are then treated statistically to calculate both the precision (reproducibility) and accuracy. The precision is usually expressed by the standard deviation, and the accuracy by the standard error.

Interlaboratory comparison of data is useful when a water analysis method is being considered, e.g., for regulatory considerations or for contribution to a data bank. By and large, collaborative testing is used to control the quality of analytical work. It is found that without interlaboratory collaborative tests errors often arise in using an analytical method that otherwise will not be detected. These errors are due to one or more of the following causes: (1) careless preparation of the sample for analysis, (2) the presence of interfering substances in one location and not in another, (3) the presence of impurities in the analytical reagents, (4) a seemingly trivial but in reality, important difference in the analytical procedure, (5) dirty equipment, and (6) use of instrumentation from different manufacturers which have different performance characteristics.

TABLE. 1. Zero and Total Drift (Ref. 6)

Test No.	Sample	Carbon Conc. (mg/ℓ)	Model	Duration (days)	Analyzer Reading (mV.) Start	Analyzer Reading (mV.) End	Full Scale (mg/ℓ)	Observed Change % Full Scale	Observed Change (mg/ℓ)	Observed Change % Full Scale/Day
1	$KHC_8H_4O_4$	0	TOC	0.5	0.56	0.56	500	0	0	8
2	$KHC_8H_4O_4$	124	TOC	2.5	20.5	21.5	400	1.8	7	0.7
3	$KHC_8H_4O_4$	192	TOC	2.1	23.9	24.8	500	1.4	7	0.7
4	$KHC_8H_4O_4$	100	TOC	14	24.5	19.0	500	-11.0	-55	-0.8
5	$KHC_8H_4O_4$	200	TC	11	12.2	13.7	1000	2.3	23	0.2
6	$KHC_8H_4O_4$	180	TC	6	11.8	11.0	1100	-1.1	-12	-0.2
7	$KHC_8H_4O_4$	190	TC	1	13.2	13.2	1000	0	0	0
8	Primary Sewage	60	TC	1	5.0	4.6	1000	-0.4	-4	-0.4
9	Ethyl Acetate	80	TOC	2.5	23.2	23.9	230	1.7	4	0.7

TABLE 2. Sensitivity of Instrument Methods Commonly Used for Analyses in Water

Instrumental Method	Sensitivity (µg/l)	
Automated Total Organic Carbon	10,000	
Polarography	100	1000
Wet Chemical Analyzer	100	1000
Molecular Absorption	100	1000
Atomic Absorption (Flame)	100	1000
Atomic Emission	100	1000
Square Wave Polarography	10	100
Sweep Voltammetry	10	100
Emission Spectroscopy (Arc)	10	100
X-Ray Fluorescence	10	100
Automated Ammonia	10	10
Pulse Polarography	1	10
Molecular Fluorescence	1	10
Spark Source Mass Spectrometry	1	10
Anodic Stripping	0.1	10
Neutron Activation	0.1	10
Atomic Absorption (Flameless)	0.1	10
Chemiluminescence	0.1	10
Emission Spectroscopy (Plasma)	0.1	10
Cold Vapor Hg Analyzer	0.2	0.2
Automated Cold Vapor	0.2	0.2
Turbitity	0.02	NTU

TABLE 3. Analytical Methods Commonly Used for the Determination of Organic Compounds in Water

Method	Approximate Sensitivity MDL[a] Instrument (gm)	Method (gm/l)
Gas Chromatography	10^{-12}-4×10^{-9}	5×10^{-9}-5×10^{-7}
Direct Aqueous GC	10^{-9}-4×10^{-9}	10^{-3}-5×10^{-6}
Gas Chromatography/ Mass Spectroscopy	10^{-9}-10^{-7}	10^{-8} 5×10^{-6}
Direct Aqueous GS-MS	10^{-9}-10^{-7}	10^{-3}-5×10^{-2}
Infrared Spectroscopy	10^{-6}-10^{-4}	10^{-5}-10^{-3}
Ultra Violet Spectroscopy	10^{-9}-10^{-7}	10^{-7}-10^{-6}
Thin-Layer Chromatography	5×10^{-8}-10^{-7}	5×10^{-7}-10^{-5}
Liquid Chromatography (UV Detector)	10^{-8}-10^{-6}	10^{-5}-10^{-3}

[a]Minimum detectable limit.

The Youden two-sample technique is commonly used for evaluating interlaboratory performance. (Ref. 5). This technique requires each participating laboratory to make one single determination on each of two samples; the number of laboratories can conveniently range up to one hundred.

In evaluating the data, both the mean value ($\bar{R}$) and the standard deviation, s, are calculated for each sample and each constituent (if more than one) using the results from all the laboratories. Next, all results exceeding $\bar{R} \pm 4s$ are rejected as indicating laboratories with systematic errors, and a new $\bar{R}$ and s calculated using the remaining data. One evaluation of the remaining data is to calculate the percent deviation from the true value.

Figure (3) shows the result on interlaboratory testing of four samples of mercury in water (Ref. 7). As seen, the between-laboratory agreements tend to deteriorate at mercury levels between 0.16 to 1.16 µg/1.

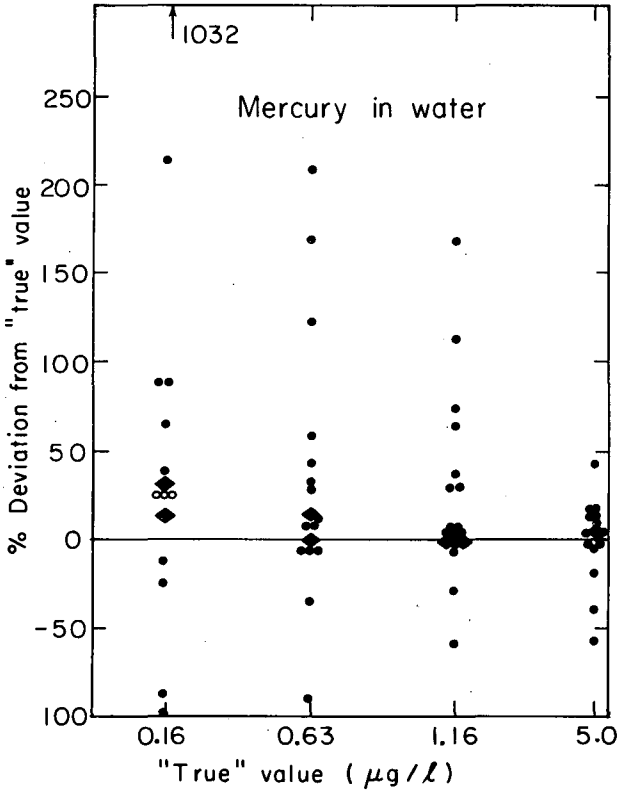

Fig. 3. Results of interlaboratory testing of four samples of mercury in water. (Ref. 7).

For interlaboratory comparison data on other pollutants and water quality standards, the reader is referred to the appropriate sections in Standard Methods, (14th Edition), and the EPA Manual.

In summary, interlaboratory collaborative tests provide valuable information on both the reliability of data, and the kind of precision and accuracy achievable.

B. SYSTEMS STANDARDIZATION

The number of steps or modules required for measuring a water quality parameter depends to a large extent on whether the analysis is made in the field or in the laboratory. For example, laboratory analysis involves measurements made on grab samples which may have an added preservative. A continuous field monitor of the sensor type, on the other hand, may be immersed directly into the water stream. Thus, calibration methods must include the entire system and not simply the instrumental measurement.

1. Laboratory Manual Instruments

Calibration methods for laboratory manual instruments can be classified as based on one of the following five types: (1) certified standards, for example, those available from the National Bureau of Standards, (2) comparison of the method being standardized with a commonly accepted method, (3) standard additions in which a small amount (e.g., µg) of the constituent is added to the water sample being analyzed, (4) synthetic standards prepared by dissolving the constituent in an aqueous solution, (5) theoretical relationships, for example coulometric analyses based on Faraday's Law. Those most commonly used for water analyses are based on certified reference standards,* calibration curves, standard additions, and synthetic standards: see Morrison (Ref. 8).

a. Certified Standard Reference Materials

Standard Reference Materials (SRM's) prepared and issued by the National Bureau of Standards are used as primary standards. The SRM's are gases, solutions or solids of carefully characterized materials containing accurately known quantities of an aqueous chemical pollutant (e.g., metal) or known magnitude of a physical parameter of water (e.g., pH).

Each SRM is designated by a distinguishing name and unique number; each sample of the SRM is of identical characterization with every other sample bearing the same designation within the limits required. When necessary, the SRM will be given a serial number and an individual calibration. In June 1975, NBS offered over 800 different SRM's; however, unfortunately only a very few are specific for water quality monitoring. Table (4) lists SRM's for water quality research and monitoring measurements. The dry, powdered orchard leaves and glass wafers are useful in calibrating the instrumental portion of the neutron activation, x-ray fluorescence, emission spectrometry and spark-source mass spectrometry techniques.

TABLE 4. National Bureau of Standards Certified SRM's for Instrumentation Calibration

SRM Number	Material	Certified Elements or Property
1641	Water solution	Hg - 1.49 mg/ℓ
1642	Water solution	Hg - 1.18 µg/ℓ
1571	Solid-orchard leaves	As - 14 µg/g
		B - 33
		Cd - 0.11
		Cu - 12
		Fe - 300
		Pb - 45
		Mn - 91
		Hg - 0.155
		Ni - 1.3
		Zn - 25
		N - 2.76%
		P - 0.21 %
614-615	Glass wafer (1-mm and 3-mm diameter)	Co - 0.71 ppm
		Cu - 1.34
		Pb - 2.32
		Ag - 0.42
682	High-purity metal	Zn
185d	Acid potassium phthalate	pH 4.004 at 25°C
186Ic, 186IIb	Potassium dihydrogen phosphate, disodium hydrogen phosphate	Mixed to give pH 6.865 at 25°C

The SRM's are of importance for both intralaboratory and interlaboratory calibration because the true value of a particular constituent is accurately known. Thus, for interlaboratory cooperative tests, the ability of the participating laboratories to get the true value (zero bias) as well as to agree with each other (e.g., precision) is determined.

b. Standard Additions

In the analysis of complex materials both matrix and interelement effects are the main contributors to systematic errors in many spectrometric methods. Therefore, the use of certified standards or the independent method of analysis approach on similar materials help to compensate for these complexities.

Another approach that is sometimes used is the method of standard additions, where a small known concentration of the desired species is increasingly added to several samples of the unknown material. The resulting samples as well as an untreated one are then analyzed. The response readings from the particular instrument are then plotted linearly against the

*For water analysis the only NBS certified standard available is for mercury.

concentrations, and the amount of unknown species present is determined by extrapolating a line to the abscissa. (Fig. 4). If the line is not linear, often a transformation can be performed such as the conversion of light absorption to absorbance. The best line which can be fitted to the data minimizes the sum of the squares of the vertical distance between data points and the constructed lines, referred to as the line of least-squares. (See Section 2).

Standard addition method is widely used in flame emission, atomic absorption, and spectrophotometric techniques.

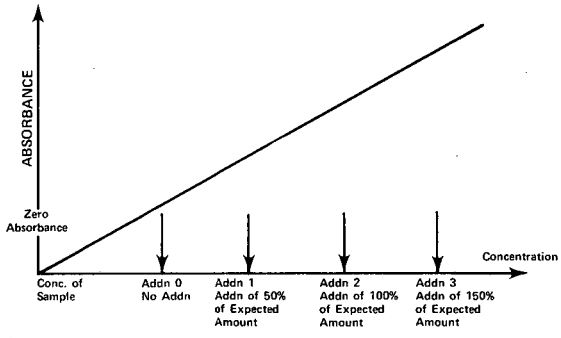

Fig. 4. Standard addition plot for atomic absorption analyses. (Ref. 5).

c. Synthetic Standards

The intent of these standards is to simulate or anticipate analyses of actual field samples. These standard synthetic samples are used for intercalibration among laboratories of instrumental methods to establish statistical precision and accuracy data. For example, Standard Methods, 14th edition, lists a synthetic standard for the dithizone method for Pb of the following composition of metal dissolved in distilled water as shown in Table (5). The sample was analyzed for Pb by 43 laboratories, with a relative standard deviation of 42.1%, and a relative error of 8.5%.

An example of a synthetic sample prepared by dissolved metals in water samples is that prepared by the Quality Assurance and Laboratory Evaluation Branch of the Methods Development and Quality Assurance Research Laboratory of the EPA in Cincinnati, Ohio. Six synthetic samples containing varying levels of Al, Cd, Cr, Fe, Mn, Pb and Zn were distributed for interlaboratory calibration of the atomic absorption method for Pb. The results were as follows (Table 6, Ref. 5).

TABLE 5

Metal	Concentration, µg/ℓ
Pb	70
Al	500
Cd	50
Cr	110
Cu	470
Fe	300
Mn	120
Ag	150
Zn	650

TABLE 6

Number of Labs	True Values µg/liter	Mean Value µg/liter	Standard Deviation µg/liter	Accuracy as % Bias
74	367	377	128	2.9
74	334	340	111	1.8
64	101	101	46	-0.2
64	84	85	40	1.1
61	37	41	25	9.6
60	25	31	22	25.7

2. Stability of Calibration

The problem of how long and under what circumstances the calibration values derived for a given analytical procedure remain valid is of importance for the critical assessment of a procedure and of the analytical results produced by it. Stability of calibration involves two aspects:

(a) the sensitivity of the analytical procedure to variations of experimental parameters, and

(b) the extent to which one has control over the parameters to keep the experimental conditions constant or to take into account the influence of changing parameters by suitable measurements and corrections.

Complex analytical procedures are usually susceptible to parameter changes, since it is difficult to reduce all of the variations simultaneously and throughout the whole range. Frequent calibration is mandatory.

3. Calibration of Automated Analyzers

Automated analyzers include both laboratory automated equipment (e.g., Technicon Auto Analyzer), and continuous field monitors (e.g., Ionics Mercury Monitor). Calibration of both classes of automated analyzers are discussed here.

Laboratory automated equipment is primarily centered around the Technicon Auto Analyzer using methods developed by the EPA. These methods are mostly based on the manual laboratory procedures given in Standard Methods, 14th edition. Calibration of the automated methods is accomplished by adding standards containing accurately known concentrations of the constituent to the sampler tray containing the samples being analyzed. For example, in the automated colorimetric phenate method for ammonia, a stock solution standard is prepared by dissolving 3.819 g anhydrous ammonium chloride in 1000 ml distilled water. From the stock solution, standard solutions are prepared to cover the concentration range of interest. These standards are loaded into the sampler tray in order of decreasing concentration of ammonia and analyzed.

Continuous field monitors are based either on sensors or an automation of manual laboratory procedures. The dissolved oxygen probe and pH electrode are examples of field monitors based on sensors. See Appendix I for recommended procedures for sensor calibration. The cyanide and phosphate field analyzers are examples of automated laboratory procedures; they are calibrated in the field using built-in standards.

C. CALIBRATION OF WATER QUALITY ANALYSIS INSTRUMENTATION

In this section specific examples of the application of systems calibration to water analysis instrumentation are given. It is not possible to cover all chemical and physical constituents; the discussion which follows centers on typical examples of important ones. For a more comprehensive coverage, the reader is referred to Standard Methods, 14th Edition; ASTM, Part 31; and The EPA Methods Manual.

1. Metals

The metal content of water samples is most commonly analyzed by laboratory instrumentation; discussion in this section will be limited to the commonly used laboratory systems. Mercury is treated separately because of the different analytical system.

a. Atomic Absorption

Standards for metals are usually prepared by dissolving pure (e.g., 99.9%) metal or metal compounds in reagent grade water which has a low background metal content (e.g., < 10 µg/ℓ) to ensure a low blank reading. Using modern methods which combine both distillation from an all-quartz apparatus and mixed-bed ion-exchange, exceptionally pure water can be obtained. Water of such high purity is a prerequisite to trace (e.g., < 100 µg/ℓ) metal analyses for it determines in part the magnitude of the blank and thus the limit of detectability (Ref. 9).

The two most commonly used atomic absorption methods for metals are standard curves and standard additions. Standardization curves are discussed first, using Cd as an example.

In Standard Methods, 14th Edition, stock Cd solutions are prepared by dissolving 100.0 mg of Cd metal in a solution composed of 20 ml distilled H_2O and 5 ml concentrated HCl. The mixture is heated to accelerate dissolution of the Cd; the resulting solution is transferred to a 1000-ml volumetric flask, and diluted to the mark with distilled water. After thorough mixing, the Cd standard solution is transferred to a polyethylene bottle. The concentration of this stock solution is 100 µg/ml (100 mg/1). From this stock solution, solutions of Cd are prepared for standardization purposes by pipetting 10.0 ml of the stock solution and 10 ml of concentrated HCl into a 1000-ml volumetric flask, and diluting to the mark with distilled water. The HCl is added to prevent the loss of Cd by hydrolysis and precipitation reactions (Ref. 2). This standard solution of Cd has a concentration of 1 mg/1; it should be prepared fresh daily.

Both the EPA and the USGS recommend preparation of stock Cd standards by different procedures than the above. A weighed quantity (e.g., 1.142 g) of reagent grade CdO is dissolved in 5 ml of HNO_3 and the solution diluted to 1000 ml with distilled water. This stock solution is further diluted to prepare the standard solutions for the calibration curve.

An example of atomic absorption calibration procedure for Pb in water is the study on the "Determination of Trace Metals in Power Plant Effluents," (Ref. 10). Measurements were made using two Perkin-Elmer Model 306 instruments equipped with both HGA-2000 and HGA-2100 graphite flameless excitation sources. Readout was accomplished using Perkin-Elmer Model 056 recorders. Standard curves were prepared from stock solutions containing 1000 mg/1 of the metal, and pipetting µl quantities into the furnace. See Figs. 5 and 6 for the Pb calibration curve. Table 7 lists the HGA-2100 operating parameters.

A good application of the standard additions method is given by Julshamn and Braekkan on determining trace metals in fish tissues (Ref. 11).

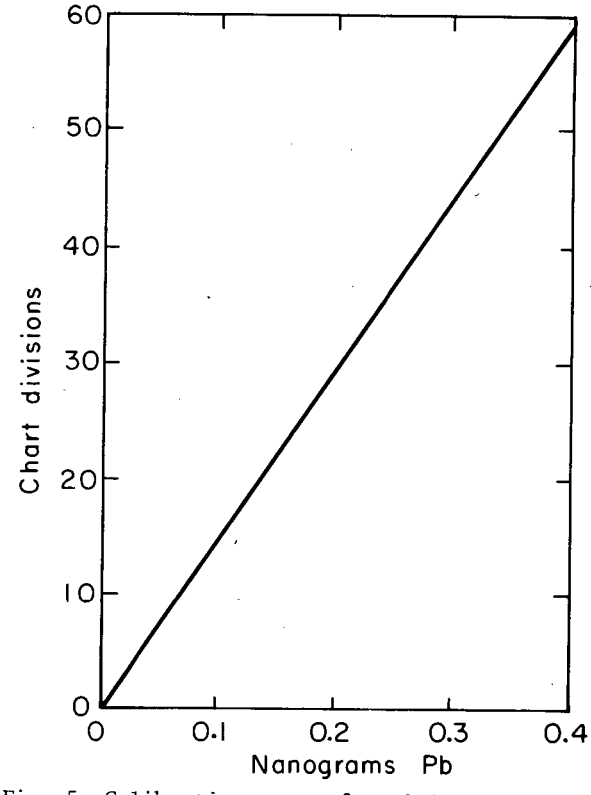

Fig. 5. Calibration curve from 0-0.4 ng Pb measured at 283.3 nm using 3X expansion. (Ref.10).

A typical calibration curve based on the method of standard additions is shown in Fig.7. All lines were plots of regression equations obtained from samples without and with the addition of 5, 10 and 15 µg Fe, corrected for

TABLE 7. HGA-2100 Operating Parameters (Ref. 10)

Element	Wavelength, nm	Spectral Band Width nm	Temperature, °C		
			Drying	Charring	Atomizing
As	193.7 (EDL @ 6w)	0.7	100	600	2400
Cd	228.8 (EDL @ 3.5 w)	0.7	100	250	1900
Cr	357.9	0.7	100	1100	2400
Cu	324.7	0.7	100	900	2400
Fe	248.3	0.2	100	1100	2100
Mn	279.5	0.2	100	900	2400
Ni	232.0	0.2	100	950	2400
Pb	283.3	0.7	100	700	2500
Se	196.0 (EDL @ 8 w)	2.0	100	700	2400

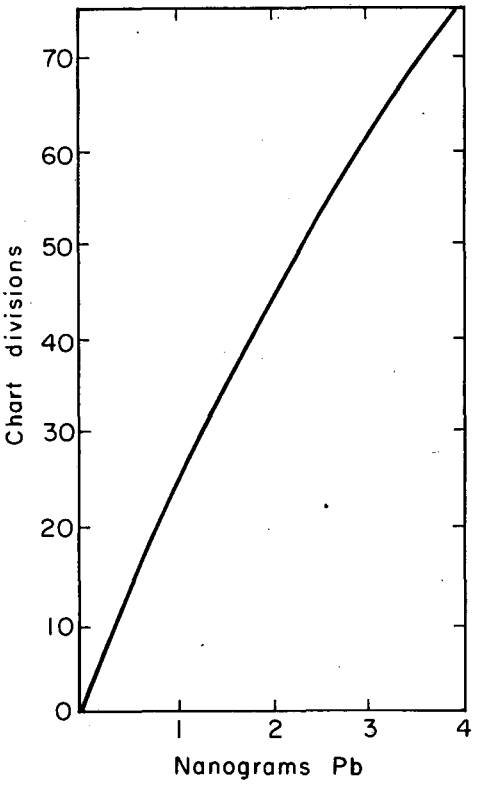

Fig. 6. Calibration curve from 0-4.0 ng Pb measured at 283.3 nm using 3X expansion. (Ref. 10).

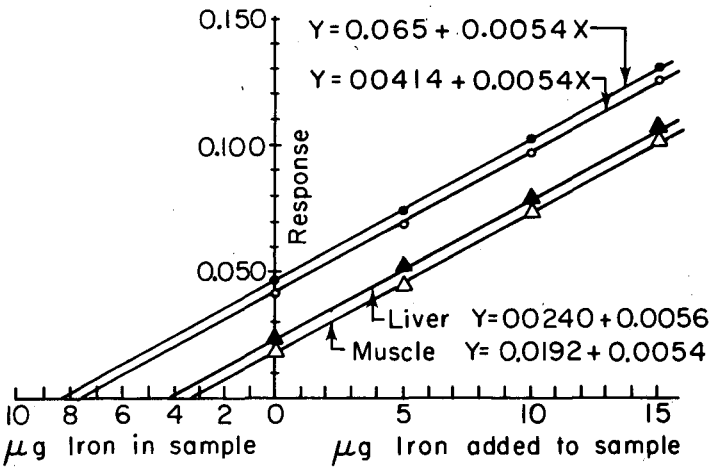

Fig. 7. Calibration curves for the determination of iron by the standard addition method. (Ref. 11).

the blank reading. The Fe content was read at the point where the lines intersect the zero response axis. The lines were calculated to fit the linear regression equation

$$y = a_0 + a_1X$$

y = response; X = µg Fe; a_0 = intercept; a_1 = slope.

All curves for Fe, Zn, Cu, Mn, Pb and Cd were highly linear with most having a correlation coefficient > 0.997. This indicated that the precision of the method was good, and that measurements were taken in the linear range of the regression curves for the different elements. See Table 8 for analytical results based on statistical treatment of the data.

TABLE 8. Regression Analysis of Curves Based on Standard Addition for Determination of Fe, Zn, Cu, Mn, Pd and Cd. (Ref. 11).

	R	α_0	α_1	1	σ(1)
Iron(Fe)					
Muscle	0.998	0.0192	0.00543	3.54	0.182
Roe	0.999	0.0414	0.00548	7.55	0.421
Soft roe	0.998	0.0365	0.00540	8.61	0.473
Liver	0.998	0.0240	0.00560	4.28	0.227
Zinc(Zn)					
Muscle	0.998	0.0241	0.00432	5.57	0.210
Roe	0.999	0.1641	0.00432	38.0	0.981
Soft roe	0.999	0.0513	0.00436	11.8	0.261
Liver	0.997	0.0251	0.00433	5.80	0.228
Copper(Cu)					
Muscle	0.999	0.0063	0.00810	0.78	0.083
Roe	0.999	0.0098	0.00805	1.06	0.100
Soft roe	0.999	0.0086	0.00815	1.22	0.110
Liver	0.997	0.0165	0.00830	1.99	0.181
Manganese(Mn)					
Muscle	0.997	0.0032	0.01170	0.27	0.081
Roe	0.999	0.0085	0.01175	0.72	0.120
Soft roe	0.999	0.0060	0.01155	0.52	0.103
Liver	0.999	0.0044	0.01195	0.37	0.083
Lead(Pb)					
Muscle	0.999	0.0018	0.01560	0.12	0.072
Roe	0.999	0.0155	0.01610	0.10	0.080
Soft roe	0.999	0.0006	0.01620	0.04	0.085
Liver	0.999	0.0024	0.01590	0.15	0.070
Cadmium(Cd)					
Muscle	0.997	0.0033	0.1463	0.023	0.0152
Roe	0.999	0.0010	0.1444	0.007	0.0130
Soft roe	0.999	0.0015	0.1450	0.010	0.0080
Liver	0.999	0.0047	0.1474	0.030	0.0141

α_R = correlation coefficient
a_0 = y = intercept, regression equation is defined as $y = a_1 X + a_0$, where X is concentration in µg/0.25 g dry matter
a_1 = slope
1 = $-a_0/a_1$ calculated for X (Y = 0) = 1
σ(1) = standard deviation = $\sigma(-a_0/a_1)$

b. UV-VIS Spectrophotometer (Colorimeter)

Calibration curves are the most commonly used method to calibrate colorimeters for metals-in-water analyses. Standard solutions are typically prepared by dissolving the pure metal in dilute acid, and generating the calibration curve (usually linear) by running the standards through the analysis procedure. The concentration of metal in the water sample usually is read from the standardization curve after correction for the blank reading.

For specific metals, the reader is referred to the appropriate sections in Standard Methods, 14th Edition, and the ASTM Annual, Part 31.

c. Neutron Activation

Calibration for neutron activation analysis is commonly carried out by exposing -- with the sample to be irradiated -- a standard containing a known weight of the metal being determined. The weight of the element being measured is then calculated from the relationship:

$$W_x = \frac{W_s A_x}{A_s}$$

W_x = Weight of element being measured
W_s = Weight of Standard
A_x = Activity of element being measured
A_s = Activity of standard.

For multielement analyses, standard solutions containing 5 to 10 elements at optimum concentration are prepared. In this way, only a few standard capsules need to be included in large set of samples being analyzed. The standards should be in as similar a matrix as possible to that of the samples; for example, saline samples such as sea water should have standards dissolved in an equivalent concentration of NaCl.

For a very good review of calibration for neutron activation, the reader is referred to the report on "Neutron Activation Techniques for the Measure of Trace Metals in Environmental Samples," by Robertson and Carpenter in the H2O--Metals section.

d. X-Ray Fluorescence

Analysis with x-ray fluorescence instrumentation is carried out on thin, solid samples (ng/cm^2 to mg/cm^2), with the higher sensitivities attained on the thinner samples. The thin specimens are important in minimizing matrix effects, for example self-absorption of the fluorescent x-rays by the sample. Good discussions of the theory of x-ray fluorescence and preparation of standards are found in the H2O--Metals section of this volume, and in the paper "Trace Element Determination with Semiconductor X-ray Spectrometers" (Ref. 12).

A recent example of calibration of x-ray fluorescence spectrometers is the application of this technique to the determination of phosphorous in natural waters. Standards were prepared by dissolving reagent grade KH_2PO_4 obtained from Fisher Scientific Co. and Mallinckrodt Chemical Works in distilled deionized water. All glassware was soaked for at least 1 hour in 6M HCl, and was never exposed to phosphate-containing detergents.

A 50.0 ml portion of sample was pipetted into a 60 ml separatory funnel; this was then followed by adding 4.50 ml conc HCl and 4 ml of 0.313 M Na_2MoO_4 $2H_2O$ to form phosphomolybdic acid. The mixture was shaken, 10 ml ethyl acetate added, and then shaken for 30 sec. After 10 min., the lower aqueous layer was removed, 10 ml of 1 M HCl added, the mixture shaken briefly, and the HCl layer removed. The ethyl acetate was then added to a 50 ml beaker, the funnel rinsed with 5 ml ethyl acetate which was added to the 50 ml beaker. Ten ml of H_2O were added to the beaker, and the contents were thoroughly stirred to mix the two layers. To the beaker, 100 ± 1 mg of silica gel was added to absorb the phosphomolybdic acid, the pH adjusted to 2.8, and the mixture stirred for five minutes. The silica gel was collected onto E. H. Sargent and Co. No. 500 filter paper (3 cm.), dried in an oven at 100 C for 10 min., and scraped into a 5 ml microbeaker containing 100 mg of cellulose powder (Whatman CF 11). Two drops of water were added, and a paste formed by stirring the mixture. The paste was pelletized under 10,000 pounds of pressure; and Mo determined by x-ray fluorescence. The Mo content is directly proportional to the phosphorous content. A typical calibration plot is shown in Fig. 8 (Ref. 13).

The plot is linear to 3000 ppb (µg/1) phosphorous. For P concentrations at the 15 ppb level, the standard deviation was 3%. For the linear portion of the curve, the correlation coefficient was 0.998 and the Student's t value was 39.4.

2. pH Value

The pH value of a water sample is usually measured electrometrically. It depends on a number of factors including the following: (1) the form of the hydrogen-ion bearing constituent (e.g., weak or strong acid), (2) the temperature of the water, (3) the presence of dissolved ions, (4) the presence of impurities such as oils, greases, or sludges, (5) the cleanliness of the glass and reference electrode system, and (6) the constancy of both electrodes.

a. Laboratory Instrumentation

The glass and reference electrode system is standardized using standard buffer solutions

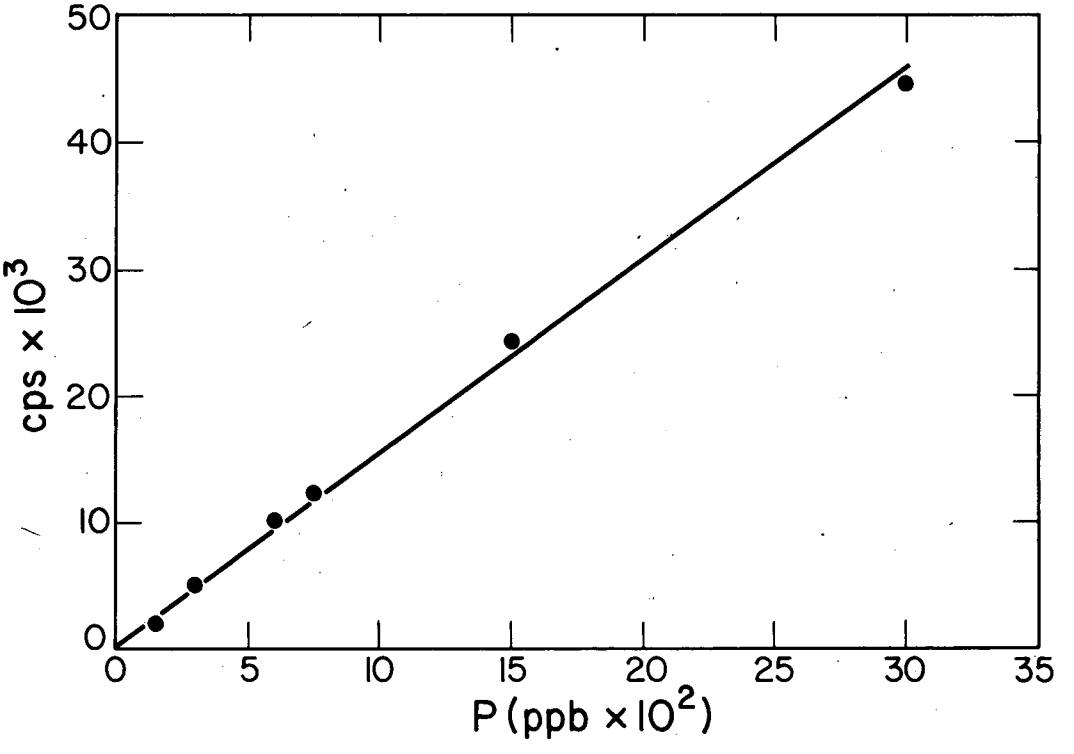

Fig. 6. Calibration curve from 0-4.0 ng Pb measured at 283.3 nm using 1X expansion. (Ref. 10).

of known pH value. The standards are prepared as needed because aged solutions may deteriorate since standard buffers have some shelf-life. Standard Methods, 14th Edition, contains a detailed discussion on preparation of buffer solutions from the buffer salts. It is recommended that certified buffer salts available from the National Bureau of Standards be used where the greatest accuracy is needed. The number of buffers should depend on the range to be covered (most water samples fall in range of 6.5-9.0).

Standard solutions are prepared by totally dissolving the correct weight of buffer power in freshly boiled distilled water with a conductance < 2μ mho at 25°C, and pH 6.7 to 7.3. The pH meter is standardized using a buffer solution with a pH value close to that of the samples.

In measuring the pH of industrial wastes, effluents and sludges, the electrodes are thoroughly rinsed with buffer solution between samples and after calibrating.

b. Continuous Field Monitors

Standardization of continuous pH monitors is discussed in Recommended Methods for Water-Data Acquisition (Ref. 14). It is recommended that the measuring system be calibrated manually at three points: pH 4, 7, and 10 using the buffer preparations described in Standard Methods, 14 Edition. See Appendix I. The calibrated accuracy of the pH measuring system is recommended to be within 1% of full scale or 0 pH unit, whichever is less, over the temperature range 0 to 40°C.

c. Manual Field Analyzers

Manual field analyzers are rugged, portable instruments that are used for pH measurements on site. The U. S. Geological Survey Methods Manual recommends that 2 or 3 standard buffers be used for calibration. (Ref. 15.) For saline water samples, a sodium correction may be required.

3. Pesticides

Analysis for trace (as low as one mg/1) quantities of pesticides in water is accomplished by laboratory instrumentation. The gas chromatographic and gas chromatographic/mass spectrometric methods are commonly used. The following is from the gas chromatographic calibration procedure given in Standard Methods, 14th Edition (Refs. 2,16):

Chlorinated pesticide stock solution standards are prepared by dissolving 100 mg of the pure material in 100 ml of ethyl acetate. From this stock, 1.0 ml is diluted to 100 ml with ethyl acetate to give an intermediate solution. A series of increasing μl amounts (1 to 5 μl) of the intermediate solution are injected into the chromatographic column, and the peak height or peak area are plotted versus pesticide concentration to give a calibration curve. Generally, peak areas give more exact results than do measurement of peak heights. For very narrow peaks, peak height measurement is recommended (Ref. 16).

The precision and accuracy for 6 chlorinated pesticides were determined by interlaboratory calibration testing. See Table 9 (Ref. 2).

TABLE 9. Precision and Accuracy Data for Chlorinated Hydrocarbon Pesticides Method (Ref. 2)

Pesticide	Conc. μg/l	No.of Labs	Relative Standard Deviation %	Relative Error %
p,p'DDT	0.50	36	38.2	5.6
	5.0	31	24.0	2.2
	29	32	24.7	2.6
Dieldrin	0.25	32	35.7	14.0
	5.0	37	42.2	7.2
	15	29	20.2	10.9
Endrin	0.10	31	38.8	16.0
	1.0	34	35.4	24.7
	10	31	16.9	8.5
Heptachlor	1.0	36	67.3	16.3
	7.5	36	41.8	19.5
	15	34	32.3	14.7
Heptachlor epoxide	1.0	33	20.6	7.0
	7.5	35	22.7	1.1
	15	36	25.4	2.5
Lindane	0.50	36	36.6	10.2
	5.0	38	42.6	13.2
	25	29	23.7	12.5

Further information on calibration of pesticides may be obtained from Standard Methods, 14th Edition, and Guidelines on Analytical Methodology for Pesticide Residue Monitoring (Ref. 16).

4. Biochemical Oxygen Demand (BOD)

Biochemical oxygen demand is included here as an example of a water quality parameter wherein the precision but not the accuracy can be determined. It is an empirical test; accuracy cannot be determined because standards which can be added in known quantities for calibration are not available.

Precision data were obtained for BOD by an interlaboratory calibration test using a glucose glutamic acid mixture. Each of 34 participating laboratories used its own seed material (settled stale sewage). The geometric mean of all results was 184 mg/1 and the standard deviation of that mean was ± 31 mg/1 (17%). (Ref. 2).

D. SUMMARY AND RECOMMENDATIONS

In summary, calibration of water quality instrumentation is largely a manual operation which involves the use of standards which contain accurately known concentrations of the pollutant. The standards are contained mainly in a solid or liquid matrix. Statistical methods are increasingly important in evaluating both intralaboratory and interlaboratory calibration procedures. Only a few standards designed for water quality instrumentation are currently available.

After reviewing the current status of water instrumentation standards and calibration procedures, some general observations are appropriate. While current standards are adequate in some respects, there are still a number of inadequacies. The optimum future standards and calibration activities should include the following:

1. Preparation and availability of certified water standards which contain pollutants at ambient level concentrations. These are needed in establishing background levels of pollutants which fall in the range < 50 µg/ℓ. The Hg 1.18 µg/ℓ solution standard will be most helpful for calibration at baseline levels.

2. Calibration methods for calibrating automated continuous field monitors. These instruments are being increasingly used both for point-source and ambient monitoring; reliable calibration procedures are needed to insure the validity of the data. The Task Group on Automatic Water-Quality Monitors has issued recommended methods for calibration of sensor-type automated monitors.

3. Use of statistical techniques for examining the accuracy and precision of trace methods, and for calculating the best calibration curve (line) for instrumental methods. Currently, calibration at trace levels have poorer precision (reproducibility) than at high concentrations. The data points are more scattered, and operator judgment in drawing a straight calibration line may vary widely.

E. ACKNOWLEDGMENTS

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G. TABLES OF MANUFACTURERS OF CALIBRATION STANDARDS

TABLE 1

Standards for Physical Parameters

Physical Parameter	Source of Standard	Manufacturer's Description	Range	Cost
	Delta Scientific	Mini-Tester, Model 22-91	0-500 ppm	$145
	Hach Chemical Company	Platinum-cobalt solution, 1414-11, 4-6 months stability	500 units	$8.75/pint
	LaMotte Chemical Products Company	1. Nessler tube, NT-C, Code 4345	Trace Amounts	$84
		2. Octet comparator, CWA, Code 7611	APHA Values	$24.95
		3. Special comparison tubes, CT-PC, Code 7523	*	$ 9.95
		4. Octet comparator, FLU, Code 5907	For lakes, rivers, bays	$19.95
Odor, Taste		Distilled Water	*	*
pH	Aquatronics, Inc.	Solution	4.0; 9.0	$3.50/pint
	Beckman Instruments, Inc. Process Instruments Div.	1. Powdered buffer	4.01-12.45	$9.00-13.00
		2. Solution	4.01; 7.00; 10.0	$5.50/quart
	Brinkmann Instruments, Incorporated	Solution	4.64; 7.15	$4.30/250 ml
	Chemtrix, Inc.	Buffer capsules	2.00-12.00	$2.75/12 capsules
	Corning	Buffer salt	4.01; 7.00; 10.00	$6.50/gram
	Delta Scientific	Color disc outfits	Each disc has 9 glass color standards, in steps of 0.2 pH or 0.5 pH	$35.00
	F & J Scientific	1. Hydrion universal indicator solution	1.0-11.0	$4.00/4 ml
		2. Hydrion paper	0.0-14.0	$1.25/dispenser
		3. Chemvelopes powder	2.00; 4.00; 7.00; 9.00	$3.50/6 envelopes
	Fil-Chem & Inc., Paul Frank Division	Tridicator pH paper	1-11; 0.25 pH accuracy	

(Continued)

TABLE 1. (Continued)

Physical Parameter	Source of Standard	Manufacturer's Description	Range	Cost
pH	Gallard-Schlesinger Chemical Manufacturing Corporation	Indicator papers	1-11, in units of 1 pH	$3.95/3 refills
	Hach Chemical Company	Buffer powder pillows	3.0-11.0	$2.20-3.20
	LaMotte Chemical Products Company	Octet comparators	0.2-13.6; in 0.2 pH increments	$9.95; $19.95
	Leeds and Northrup	Solutions	4.008; 6.865; 7.413; 9.18	
	The London Company	Buffer package	1.68-9.18	
	National Bureau of Standards	SRM 185c	pH 4.004	
		SRM I 861e	pH 6.863	
		SRM II 1861c	pH 7.415	
		SRM 187b	pH 9.183	
		SRM 188	pH 3.557	
		SRM 189	pH 1.679	
		SRM 191	pH 10.01	
		SRM 922	pH 7.699	
Specific Conductance	Beckman Instruments, Inc. Cedar Grove Operation	"Standard" cells; CEL-A-Y100, CEL-A-Y87	0:0100to 1.00 cm^{-1}	
	Hach Chemical Company	Sodium chloride solution, 1000 mg/l.; stability > 12 months	*	$1.20/4 oz.
Temperature	Fenwal Electronics	Standardized resistance-temperature curves	40° F-100 °F	*
	National Bureau of Standards	Thermometers	Various	*
Turbidity	Amoco Service Co.	Amoco SNT (Styrene divinylbenzene	5.0 to 75.00 FTU	$100-$500 per 802
	Hach Chemical Company	1. Standard reflectance rod	5.0 JTU	*
		2. Hexamethylene-tetramine Hydrazine sulfate		$12.00/500 gram $ 2.45/20 grams
	Hellige, Incorporated	Silica suspension	0-100 ppm	$57/quart

TABLE 2.

Standards for Chemical Parameters

Chemical Parameter	Source of Standard	Manufacturer's Description	Range	Cost
Metals	Alfa Inorganics, Inc.	Ultrapure metal	*	*
	Alpha Analytical Lab.	Solutions	1000 mg/1; 5000 mg/1	$18-68 per 1000 ml
	Apache Chemical, Inc.	Ultrapure metal	*	*
	ArRo Laboratories, Inc.	Solutions		
	Atomergic Chemetals Co.	Ultrapure metal	*	*
	J.T. Baker Chemical Co.	Solutions	1000 mg/1	$20/500 ml
	Brinkmann Instruments, Incorporated	Ultrapure metal	*	*
	Columbia Scientific Industries	Thin specimen x-ray calibration standards	*	*
	Conostan Dividion, Continental Oil Co.	Metallo-organic standards	10-5000 mg/ℓ	$20-$560
	Cominco American, Inc.	Ultrapure metal	*	*
	F & J Scientific	Solutions	1000 mg/1	$15-60 per 500 ml
	Hach Chemical Company	Solutions for Hg and Pb only	100 mg/1 Pb; 100 mg/1 Hg	$5.00/pint $3.50/pint
Cu,Mo	Hazen Research, Inc.	HRI Analytical standards	Cu: 0.078 to 0.94% Mo: 0.051 to 0.30%	$100 per 400 gram
	Materials Research Corp.	Ultrapure metal	*	*
	MCB Manufacturing Chemists	Solutions	1000 mg/1	*
	National Bureau of Standards	1. SRM 1571 orchard leaves		*
		2. SRM 606-619; trace elements (Cd, Pb only)		*
	Perkin-Elmer, Coleman Instruments Div.	Hg solution	*	$5.50/450 ml
	Spex Industries, Inc.	Ultrapure metal	*	*

TABLE 2. (Continued)

Chemical Parameter	Source of Standard	Manufacturer's Description	Range	Cost
Pesticides	Analabs, Inc.	Pesticide Standards	Solid; 0.1 to 1000 mg/ℓ	Various
	Chem. Service, Inc.	Purified Pesticides	Solid	Various
	PolyScience Corporation	1. Solution, 1.0% (w/w) in benzene	*	$65-70/5 ml
		2. Purified pesticide	*	*
Phenols	Hach Chemical Company	Phenol, ACS	*	$7.75/lb
	PolyScience Corporation	Mixture 175; Phenols (benzene, phenol, m-cresol, o-ethylphenol, p-ethylphenol)	*	* $60/5 ml; some 10 ml
Nutrients	Hach Chemical Company	Solutions;		
		1. NH_3 - N	1 mg/l	*
		2. NO_3 - N	0.3 mg/l	*
		3. PO_4 - P	1 mg/l	*
Polychlorinated Biphenyls	Analabs, Inc.	99% pure PCB Isomers	*	Various

H. APPENDIX

Recommended Methods for the Acquisition of Data Using Automatic Water-Quality Monitors (Ref. 14)

INTRODUCTION

The purpose of this document is to set forth criteria for the operation of water-quality monitors so that the data generated by the monitors will meet acceptable levels of accuracy.

The system performance requirements outlined under this chapter are not to be considered as engineering specifications. It should be recognized that in order to meet specific needs of operation, enforcement, or management, data must sometimes be collected under more rigorous criteria of accuracy and transient response than those prescribed in this document.

General

Automatic water-quality monitors of the electro-chemical and electro-physical types provide the most economical means of obtaining continuous or time-series reporting of certain water quality characteristics. Monitors of this type consist of three basic sections: the sensing elements, the signal-conditioning elements, and the data logging or display section. The sensing elements may be immersed directly in the stream, but the more common approach is to pump the sample to a sensor chamber in which the elements are located. The signal-conditioning elements convert the signals from the sensors to an appropriate voltage level proportional to the measured variable. The data logging or display section presents the measured value, usually in engineering units.

Parameters

A variety of electro-chemical and electro-physical sensors are available. The reliability of some of these for use with water-quality monitors has been demonstrated. Others developed for laboratory use may be adaptable to automatic monitoring but as yet are unproven for this application. Active research is being conducted for developing sensors to measure other parameters.

Existing sensors - unproven

- Water temperature
- Specific conductance
- Dissolved oxygen
- pH
- Chloride ion
- Turbidity
- Oxidation-reduction potential, or redox potential
- Solar radiation

Existing sensors - unproven

- Bromide ion
- Cadmium ion
- Calcium ion
- Cupric ion
- Cyanide ion
- Fluoride ion
- Fluoroborate ion
- Iodide ion
- Lead ion
- Nitrate ion
- Perchlorate ion
- Silver ion
- Potassium ion
- Sodium ion
- Sulfide ion
- Thiocyanate ion
- Water hardness

Other sensors (under development)

- Ammonia
- Phenol
- Phosphate
- Nitrite
- Sulphate

SCOPE

This recommendation deals with system performance requirements, sampling techniques and calibration methods for automatic water quality monitors which employ electro-chemical and electro-physical sensors to measure one or more water-quality parameters.

UNITS OF MEASUREMENT

The units of measurement used in this recommendation are degrees Celsius or Fahrenheit, micromhos, milligrams per liter, pH units, JTU (Jackson Turbidity Units) millivolts, and gram calories per square centimeter per minute.

DEFINITIONS

The following definitions will be used throughout this document.

Calibrated Accuracy

The calibrated accuracy is the difference between the indicated parameter value and its actual value. It is determined by calibrating the measuring system with an uncontaminated sensor as outlined under the section in this document entitled, "System Calibration."

Transient Response

The transient response is the rate at which the system responds to a step change. It is a function of the time constant of a first order differential response which takes the exponential form of $1 - e^{-t/T}$ where t = time and T = time constant. Although not all measuring systems follow a first order differential response, the time constant indicated for each parametric measuring system is intended for the purposes of this document to establish a minimum rate of response which all measuring systems must equal or exceed throughout the full transient period of 0 to 5T.

Stability

Stability is a measure of the length of time a measuring system, once calibrated, continues to measure the actual parameter value within the calibrated accuracy without the need for adjustment or recalibration. Stability performance is based upon the measurement of standard calibrating solutions with an uncontaminated sensor.

Temperature Compensation

Temperature compensation is an adjustment which corrects for the effect of temperature on the measuring system. In addition it may also adjust the measured value of a parameter to a selected temperature based on a known parameter-temperature relationship. Temperature compensation may be incorporated into the measuring system so that the value reported is the adjusted value. If this approach is not used, then manual or algebraic methods are necessary to obtain the adjusted value.

Contamination

Contamination is any fouling of a sensor which causes its calibrated output to shift by a discernible amount.

Representative Sample

A representative sample is a water sample whose measured values are characteristic of the body of water from which the sample has been taken.

Degradation

Degradation is any physical, chemical, or biological process which causes the characteristics of the water sample at the sensor to vary from those at the intake. For the purpose of this document any variations greater than those listed in the table below are considered excessive.

Parameter	Difference between Measured Value at the Sensor and at the System Intake
Water Temperature	±0.1°C
Specific Conductance	±0.5% of full scale
Dissolved Oxygen	±0.15 mg/l
pH	±0.05 pH unit
Chloride Ion	±1.0% of full scale
Turbidity	±1.0% of full scale
Oxidation-Reduction Potential	±6 millivolts

SYSTEM PERFORMANCE

The criteria set forth in this section pertain to the system from the sensor to the data logger, and apply to the system over environmental operation conditions ranging from -10° to 50°C with humidity levels up to 99%. Any exceptions to the above are noted in the appropriate section. For details on calibration methods for each of the following parameters, see the appropriate section under System Calibration.

Water Temperature

Calibrated Accuracy

The calibrated accuracy of the temperature measuring system shall be within 1% of full scale of ±0.5°C whichever is less.

Transient Response

The time constant of the temperature measuring system shall not be greater than one minute.

Stability

The temperature measuring system shall retain its calibrated accuracy for a period of not less than 4 weeks.

Specific Conductance

Calibrated Accuracy

The calibrated accuracy of the specific conductance measuring system shall be within 3% of full scale over the temperature range of 0 to 40° C.

Transient Response

The time constant of the specific conductance measuring system shall not be greater than 2 minutes.

Stability

The specific conductance measuring system shall retain its calibrated accuracy for a period of not less than 4 weeks.

Temperature Compensation

The data from the specific conductance measuring system shall be temperature compensated according to the characteristics of potassium chloride solution and normalized to 25° C.

Dissolved Oxygen

Calibrated Accuracy

The calibrated accuracy of the dissolved oxygen measuring system shall be within ±1% of full scale or ±0.1 mg/1, whichever is greater.

Transient Response

The time constant of the dissolved oxygen measuring system shall not be greater than 2 minutes.

Stability

The dissolved oxygen measuring system shall retain its calibrated accuracy for a period of not less than 4 weeks.

Temperature Compensation

The dissolved oxygen measuring system shall be temperature compensated so as to meet the accuracy requirements as outlined in the section under Calibrated Accuracy, above.

pH

Calibrated Accuracy

The calibrated accuracy of the pH measuring system shall be within 1% of full scale or 0.1 pH unit, whichever is less, over the temperature range of 0 to 40° C.

Transient Response

The time constant of the pH measuring system shall not be greater than 2 minutes.

Stability

The pH measuring system shall retain its calibrated accuracy for a period of not less than 4 weeks.

Temperature Compensation

The pH measuring system shall be temperature compensated so as to meet the accuracy requirements as outlined under Calibrated Accuracy, above.

Chloride Ion

Calibrated Accuracy

The calibrated accuracy of the chloride ion measuring system shall be within ±5% of full scale.

Transient Response

The time constant of the chloride ion measuring system shall not be greater than 2 minutes.

Stability

The chloride ion measuring system shall retain its calibrated accuracy for a period of not less than 4 weeks.

Temperature Compensation

The chloride ion measuring system shall be temperature compensated so as to meet the accuracy requirements as outlined in the section under Calibrated Accuracy, above.

Turbidity

Calibrated Accuracy

The calibrated accuracy of the turbidity measuring system shall be within ±5% of full scale over the temperature range of 0 to 40° C.

Transient Response

The time constant of the turbidity measuring system shall not be greater than 1 minute.

Stability

The turbidity measuring system shall retain its calibrated accuracy for a period of not less than 4 weeks.

Oxidation-reduction Potential (ORP), or Redox Potential

Calibrated Accuracy

The calibrated accuracy of the ORP measuring system shall be within ±12 millivolts when the standard buffer solutions are measured as noted in the section under System Calibration.

Transient Response

The time constant of the ORP measuring system shall not be greater than 2 minutes.

Stability

The ORP measuring system shall retain its calibrated accuracy for a period of not less than 4 weeks.

SYSTEM CALIBRATION

Calibration data for all measuring systems shall be provided in the manner described in the following paragraphs.

Water Temperature

Method

The water temperature measuring system shall be calibrated by immersing the sensor in a beaker of water and comparing the output of the measuring system to that obtained by a good grade, mercury-filled thermometer, either centigrade or Fahrenheit, which has been checked against a precision thermometer certified by the National Bureau of Standards.

Calibration Points

The temperature measuring system shall be calibrated at three points. One point is obtained by placing the sensor in a container of stirred water near zero degrees C (obtained by adding ice to a container of water). A second calibration point shall be obtained by placing the sensor in a container of stirred water sufficiently warm to produce a reading near the full scale value of the measuring system. The third point should be obtained by placing the sensor in a container of stirred water that will produce a reading near mid-scale.

Specific Conductance

Method

The specific conductance measuring system shall be calibrated by immersing the sensor in a beaker of potassium chloride standard solution and comparing the output of the measuring system to the known value of the standard solution. The potassium chloride solution should be prepared in accordance with the instructions given in Standard Methods for the Examination of Water and Waste-water, Thirteenth Edition, 1971.

Calibration Points

Each applicable range of the specific conductance measuring system shall be calibrated at three points by employing potassium chloride standard solutions at or near 15%, 50% and 100% of full scale. Each range shall be checked for temperature compensation using solutions of potassium chloride having values of specific conductance near the midscale of each range.

Dissolved Oxygen

Method

The dissolved oxygen measuring system shall be calibrated by immersing the sensor in a beaker of air-saturated water and comparing the output of the measuring system to that obtained by an analysis of the water. The water shall be stirred or made to flow with sufficient velocity such that any increase in flow or stirring shall not cause a change in the sensor output. The analysis shall be made in accordance with the Alsterberg modification of the Winkler method of dissolved oxygen determination. (Reference: Standard Methods for the Examination of Water and Wastewater, Thirteenth Edition, 1971; Methods for Chemical Analysis of Water and Wastes, 1971, Environmental Protection Agency; and Techniques of Water-Resources Investigations of the United States Geological Survey, Book 5, Chapter A1: "Methods for Collection and Analysis of Water Samples for Dissolved Minerals and Gases." The water must be free of interfering substances; therefore, the use of distilled water is recommended.

Care must be taken to allow adequate time in each test for the sensor to reach equilibrium.

Calibration Points

The measuring system shall be calibrated at three points: One preferably at the zero level, one at approximately one-third of full scale, and one at approximately two-thirds of full scale. The zero level is obtained by adding a few crystals of cobalt chloride ($CoCl_2$) to a beaker of saturated sodium sulfite (NA_2SO_3) solution. Various concentrations of oxygen in air saturated water can be obtained by changing the water temperature. See "Standard Methods," pp. 480-1 for table showing saturated values at various temperatures.

pH

Method

The pH measuring system shall be calibrated by immersing the sensor in a beaker of standard pH buffer solution and comparing the output of the measuring system to the known value of the buffer solution. The buffer solution shall be prepared in accordance with the instructions given in Standard Methods for the Examination of Water and Wastewater, Thirteenth Edition, 1971.

Calibration Points

The pH measuring system shall be calibrated at three points, using buffer solutions having nominal values of 4, 7, and 10 pH units.

Chloride Ion

Method

The chloride ion measuring system shall be calibrated by immersing the sensor in a standard sodium chloride solution and comparing the output of the measuring system to the known value of the standard solution. The standard solution shall be prepared in accordance with the instructions given in Techniques of Water-Resources Investigations of the United States Geological Survey, Book 5, Chapter A1: "Methods for Collection and Analysis of Water Samples for Dissolved Minerals and Gases."

Calibration Points

The chloride ion measuring system shall be calibrated at three points by employing standard solutions at or near 10%, 50%, and 100% of full scale of the range being used.

Alternate Method (Titrimetric)

The chloride ion measuring system shall be calibrated by titration of a water sample obtained from the monitoring system and using methods given in Standard Methods for the Examination of Water and Wastewater, Thirteenth Edition, 1971.

Turbidity

Method

The turbidity measuring system shall be calibrated by immersing the sensor in a beaker of Formazin solution and comparing the output of the measuring system to the known value of the standard Formazin solution. The stock Formazin solution shall be prepared in the following manner:

(1) Dissolve 10.00 grams of reagent grade hydrazine sulfate (N_2H_4, H_2SO_4) in 900 ml of distilled water
(2) Dissolve 100.00 grams of pur hexamethylene tetramine $(CH_2)_6N_4$ in 900 ml of distilled water
(3) Pour the two solutions into a 2000 ml volumetric flask and dilute to 2000 ml with distilled water
(4) Allow the solution to stand for 48 hours at 20° to 22°C (68° to 72°F) during which time the suspension will develop.

The following table gives the relationship between each of the listed dilutions of the stock solution and its corresponding turbidity (in Jackson Turbidity Units).

JTU	ml of stock suspension diluted to 1.000 liter with turbidity-free water
3000	750
2500	625
2000	500
1500	375
1000	250
500	125
400	100
300	75
200	50
150	37.5
100	25

NOTE: The Formazin stock suspension is stable for approximately two weeks whereupon it should be discarded. The diluted samples are stable for no more than one week.

Calibration Points

The turbidity measuring system shall be calibrated at three points by employing standard solutions at or near 20%, 50% and 100% of full scale of the range being used.

NOTE: The zero point may be checked by immersing the sensor in distilled water.

Alternate Method

The turbidity measuring system shall be calibrated by obtaining a water sample from the monitoring system, measuring its turbidity value with a commercial turbidimeter, and then comparing this value with the output of the monitor measuring system. The accuracy of the commercial turbidimeter shall be as specified under the section on System Performance and shall be calibrated in accordance with the method under System Calibration. When possible the method described under that section should be used in preference to the alternate method also described under that section.

Oxidation-reduction Potential (ORP), or Redox Potential

Method

The oxidation-reduction potential (ORP) measuring system shall be calibrated by immersing the sensor in a beaker of standard pH buffer solution to which quinhydrone crystals have been added and comparing the output of the measuring system to the known value of the buffer solution. The buffer solution shall be prepared in accordance with the instructions given in Standard Methods for the Examination of Water and Wastewater, Thirteenth Edition, 1971.

Calibration Points

The ORP measuring system shall be calibrated at two points using buffer solutions containing quinhydrone and having nominal values of 4 and 7 pH. The predictable potential of these solutions is a function of the temperature and the type of reference electrode used. For example:

Quinhydrone electrode to saturated calomel electrode potentials $E = 0.4529 - (0.000198322T^{\circ}$ Abs.) pH.

pH	Volts 15° C	Volts 20° C	Volts 25° C
1.0	+0.396	+0.395	+0.394
4.0	+0.255	+0.221	+0.217
7.0	+0.053	+0.046	+0.040

When an Ag-Ag Cl reference electrode is used, 0.046 volts should be added to the values listed above. (E Ag. Ag Cl = E calomel +0.046).

SYSTEM MAINTENANCE

The criteria and recommended methods set forth in this document are intended to ensure use of reliable monitoring instruments capable of generating water-quality data that will meet acceptable levels of accuracy. However, the accuracy of field data depends not only upon the representativeness of the sample, the system performance (calibrated accuracy, transient response, stability and temperature compensation) and the method of calibration as outlined under sections entitled Sample, System Performance and System Calibration, but also upon the maintenance of the system. Preventive maintenance on a regularly scheduled basis for the intake system and the measuring system and sensors is necessary if a monitor is to operate within its system performance capabilities.

Intake System Maintenance

Routine cleaning of the intake system is essential, with frequency depending upon local conditions. Manual backflushing should be included on a scheduled maintenance program if an automatic backflushing feature is not included in the system design. It is important that the intake screening be kept free of debris. The manufacturer's recommended maintenance procedure should be followed for the pump, and installation must be sure that it can be easily removed for maintenance, repair, or replacement.

Sensor and Measuring System Maintenance

To maintain sensor performance and to ensure measuring system stability at an acceptable level, close surveillance and frequent servicing are required. It is important that sensor contamination be kept to a minimum and that frequent calibration checks be made for all parameter measuring systems. Systems having temperature-compensating elements should be occasionally checked to see that these elements are functioning correctly. The calibration checks should be performed at a minimum of three widely spaced temperature points. Experience indicates a reasonable interval between maintenance visits to monitor field installations to be approximately one week. However, no set schedule can be specified because of varying local conditions. On such maintenance visits, the differences between reported and actual values of a parameter both before and after maintenance should be determined. This information will be invaluable in computing the finalized data.

From time to time, during different seasons and under different flow conditions, checks should be made to determine that degradation of the sample between the system intake and the sensor sampling chamber does not exceed the limits outlined in the section on degradation.

RECOMMENDATIONS

Sensors now in use for measuring water-quality parameters are being continually improved to meet the demands for increased reliability and precision in automatic monitoring applications. In recognition of these improvements in the state-of-the-art and also in recognition of the frequently changing needs of water-quality management, any set of methods such as those set forth in this report cannot be considered as final. Therefore, it is recommended that there be periodic review of new developments in automatic water-quality monitoring so that the present methods can be revised accordingly.

It should be noted that the National Weather Service and others in private industry now have facilities for laboratory calibration of solar radiation sensors. However, additional study will be required before an acceptable procedure for field calibration of solar radiation sensors can be included in this report as a recommendation.

CONTENTS

METALS-IN-WATER MONITORING INSTRUMENTATION

CONTENTS

INTRODUCTION

Metals in water are attaining increasing importance as pollutants of man's aqueous environment. Because metallic pollutants in water at even trace levels can have disastrous effects on our health, it has become important to measure their quantities accurately and precisely. This section of the WATER volume will discuss the metals which pollute our waters - and the instrumental techniques of analyzing for them.

Part I encompasses general material on metals in fresh, waste and saline waters. It considers their characteristics and forms (A), their source and pathways in the aqueous ecosystem (B), their effects (C), and methods of control (D).

Part II gives material concerning some selected metals which are considered particularly major pollutants. Each section in part II will describe the metal as it exists in aqueous ecosystems, its major detrimental or positive effects and the major considerations involved in analysis. The sections are not intended as extensive or comprehensive reviews but as introductions to the topic and the literature.

Part III covers the systems used for determining metals in water. It describes only those parts of metal monitoring systems which differ from monitoring systems in general.

Part IV, Instrumentation, describes the instrumental techniques which are used to determine metals in water: Atomic Spectroscopy (A), UV-visible absorption spectrometry (B), and On-Going and Developing techniques (C) which include X-Ray Fluorescence (1), Neutron Activation Analysis (2), and Electrochemical Techniques (3) such as anoidic stripping voltammetry.

In part V are the instrument notes. First, those for atomic spectroscopy and second those for UV/vis instruments. Each group is set off by a green sheet on which is a table of all the instruments that follow and some of the more important specifications.

I. GENERAL CONSIDERATIONS CONCERNING METALS IN WATER

This discussion encompasses the forms, sources, effects and controls of metals in water. In short it describes what the metals are, and why and how they are monitored.

A. Characteristics of Metals in Water

Metals are commonly defined as lustrous and malleable elements, having resistivities between 10^{-4} and 10^{-6} ohm-cm. Table 1 lists the metals which the EPA currently considers important in the aqueous environment and which are analysed using the instrumental methods considered in this section, Metals-in-Water; primarily atomic spectroscopy, UV-visible absorption spectroscopy and several developing techniques.

1. Physical State of Metals and Metal Compounds in Water

Metals and metal compounds can exist as suspensions and colloids, (i.e. insoluble particulates), in solution or in an equilibrium between the solid and liquid state. A solid suspended in water will settle to the bottom of a container upon standing; a colloid will not, but both can be separated from water by passing the solution through filters. According to EPA's arbitrary definitions a compound which will pass through a 0.45 μm filter is in solution. This size filter will actually allow many fine colloids to remain in the solution, leaving a turbid sample, which could actually be separated using finer filters. The separation of metal compounds dissolved in water generally requires chemical means, such as precipitation, ion exchange, or electrical means.

Many of the physical properties of solutions and suspensions, such as turbidity and conductivity, are not dependent upon the particular compound in solution. These have been grouped together as "physical properties" and are discussed more specifically in the "Physical Properties" section of the WATER volume. Chemical characteristics, which may or may not depend upon physical state, are discussed below in Section 2.

2. Chemical Characteristics of Metals and Metal Ions in Water

Metals in their elemental form have no net charge and are said to be in the zero oxidation state, Me(0).* Some metals, such as iron, mercury, and gold exist in water in elemental form as suspensions or colloids; their surfaces are in constant interaction with the solution surrounding them.

The majority of the metals in water are not in the elemental state, but are in a different oxidation state, that is with one or more electrons removed from an outer shell. Some metals can exist only in one oxidation state in water. The alkali metals, for example, sodium or potassium, are highly stable when singly ionized as Na(I) or K(I). If introduced

*This notation implies that the metal, Me, is in the zero oxidation state, (0). A metal which has been oxidized, for example, potassium^{+1} would be written K(I).

Table 1. Metals for which the EPA recommends instrumental techniques discussed in this section (40 CFR 136).

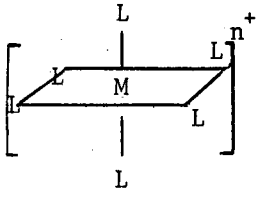
Aluminum	Indium	Rhodium
Antimony	Iron	Ruthenium
Arsenic	Lead	Selenium
Barium	Magnesium	Silica
Beryllium	Manganese	Silver
Boron	Mercury	Sodium
Cadmium	Molybdenum	Thallium
Calcium	Nickel	Tin
Chromium	Osmium	Titanium
Cobalt	Palladium	Vanadium
Copper	Platinum	Zinc
Gold	Potassium	

to water as elements, they can react explosively to form the single ionized state as Na^+ or K^+:

$$K(0) + H_2O \xrightarrow[H_2O]{} K^+ + OH^- + 1/2\ H_2\uparrow .$$

The metal easily loses an electron, but to remove another electron from an alkali metal would require more than ordinary chemical means. Other metals, such as iron or chromium, can exist in several oxidation states, sometimes simultaneously. For example, chromium can exist in water as Cr(0), Cr(II) Cr(III) or Cr(VI) depending upon the surrounding solution.

Metals and metal ions in water form a variety of compounds. They may form simple salts (sodium chloride or copper sulfate), complex ions or coordination complexes, organometallics or polymers. These classifications are not mutually exclusive. Complex ions are made up of several atoms, including the metal atom(s), which under normal aqueous conditions function as a chemical unit, for example $[Cr_2O_7]^=$. Coordination complexes involve a central metal ion, M, surrounded by complexing agents called ligands, L, which are bonded together:



The complex formed may be positive, $[(Cu(NH_3)_4]^{++}$, negative, $[Fe(CN)(NO)]^{-3}$ or neutral, $[Pt(NH_3)_2Cl_2]$. The ligands may be inorganic; Cl^-, NH_3, or $(OH)^-$; organic, such as ethylenediamine (en = $NH_2CH_2CH_2NH_2$) or diethydithiocarbamate (dedtc = $(C_2H_5)_2NCS_2$), charged or neutral, simple or polymeric. They may be substances found in the formative solution or the solvent itself. When introduced into water, the complexes may be insoluble, forming a suspension; they may be partly soluble existing in a state of liquid-solid equilibrium; or they may be soluble and stable with the ion pairs separating or they may be unstable in the particular aqueous solution and react with it to form other complexes.

Organo-metallics are compounds formed between a metal or metal ion and an organic molecule. The compound may be a coordination complex such as $[Co(en)_3]Cl_3$*, or it may be more simple as in CH_3MgBr. Organometallics often are biologically important; an example is desferri-ferrichrome (Fig. 1), which may play an important part in biosynthesis of iron (Ref. 1).

Metals in solution exist in a complex equilibrium with the other substances in solution. The solution is in equilibrium with the

* en = ethylenediamine, $NH_2CH_2CH_2NH_2$.

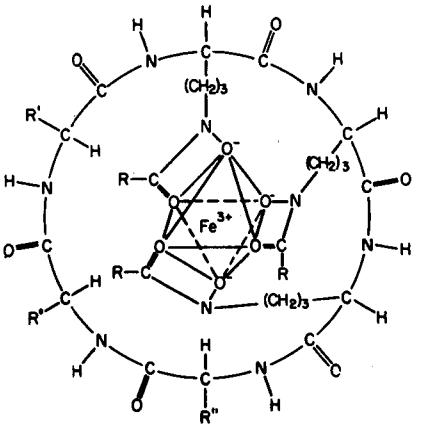


Fig. 1. Desferri-ferrichrome (reproduced from Neilands, [Ref. 2] with permission by Birkhauser Verlag, Basel, Switzerland, copyright 1964).

vapor phase, dissolved gases and the atmosphere and with the solid phase, suspended and colloidal solids and the surrounding land mass (Fig. 2). (For a detailed discussion of the equilibria involved, see Refs. 1-5). In order to predict the species present and their movement in a given water supply, it is often necessary to use computer modeling techniques (Refs. 6-11). To make predictions as to the nature of the system, the modeling program will use the species present, hydrodynamic information, the geochemistry of the surrounding environment, and numerous thermodynamics and kinetic expressions based upon known chemical reactions or half reactions of the species.

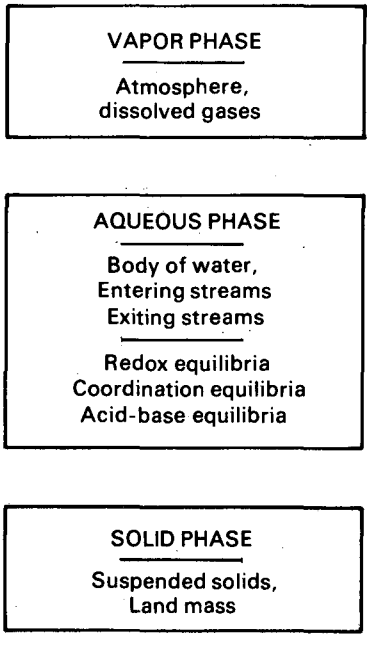


Fig. 2. Equilibria effecting metals in natural waters. (XBL 7810-11540)

3. Metal and Metal Ion Solubility, Coordination and Oxidation State in Water

There are numerous factors affecting the state of metals and metal ions in water. Several of the most important in terms of the environment are discussed below:

• Temperature. The temperature of the water affects the solubility of the metals or metal ions in water, the reactions which they undergo, and their effect on the environment.

• Pressure. The atmospheric pressure, which varies considerably with the altitude of the water supply, changes the solubility of gases in solution, e.g., the liquid-vapor phase equilibria. This in turn, affects the metal-ion equilibria involving those gases. A good example is the Pb-CO_2-water system shown in Fig. 3.

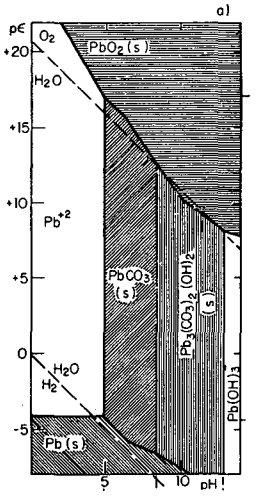


Fig. 3. pH-pE diagram of the Pb-H_2O-CO_2 system (reproduced from Stumm and Morgan [Ref. 1] with permission by John Wiley and Sons, New York, N.Y., copyright 1970).

• Common Ion Effects. The product of the ion concentrations of a partly soluble salt in solution is (to first approximation) a constant. For example, the equilibrium of $Ca(OH)_2$ in water can be written:

$$Ca(OH)_2 \text{ (solid)} \underset{H_2O}{\rightleftharpoons} Ca^{+2} + 2(OH)^-.$$

The solubility product constant $K_{sp} = [Ca^{+2}][OH^-]^{2*}$. The addition of either Ca^{+2} or $(OH)^-$ will force the precipitation of $Ca(OH)_2$.

• Antagonistic and Synergistic Ion Effects. The presence of certain metal ions can cause either greater (synergistic) or less (antagonistic) solubility of other metals. For example, the presence of $CaHCO_3$ or $MgHCO_3$ reduces lead solubility but $Ca(OH)_2$ increases it (Ref. 11).

• Effect of Pollutant Concentration. Depending on the concentration of a metal ion, the metal can occur in different forms. Figure 4 depicts the $Fe(OH)_3$ - water system, showing which species of Fe^{+3} are present at various pH and [Fe].* From the diagram, it is easy to see that at pH4, $Fe_2(OH)_2^{4+}$, $Fe(OH)_2^+$, $Fe(OH)^{2+}$, and $Fe(OH)_3$ all exist in water solution depending on the concentration of $Fe(OH)_3$. When the log of the $Fe(OH)_3$ ion concentration is ~-4.5, $Fe(OH)_3$ is present; if log C is ~ -10, than $Fe_2(OH)_2^{4+}$ will be present.

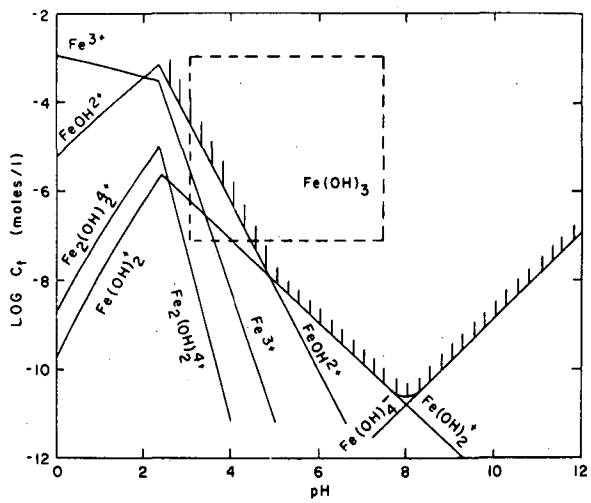


Fig. 4. Log concentration-pH solubility diagram for ferric hydroxide (reproduced from Leckie and James [Ref. 6] with permission by Ann Arbor Science Publishers, Ann Arbor, MI, copyright 1974).

(XBL 787-9780)

• pH. The pH is the measure of acidity or basicity of a solution. Technically it is the negative of the log of the hydrogen ion concentration, -log $[H^+]$. pH can be used to control the species and oxidation states of the metals in a solution and the reactions which they undergo. Indeed, the pH can be used to control the nature of the solution.

Various aqueous environments have different pH. Acid mine waters are often ~ pH 2 (acidic), whereas ground waters are sometimes ~ pH 12 (basic). Figure 4 shows the effect of pH on which form of Fe^{+3} is present. When the log of Fe^{+3} concentration is -8, and the pH is 1, $Fe(OH)_2^+$ is present; at pH 4.24, Fe^{+3} is present.

• Redox Agents. The term "redox" refers to the oxidizing or reducing nature of a solution. A reducing agent tends to donate electrons to a species:

$$M^+ + red \rightarrow M + ox$$

red = reducing agent
ox = oxidized form of the reducing agent.

An oxidizing agent tends to take electrons:

$$M^+ + ox \rightarrow M^{++} + red$$

ox = oxidizing agent
red = reduced form of an oxidizing agent.

The redox environment of the metal or metal affects both the oxidation state of the metal and the complexing agents in the solution. The redox potential of a solution is often expressed as pE (Ref. 1), the negative of the log of the electron activity. Large positive values represent an oxidizing environment, while small or negative values indicate a reducing solution. Figure 5 shows the range of values of pE for certain aqueous environments. Redox agents may be metals or metal ions or in fact, many of the other agents in the aqueous environment.

• Complexing, Chelating, and Sequestering Agents. Many species in water can act as complexing, chelating, or sequestering agents. Complexing agents are atoms, molecules or ionic species which surround and are bonded to a metal atom by a coordination bond, often involving the overlap of a filled orbital on the coordinating species (ligand) and an unfilled d or f shell on the metal atom. Since the definition of a coordination complex is rather loose, the definition is more often by usage. Chelates, by agreement, are ligands, which coordinate through more than one site. Sequestering agents are ligands or chelates which prevent detection of the metal by a particular instrumental technique. These agents surround a metal ion in solution, diffusing and supporting its charge, thereby lending it stability. Complexing agents in water can be single inorganic ions such as halides (Cl, I^-), cyanide or gases (CO, N_2 or NH_3) or large organic molecules such as salicylate, or EDTA (ethylenediamine tetraacetic acid).

A metal ion in solution if not complexed by other ions will be complexed (surrounded) by water molecules. The exact degree of solvation can be quite extensive. Figure 6 shows the predicted solvation about a sodium ion. The H_2O molecules in areas A and B are extensively bonded.

* [M] implies the concentration of species M.

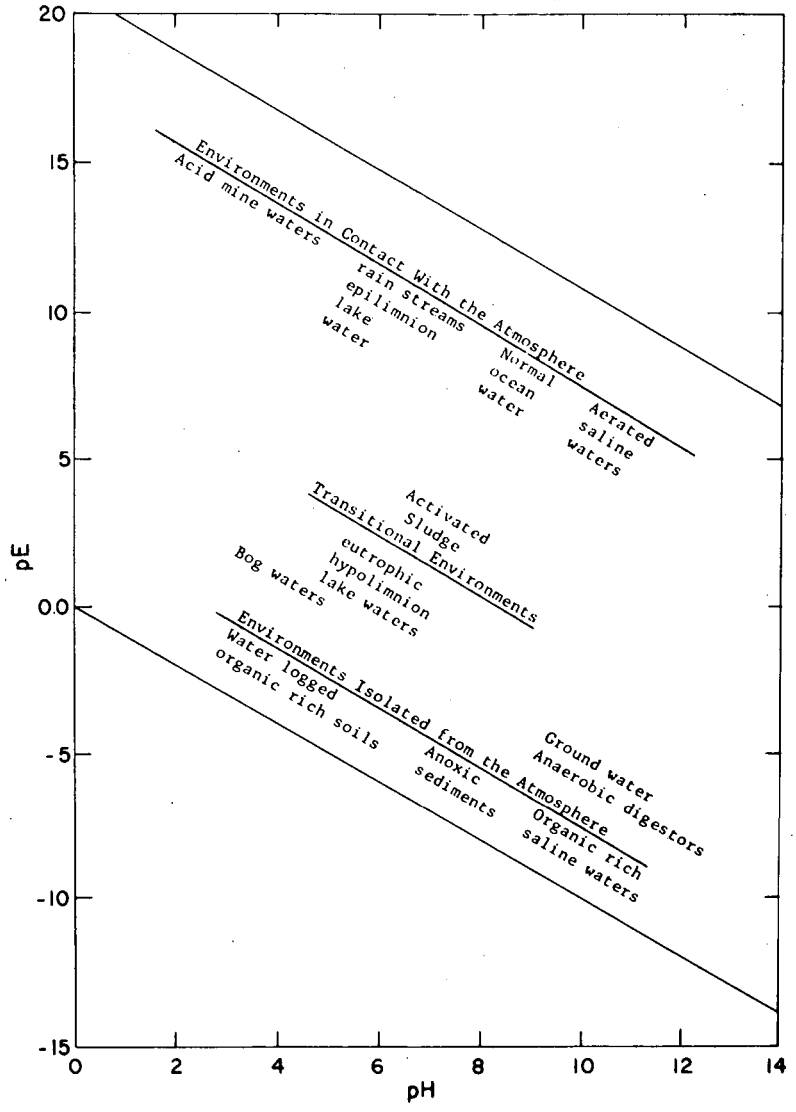


Fig. 5. Relative positions of various environments as characterized by pH and pE (reproduced from Leckie and James [Ref. 6], with permission by Ann Arbon Science Publishers, Ann Arbor, MI, copyright 1974). (XBL 787-9779)

Microorganisms. Microorganisms can act as redox agents or complexing agents. Often the exact mechanisms by which they act are not known; however, many of the reactions mediated by microorganisms are environmentally important. Perhaps one of the most important is the conversion of inorganic mercury (of only moderate toxicity, and solubility) to methyl mercury, which is highly toxic and readily absorbed into animal tissues (Refs. 13, 14). The net reaction is:

$$HgCl_2 + \text{microbial action} \rightarrow CH_3HgCl$$

but the mechanism has not been established.

B. Sources and Pathways of Metals in Water

Pure water, that is liquid H_2O, is not found in the natural environment. Pollutants, including metals and metal compounds, are introduced into the natural water from a variety of sources (Ref. 15). They may pass directly into the body of water or may reach it by other means. The pollutant, when it enters this ecological cycle, may be brought into contact with man who may recycle it. Figure 7 shows the sources and pathways of metallic pollutants in the environment. This section briefly discusses first, the sources of metals and metallic compounds (henceforward "metals")

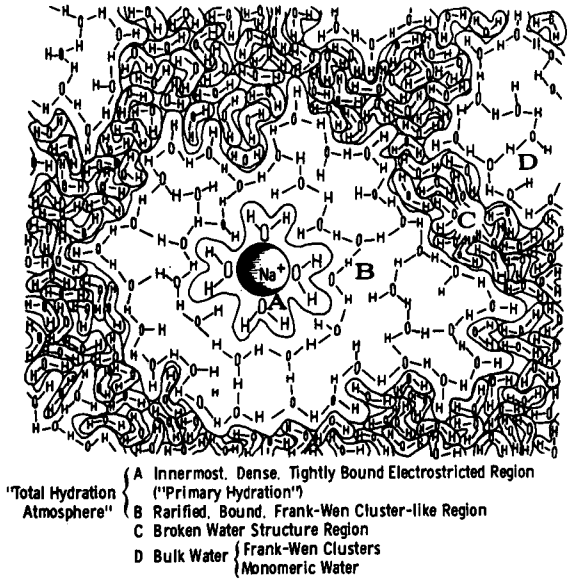


Fig. 6. The local water structure of the Na^+ ion at 25°C and 1 atmosphere (reproduced from Horne [Ref. 3] with permission by Marcel Dekker, Inc., New York, N.Y., copyright 1972).

in the aquatic environment (Section 1), and then the pathways by which they may reach man and his environment (Section 2). The specific paths and sources for certain metallic pollutants will be discussed in the section on the specific metal.

1. Sources of Metals in Water

Metals are introduced into the aquatic environment from a number of sources, both natural and anthropogenic. Surface waters such as lakes, rivers, streams and estuaries, can receive pollutants from connecting bodies of water, from precipitation or by dissolving or leaching them from the surrounding landmass. Ground waters can be contaminated by pollutants leaching through the surrounding land mass or by direct connection to a pollutant stream.

This section will discuss the "background" metal concentration of natural waters, i.e. the concentration of metals normally associated with a body of water, and the natural sources of metals in that water. Next it will describe the anthropogenic sources of water. Sources of natural pollution, which involve movement of pollutants from the atmosphere, landmass or other bodies of water into the body of water of concern, can become the vehicles for introducing anthropogenic pollutants.

a. Natural Sources

(1) Surface waters. A body of water is in constant equilibrium with its boundaries, the landmass, the atmosphere, and connected sources of water. Metals may be introduced into it from the atmosphere in many ways. The simplest is the settling of contaminants which have been suspended in the air by natural events: the wind, volcanic eruptions (Refs. 16 and 17), or geothermal emissions (Ref.18). Precipitation (Refs. 15, 19-23), either snow (Ref. 23) or rain, will introduce metals into surface waters either by direct runoff, as particular erosion, leaching from the soil or by filtering through the soil, introducing pollutants already in the rain.

A particularly important source of metals is the bottom sediment which may introduce suspended particulates or gradually release metals as dissolved salts. The salts may be dissolved by chemical or biological action.

Rivers and streams entering a body of water, introduce any materials which have been introduced into them. It is also possible for pollutants to migrate up a river. In periods of drought, salts from an estuary move up river, posing a serious problem to humans, industrial and agricultural consumption. Under natural conditions, surface fresh-waters are generally very low in concentrations of metals (Table 2) and natural salt-waters are only high in the summed concentration of certain metals: Na^+, K^+, etc.

(2) Ground waters. Ground waters can be naturally fresh with only low levels of Na^+, K^+ and trace metallic pollutants. However, occasionally they may be saline, such as geothermal brines. Metals may be introduced to the aquifer by simple action of the water on the surrounding landmass, or by addition of metal containing water leached through the soil. A major natural introduction of metallic pollutants can occur by the disruption of the surrounding rock in an earthquake which allows the mixing of a saline with a fresh water aquifier, or introduction of other pollution sources (atmospheric, aqueous or otherwise).

To recapitulate, metals may be introduced into surface waters by natural equilibrium processes between the body of water and the atmosphere, landmass and connected water mass, or by water flow into a particular body of water through rivers, streams or by precipitation. They may be introduced into ground water by equilibrium processes with the surrounding landmass, by leaching or by disruption of the rock surrounding an aquifer.

b. Anthropogenic Sources of Metals in Water. Man's industrial activities are the greatest source of metals in water. So great is his contribution to the natural waters that the Rhine river has been termed "Europe's Great Sewer" (Ref. 25). The ocean waters of Japan and Sweden, once a source of

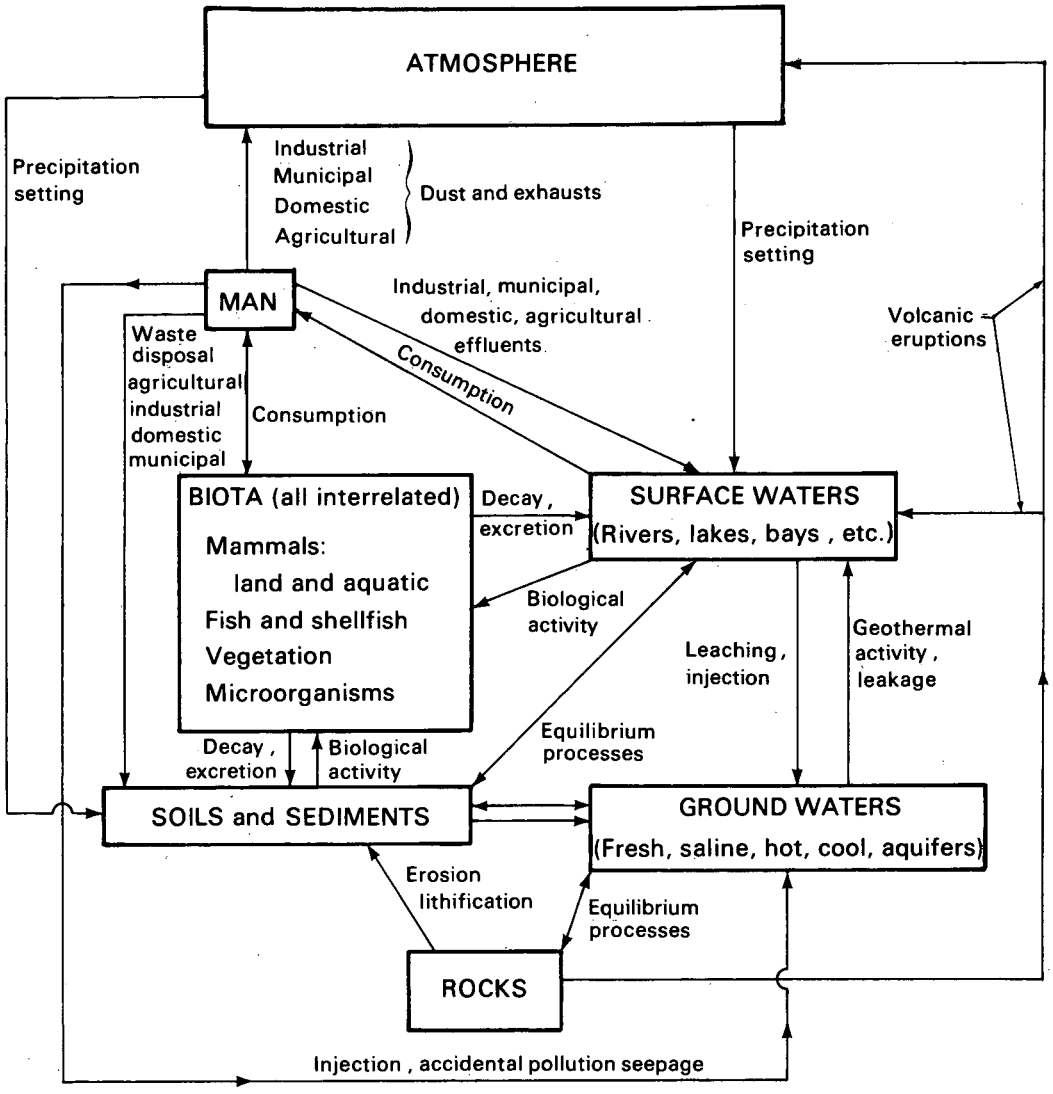


Fig. 7. Sources and pathways of metallic pollution in the ecosystem.
(XBL 7812-13452)

food and livelihood, have become the source of mercury pollution leading to Minamata disease.

Anthropogenic sources must be viewed two ways: mode of generation and manner of introduction. For simplicity five modes of generation are usually considered; industrial, domestic, municipal, agricultural or silvitural and recreational. The pollutants generated are introduced into the water supply directly or indirectly. The source may be a point source with a single point of discharge or more general diffuse emission (non-point source).

(1) Industrial. Table 3 lists some of the metals which legally may be introduced by various industries in their waste streams, and also includes a list of metals used by those industries but whose discharge is not permitted. The U. S. Environmental Protection Agency has considered thirty-five metals (Table 1) as important enough pollutants to publish analytical methods to be used for monitoring their discharge (see Section d, Controls). Most of the thirty-five are mentioned specifically on 40 CFR Parts 400-459, the Regulations governing point source categories and industrial discharges. The particular industries associated with certain metals will be discussed in Section II on Specific Metals in Water.

Waste streams may directly discharge into a surface water or be injected into an aquifer, an underground source of water. Injection is

Table 2. Range of concentrations for selected trace metals in U. S. surface waters (data presented in Kopp and Kroner, Ref. 24).

Metal	Concentration Range (μg/ℓ)
Aluminum	11.6 - 71.4
Arsenic	20 - 308
Barium	17 - 90
Beryllium	0.02 - 0.28
Boron	19 - 289
Cadmium	2 - 50
Chromium	4 - 25
Cobalt	1 - 36
Copper	9 - 23
Iron	19 - 173
Lead	4 - 39
Manganese	2.7 - 232
Molybdenum	15 - 145
Nickel	3 - 56
Silver	0.3 - 5.8
Vanadium	9 - 171
Zinc	16 - 205

usually into aquifers whose water is unfit for human consumption. A fresh water aquifer can be polluted through injection at an improper level, or injection into an aquifer which is not fully surrounded by rock mass, thereby allowing seepage. Pollution can develop further if well pipes corrode or the aquifer is cracked by earth movement.

Metallic pollution is added to the aqueous environment indirectly through industrial emission to the atmosphere. Industries belch volumes of metallic pollutants into the air. For example, Table 4 shows the metallic components of flyash associated with coal-powered steam penetration plants. Eventually these pollutants settle to the surface water directly or are introduced through precipitation which can go directly into the body of water. They also may leach through the soil into surface and ground water. This can be an important factor in producing high levels of metals (e.g., mercury) in surface waters. Table 5 shows the concentration of various metals in the rain water in certain light industry areas. Taller smoke stacks which are used to prevent high concentrations of air pollutants tend to spread the pollutants to a greater area, polluting more bodies of water.

Buried industrial waste or waste stored in slurry ponds can be eroded or leached into the surface or underground aquatic ecosystem. This problem can be particularly insidious since it is so long-term. Arsenic introduced to the soil in 1934 in Minnesota was identified as the source of water pollution in 1972 (Ref. 27).

(2) Domestic and Municipal. In today's urban society domestic users are rarely direct sources of pollutants to the water supply but contribute to the municipal wastes. Rural users are more likely to intro-

Table 3. Metals used in various industries.

Point Source Category	Discharge Permitted[a]	Discharge Not Permitted[b]
Textile Industry (410)	Cr	
Electroplating (413)	Cd, Cu, Au, Ir, Fe Pb, Ni, Os, Pd, Pt, Rh, Ru, Ag	Al, Cr,
Inorganic Chemicals (415)	As, Cr, Cu, Fe, Pb, Hg, Ni	Al, Cd, Sn, Zn
Fertilizers (418)		Al, As, Cd, Cr, Ca Fe, Hg, Mn, Pb, Ni Zn
Organic Chemicals (414) and Petroleum Refining (419)	Cr	Al, As, Cd, Cr, Cu Fe, Pb, Ni, Zn
Iron and Steel Mfg. (420)	Cr, Fe, Mn, Ni, Pb, Sn, Zn	As, Cd, Cu, Hg, Sb
Non-Ferrous Metals Mfg. (421)	As, Cu, Pb, Cd, Se, Zn	Al, Ag, Cr, Hg, Sb
Phosphate Mfg. (422)	As	
Steam Electric Power Generation (423)	Cr, Cu, Fe, Zn	
Ferroalloys (424)	Cr, Mn	
Leather Tanning (425)	Cr	
Glass Mfg. (426)	Pb	Cr
Rubber Mfg. (428)	Cr, Pb, Zn	
Timber Products (429)	Cu, Cr, As	
Pulp, Paper, and Paper-Board (430)	Zn	Cr, Cu, Hg, Pb, Ni
Coal Mining (434)	Fe, Mn	
Ore Mining (440)	Al, As, Cd, Cu, Fe, Hg, Ni, Pb, Zn	
Photographic (459)	Ag	

[a]Permitted discharges are listed in 40 CFR 400-459, current July 1, 1977.

[b]Metals associated with the industries mention, but whose discharge is not permitted was determined by comparison of the permitted discharges with the metals mentioned in Ref. 25.

duce metallic wastes directly into streams or lakes through malfunctioning cesspools. The municipal contribution to metallic wastes can be extensive and manifold. Most important sources are the publicly owned treatment works (POTW's) which treat sewage from domestic and industrial users. The direct contribution to water depends largely upon the industries attached to the system. Palo Alto, California has an unexpectedly high level of gold and silver (20-32, 630-680 mg/ℓ respectively) in its sewage system probably due to the high level of electronics industries in the area. (Ref. 28) Table 6 shows the concentration of other metals found in several U. S. sewage systems.

A second municipal contribution to metallic pollution is through transportation systems - street and road runoff and automo-

Table 4. Metallic pollution found in steam electric power generation atmospheric emission (data presented in Ref.26).

Metal	Flyash-Coal-Fired (ppm)
Aluminum	60,000 - 140,000
Antimony	0.6 - 3.7
Arsenic	3 - 15
Barium	2,000 - 5,000
Beryllium	3 - 7
Boron	200 - 700
Cadmium	1
Calcium	32,000 - 120,000
Chromium	20 - 150
Cobalt	7 - 20
Copper	36 - 128
Iron	24,000 - 77,000
Lead	20 - 70
Magnesium	6,000 - 13,500
Manganese	100 - 300
Mercury	Vaporizes
Nickel	10 - 70
Potassium	7,500 - 12,500
Selenium	Vaporizes
Silicon	200,000 - 300,000
Sodium	750 - 15,000
Thallium	1.1 - 1.7
Titanium	3,000 - 7,000
Vanadium	70 - 150
Zinc	50 - 105

bile fumes can introduce lead and other metals into the nearby waters. A study of Israeli rivers has proposed the automobile as the major source of lead pollution in certain parts of the Yarkon River (Ref. 29).

(3) Agriculture and silviculture. These disrupt ground cover, which promotes erosion. Metals are also introduced into the soil as pesticides, preservatives or dust control chemicals, such as calcium chloride. All these can be leached or eroded into the water supply. By the same mechanism, man's recreation also adds metal pollutants from outboard motors, beer cans, and numerous other sources.

Table 5. Data on rain water and air dust composition in the literature (data presented in Ruppert, Ref. 21).

Metal	Concentration Range Observed in Rain Water μg/ℓ
Aluminum	89 - 1500
Cadmium	0.5 - 18
Calcium	300 - 3000
Chromium	0.1 - 14
Copper	0.4 - 23
Iron	10 - 1440
Lead	5.4 - 39
Magnesium	200 - 1400
Manganese	0.19 - 43
Mercury	0.04 - 1.5
Molybdenum	0.06 - 0.44
Nickel	3.6 - 6
Potassium	12 - 1000
Silicon	70 - 7000
Silver	0.01 - 0.24
Sodium	150 - 2300
Vanadium	1.4 - 4.7
Zinc	3 - 85

2. Paths of Metals in Water

Once the metallic pollutants reach the aqueous environment, they are taken up by the ecosystem. Figure 7 shows a simplified diagram of the paths which can affect the distribution of the metallic pollutant. The specific processes depend upon the particular pollutant and are discussed in Section II. For good general discussions of this topic, see Refs. 12, 30.

Figure 7 illustrates the complex paths of the pollutant. Six classes of uptake agent can be identified: sediments and soils, and the biota, vegetation, microorganisms, fish and shellfish, mammals and man. All can take up metallic pollutants directly. (They all can - and do - return them to the system). It has become increasingly clear that the effect of the pollutant on each of these classes is important per se. However for simplicity, the path of the pollutant will be discussed in its relationship to man. Under Specific Metals in Water, Section II, the important effects of the particular metals on vegatation, fish and wild life will also be discussed.

Man can, of course, consume water containing metallic pollutants directly, or they may reach him through the food cycle. By going through the cycle, the metallic pollutants are often concentrated or converted to other forms (for example: inorganic Hg $\xrightarrow{\text{microorganisms}}$ organic mercury) (Ref. 31) or concentrated to detrimental levels. The

Table 6. Trace metals concentrations found in sewage treatment plants in three U. S. Cites in 1963 (data presented in Williams, Aulenbach and Clesceri, Ref. 15).

City	Metal	Average Total Metal-8 hr. Composite, µg/ℓ		
		Sewage	Primary Effluent	Secondary Effluent
Grand Rapids, Michigan	Chromium	3800	3500	2600
	Copper	1600	1400	1600
	Nickel	2100	1900	1800
	Zinc	1500	1000	700
Richmond, Indiana	Chromium	300	700	100
	Copper	200	300	50
	Nickel	30	100	20
	Zinc	300	300	100
Rockford, Illinois	Chromium	2700	1800	1200
	Copper	1700	1700	1600
	Nickel	1000	1000	1000
	Zinc	3700	2100	1400

following sections briefly discuss the various agents in the food cycle and the effect they have on the metallic pollutants in the cycle.

a. Sediments and Soils. By various means, direct adsorption, precipitation (gravitational sinking) or deposition of decaying vegetal and animal matter, metallic pollutants are concentrated on the bottom sediments. There is a dynamic equilibrium between the bottom solids and the aqueous solution. Sediments containing metals can often remain a source of pollutants long after the initial source has been stopped.

When it is chemically possible metals from sediments are released into the body of water (Refs. 17, 32). This release can be enhanced or hindered by common ions pH and temperature effects (Ref. 33). Predicting and examining the relation of the bottom sediment to the mass of water has become an important consideration (Ref. 34). Metals contained in bottom sediments are also taken up by bottom vegetation, microorganisms, fish and mammals which are bottom gleaners.

Metals in the water used for irrigation are deposited in the soil. They can then be leached back into the pollutant source or other ground (Ref. 27) or surface waters (Ref. 29). Or they can be taken up by the vegetation (Ref. 35).

b. Vegetation. Metals in soils or bottom sediments are taken up by vegetation. Studies are currently underway examining the exact extent of this mechanism to determine its potential danger or value to man. Waters with higher metal concentrations can enhance growth and productivity, or can destroy the plants. Metals which are taken up may be concentrated (Ref. 30). The plants in turn are consumed by most other agents in the food chain, microorganisms, fish and shellfish, mammals and man.

c. Microorganisms. Phytoplankton, zoo-plankton and invertebrate benthos frequently consume the metallic pollutants. In the microorganisms the metals are often concentrated or converted to organic forms. Microorganisms containing metallic pollutants are then consumed by man, mammals and fish. Or the microorganisms can release the metal (inorganic or organic) back into the water supply.

Table 7. Concentration factors for selected metals in a variety of aquatic organisms (data presented in Ref. 37).

Metal	Species	Concentration Factor
Beryllium	Benthic Algae	100
	Phytoplankton	1000
	Zoo Plankton	15
Cadmium	Oysters	1800
	Fish	1000
Chromium	Benthic Algae	1600
	Phytoplankton	2300
	Zooplankton	1900
	Molluscs (soft parts)	440
	Fish	70
Manganese	Molluscs	12,000
Mercury	Fish	16,600 - 27,800

d. Fish and Shellfish. Fish and shellfish which consume metals directly from the microorganisms or vegetation in the water often further convert inorganic forms to organic forms. However, their most serious effect with respect to man is to concentrate the pollutants. American oysters grown in seawater containing 0.005 mg/ℓ cadmium have been found to accumulate 10.75 ppm in forty weeks, a concentration factor of 2,000 in less than one year (Ref. 36). The concentration factor is highly dependent upon species and metals. Table 7 contains concentration factors for several species and metals and illustrates the range observed. Fish and shellfish are then of course consumed by other agents in the food cycle, mammals and man.

e. Mammals and Man. The cycle as it has been established is continued. Man and other mammals consume water, vegetation, fish and shellfish, and each other. The metals are either accumulated or excreted and returned to the cycle.

C. Effects of Metals in Water

The effect of metallic pollutants in water may be far reaching depending on the pollutant and the species affected. Effects may be felt anywhere in the ecosystem. Deleterious effects can range from minor irritations to major disruptions of the ecosystem, from an unpleasant taste to death. Some metals such as arsenic and mercury cause systemic effects in man. Others such as chromium or cadmium are suspected carcinogens. Still others, such as boron, are essentially non-toxic to man but affect vegetation.

The effect of the metal may be enhanced by the presence or absence of other metals, oxidation state or form (inorganic or organic). Zinc or copper poisoning appears less in hard water; chromium is a possible carcinogen only in the +6 oxidation state. Organic methyl mercury appears to be significantly more harmful than inorganic mercuric chloride or elemental mercury.

Table 8. Water quality criteria for metals in water.

Metal	Public Water Supplies, Recreational and Aesthetic Use[a]	Fresh Water Aquatic Life and Wildlife	Marine Aquatic Life	Agricultural Uses	Industrial Uses[d]
Aluminum	–	–	0.01× 6 hr LC[e]50[b] 200 µg/ℓ, min risk	livestock < 5.000 µg/ℓ[b] irrigation cont. 5,000 µg/ℓ	Boiler & cool water 3,000 µg/ℓ[b] Copper leach sol'n 12×10[6] µg/ℓ
Antimony	–	–	> 200 µg/ℓ hazardous	–	–
Arsenic	50 µg/ℓ[c] (health)		0.01×96 hr LC50[b] 10 µg/ℓ, min risk	livestock - 200 µg/ℓ[b] irrigation - 100 µg/ℓ[c]	–
Barium	1000 µg/ℓ[c]		0.01×96 hr LC50[b] < 500 µg/ℓ, min risk	irrigation - cont. 100 µg/ℓ	–
Beryllium	–	Soft water - 11 µg/ℓ[c] hard water - 1100 µg/ℓ		irrigation - cont. 100 µg/ℓ[c]	–
Boron	insufficient data[b]	–		irrigation - sensitive crops 750 µg/ℓ[c]	–
Cadmium	10 µg/ℓ[c] (health)	Soft water - 0.4 µg/ℓ[c] sensitive species hard water - 1.2 µg/ℓ	5.0 µg/ℓ[c]		–
Calcium	–	–	–	–	–
Chromium	50 µg/ℓ[c] (health)	100 µg/ℓ[c]	0.01×96 hr LC50[b] 50 µg/ℓ min risk 10 µg/ℓ oyster areas non-toxic shot[b]	livestock - 1000 µg/ℓ irrigation - cont. 100 µg/ℓ	–
Cobalt	–				
Copper	1000 µg/ℓ[c]	0.01×96 hr LC50[c]	0.01×96 hr LC50[c] 10 µg/ℓ, min risk[b]	livestock - 500 µg/ℓ[b] irrigation - cont. 200 µg/ℓ[b]	–
Iron	300 µg/ℓ[c]	1000 µg/ℓ[c]	50 µg/ℓ, min risk[b]	irrigation - 5,000 µg/ℓ[b]	Textile Industry 300 µg/ℓ Copper leach sol'n 12×10[6] µg/ℓ[b]
Lead	50 µg/ℓ[c] (health)	0.01×96 hr LC50[c]	0.2×96 hr LC50[b] 10 µg/ℓ, min risk[b]	livestock - 100 µg/ℓ[b] irrigation - cont. 5,000 µg/ℓ[b]	–
Magnesium	–	–	–	–	Petroleum Industry 85,000 µg/ℓ[b] Copper leaching sol'n 12×10[6] µg/ℓ
Manganese	50 µg/ℓ (welfare)[c]	–	100 µg/ℓ (marine mollusk consumers)[c]	irrigation - cont. 200 µg/ℓ[b]	Brackish cooling water 20 µg/ℓ[b] Boiler makeup water 10,000 µg/ℓ[b]
Mercury	2.0 µg/ℓ (health)[c]	0.05 µg/ℓ[c]	0.10 µg/ℓ[c]	livestock - 10 µg/ℓ[b] (human consumption)	–
Molybdenum	–	–	0.02×96 hr LC50[b]	livestock - insufficient data[b] irrigation - cont. 10 µg/ℓ[b]	–
Nickel	–	0.01×96 hr LC50[c]	0.01×96 hr LC50[c]	irrigation - cont. 200 µg/ℓ[b]	–
Potassium and Sodium	–	–	–	–	Petroleum Industry 230 mg/ℓ Oil injection recovery water 42,000 mg/ℓ
Selenium	10 µg/ℓ[c]	0.01×96 hr LC50[c]	0.01×96 hr LC50[c]	livestock - 500 µg/ℓ irrigatic - cont. 20 µg/ℓ	–
Silica	–	–	–	–	Brackish cooling water 25,000 µg/ℓ Boiler makeup water 150,000 µg/ℓ
Silver	50 µg/ℓ[c]	0.01×96 hr LC50[c]	0.01×96 hr LC50[c]	insufficient data[b]	–
Thallium	–	–	0.05×20 day sublethal test[b] 50 µg/ℓ, min risk[b]	–	–
Vanadium	–	–	0.05×96 hr LC50[b]	livestock - 100 µg/ℓ irrigation - cont. 100 µg/ℓ	–
Zinc	5000 µg/ℓ (welfare)[c]	0.01×96 hr LC50[c]	0.01×96 hr LC50[b] 0.001×96 hr LC50[c] Cu,Cd[b] 20 µg/ℓ, min risk[b]	livestock - 25,000 µg/ℓ irrigation - cont. 2000 µg/ℓ	–

[a] For all metals, the recommended criteria for waters used for recreation and aesthetic purposes are the same as those for domestic consumption.

[b] Ref. 30

[c] Ref. 37

[d] Since there is a large range of industries and requirements for water use, only the maximum and minimum values that have been used (Ref. 42) are listed.

[e] An LC or TL is a lethal concentration and represents a tolerance limit. The hours before LC refer to the number of hours that a percentage of specimens live in a solution containing that particular concentration of pollutant. The number following LC, ex: LC50, refers to the percentage of specimens which can live at that concentration. The 96-hour LC50 is the concentration at which 50% of the specimens can live after 96 hours. The concentration is determined using the most sensitive species to be subjected. To achieve safety the LC is then multiplied by an application factor.

It has become increasingly clear that any disruption of the natural ecological cycle can be deleterious and that establishing long term effects of various pollutants is extremely difficult. Current EPA goals for control are "zero-discharge" by 1985, a goal which in many cases may be unrealistic. In the meantime, interim regulations have been and are being developed (discussed in greater detail in Section A4 and the introduction of this volume) based upon water criteria developed to prevent deleterious effects. These criteria and their bases are discussed in three development documents: McKee and Wolf, (Ref. 12), Water Quality Criteria (Ref. 30) developed in 1972 by the National Academy of Sciences and National Academy of Engineers (NAS/NAE report), and Quality Criteria for Water (Ref. 37) published by the EPA in 1976. All these provide excellent references for deleterious effects of metallic pollutants as well as introductions to the literature. Section II does not attempt to duplicate their efforts but to summarize some of their conclusions and consider some of the more current literature.

In this section, the possible deleterious effects will be discussed with reference to the water usage. Section 1 will consider human uses (public water supplies, recreational and aesthetic uses). Section 2 discusses the effect of metallic pollutants on fresh water

and marine fish and wildlife. Section 3 considers agricultural usage and 4 industrial uses. Each section will consider a) possible deleterious effects, b) methods of determining deleterious effects (where applicable) and c) requirements for use. The specific effects of particular metals are considered in Section II. Table 8 lists the metals currently regulated by the EPA, the recommended water quality criteria and the reasons for their establishment.

In reviewing the table, it is important to remember that the criteria are often based on recognizably insufficient information. The absence of a criterion often indicates that the data were so scanty that even an educated guess was impossible.

For simplicity, health effects may be described by several terms: (Ref. 30)

Acute - a stimulus severe enough to cause an effect quickly.
Chronic - a stimulus which involves a long term effect (also often used to describe a long term stimulus).
Lethal - fatal, causes death
Sublethal - does not cause death
Cumulative - successive small stimuli increase or bring about the effect.

1. Waters for Human Use: Public Water Supplies, Recreational and Aesthetic Uses

The criteria for public water supplies are usually based upon health and safety considerations (Table 8). However, some may be determined by the inconvenience the pollutants cause; the stains caused by manganese, scaling caused by hard water or the taste of iron salts. For all "metallic pollutants in water used for recreational or aesthetic purposes," the recommended criteria are based on safety for human consumption.

There are several ways of determining the effect of metallic pollutants on humans. Most common, and too often tragic, are the results of accidential or occupational exposures. For example, the mercury poisoning associated with Minamata disease, or cadmium poisoning postulated as the cause of Itái-itái disease. Experiments are rarely performed on humans so that often the results of trials on test animals, such as rats, pigs or monkeys are extrapolated to fit humans. This is at best a risky method since sometimes responses are not equivalent. The hardest effects to judge are those based on chronic low-level exposure. It will be many years before ample data are available in this field. Table 9 lists the 1975 interim drinking water criteria for metals and indicates the levels which are currently considered safe for human consumption of two liters/day for 20 years.

Table 9. National interim primary drinking water regulations for metals (40 CFR 141).

Metal	Level in µg/ℓ
Arsenic	50
Barium	1000
Cadmium	10
Chromium	50
Lead	50
Mercury	2
Selenium	10
Silver	50

2. Effects of Pollutants on Wildlife, Both in Water and on Land

The NAS/NAE report (Ref. 30) categorizes the effects of metallic pollutants as lethal or sublethal (including effects on migrations, behavior, incidence of disease, life cycle, physiological processes, genetic effects, nutrition food chains, ecosystem and food value for human use). The effects are determined by bioassay techniques, which are described more thoroughly in Standard Methods (Ref. 38). Most toxicity data are reported as median tolerance limits, TL50, implying that within a particular time limit (usually 96 hours) half the species present survive (96-hour TL50). Sometimes longer term exposures are necessary. Criteria are often based upon the 96-hour TL50 of the most sensitive species multiplied by a confidence factor.

3. Agrcicultural Uses

The effect of metallic pollutants on water used for agriculture can also be lethal (to the plant) or sublethal (affecting the growth rate, crop-yield or fitness for human consumption). The effect of metallic pollutants is strongly dependent upon climate and the temperature and humidity of the area. Also, it is dependent upon the nature of the soils. Neutral or alkaline soils usually have a greater tolerance, as do fine textured soils. Table 10 shows the recommended maximum concentration of trace elements in irrigation waters.

The table differentiates between the pH of the soils, the texture of the soil and the type of irrigation (supplemental or continuous).

Table 10. Recommended maximum concentrations of trace elements in irrigation waters[a] (Ref. 30).

Element	For waters used continuously on all soil (mg/ℓ)	For use up to 20 years on fine textured soils of pH 6.0 to 8.5 (mg/ℓ)
Aluminum	5.0	20.0
Arsenic	0.10	2.0
Beryllium	0.10	0.50
Boron	0.75	2.0
Cadmium	0.010	0.050
Chromium	0.10	1.0
Cobalt	0.050	5.0
Copper	0.20	5.0
Fluoride	1.0	15.0
Iron	5.0	20.0
Lead	5.0	10.0
Lithium	2.5[b]	2.5[b]
Manganese	0.20	10.0
Molybdenum	0.010	0.050[c]
Nickel	0.20	2.0
Selenium	0.020	0.020
Vanadium	0.10	1.0
Zinc	2.0	10.0

[a]These levels will normally not adversely affect plants or soils.

[b]Recommended maximum concentration for irrigating citrus is 0.075 mg/ℓ.

[c]For only acid fine textured soils or acid soils with relatively high iron oxide contents.

It might be pointed out that with renewed interest in ground water, soils which are alkaline and fine textured may protect the plants, but may allow quicker leaching into the ground water. If this is the case, the criteria may again be changed.

4. Effects of Metals for Industrial Use

The EPA currently lists forty-two industries as point sources, with some 250 subcategories. The requirements and, therefore, the effects of various pollutants and the industries are as varied as the industries themselves. Table 11 summarizes intake characteristics for waters used in various industries.

Industrial use of water and the effect of metallic pollutants is discussed in some detail in the NAS/NAE report. For the water needs of particular industries the reviewer is referred to the development documents of effluent guidelines for various point source cate-

Table 11. Ranges in recommended limiting concentrations for industrial process water (data presented in Ref. 39).

Use	[Iron as Fe] µg/ℓ	Manganese as Mn (µg/ℓ)	Iron plus Mn (µg/ℓ)	Hardness as $CaCO_3$
Air conditioning	500	500	500	–
Baking	200	200	200	a
Brewing	100	100	100	b
Carbonated beverages	100-200	200	100-400	200-250(mg/ℓ)
Dairy	100-300	30-100	–	180(mg/ℓ)
Ice Mfg.	200	200	200	–
Food processing	200	200	200-300	10-250(mg/ℓ)
Paper products	100-1000	50-500	–	100-200(mg/ℓ)
Synthetics	0-50	0-50	0-50	8-55(mg/ℓ)
Sugar	100	–	–	low
Farming	100-200	100-200	200	50-500(mg/ℓ)
Textiles	100-1000	50-1000	200-1000	0-50(mg/ℓ)

[a]Some calcium is necessary for yeast action. Too much hardness retards fermentation, but too little softens the gluten to produce soggy bread. Water of zero hardness is required for some cakes and crackers.

[b]For dark beer alkalinity as $CaCO_3$ may be 80 to 150 mg/ℓ.

gories published by the EPA. They not only discuss the needs but the effects of the pollutants upon the industry, the various metals which are used throughout the system, and the means of controlling discharges. While it is beyond the scope of this volume to discuss them all, the reader who must monitor the effluents, direct or indirect, of certain industries should know about these documents and use them extensively to be aware of possible metals which may inadvertently be released into the system.

D. Controls of Metals in Water

There are three important means of controlling metallic pollution: natural, regulatory, and process methods of control. The natural water system is remarkably able to purify itself. Natural sedimentation and pH controls remove many metals from water directly (Ref. 41). Bacteria in the water system are able to to remove some of the metals from waste water (Ref. 42). Man's discharges in the aqueous system have long exceeded the ability of the water to purge itself, so man must now clean both his discharges and his waters. To this end, regulatory controls and systemic controls, i.e. physical, chemical or biological processes used to remove chemicals from discharge stream, must work in tandem.

1. Regulatory Controls

Regulatory controls set guidelines outlining the amount of discharge allowed, how to remove any excess pollutants (Refs. 43-47), methods and schedules for monitoring to determine compliance, and penalties for failure to achieve compliance.

Regulatory controls, and the philosophy behind them, have been discussed in the Introduction of this volume, and briefly mentioned, with respect to the effects of metallic pollution, in Section C of the metals-in-water section. Table 8 lists the recommended criteria for metals, and Table 9, the National Interim Drinking Water Standards for metals. The particular receiving water standards, which are operable, are necessarily dependent upon local conditions: state and local

agencies, soil, climate, and sources of pollutants within the area.

Currently, discharge standards are dependent upon industry and on local conditions. In that respect, they are strongly based on the controls discussed in part 2 of this section, "Process Controls", since they are based on the "Best Practicable Technology Currently Available" (BPTCA) or the "Best Available Technology Economically Achievable" (BATEA). The import of local conditions is considered when the industry applies for a National Pollution Discharge Elimination System (NPDES) permit which may require more stringent controls.

Regulatory controls are supported by monitoring systems to determine compliance and are required by federal regulation. The systems and analytical techniques actually used for metals are discussed in Part III, Monitoring Systems, which considers the theoretical background of the techniques and Part IV, Instrumentation, which describes the actual instrumentation available for determining metals in water.

2. Process Controls

Controls of discharges by controlling the process or treating the effluent depend largely upon the source of effluent. Although process controls are strongly dependent upon the discharges, the techniques involved may be grouped as controls for point sources and for non-point sources. Point sources include industrial discharges, publicly owned treatment works (municipal) and some domestic usage. Non-point sources may involve rain runoff (industrial, municipal, agricultural including silvicultural), rain out or settling mechanisms (pollutants evolved from any source of air pollution-industiral, municipal, agricultural, domestic or recreational), leaching mechanisms (pollutants derived from any source of pollution which is deposited within or on the earth) and general anthropogenic deposition (pollutants from man's more erratic disposal of his products-garbage thrown in rivers, on highways, etc).

Point sources are simpler to control (section (a) below) because the regulatory agent has greater ability to monitor and determine the exact discharge. The agent in charge of purifying effluents has a single defined set of sources of pollutants.

Non-point sources are more difficult to control because the discharge involved is more diffuse and therefore is difficult to define and monitor. Discharges are often very long term and have long since terminated when their effect is discovered. Methods of control are discussed in Section b.

a. Point Source Controls. Specific processes used for control of point source discharge vary from industry to industry and between industry and POTW's. The reader interested in a particular industry should refer to the EPA "Development Documents for Effluent Guidelines and Pretreatment Standards" for the point source category of interest.

There are some basic methods and philosophies for control which apply to most point sources (Refs. 25, 39, 48-53). First, there are controls which are applied to an already existing system or process. They may be external, that is applied before or after a particular process step, or internal, added to process chemicals to produce more tractable effluents. These "applied" controls work with a process or plant which might as easily function without them.

A second philosophy of control is the industrial plant or system of control which is designed around the idea of water management and utilization. Often the techniques for removal of pollutants from the water are similar, but the water use and effluent management is maximized.

Purification is usually based on a theory of cleaning by degree (Refs. 25, 39, 48-53). Initially the larger of the suspended particles are removed by screening grit chambers, or sedimentation. Much of the dissolved metals are collected after precipitation. Several techniques are used:

- Aeration: removal of CO_2, precipitating salts soluble in only slightly acidic solution.

- Softening: addition of lime and soda ash, which involves many calcium and magnesium salts as $CaCO_3$ and $MgCO_3$. This process is hindered by extreme cold (Ref. 54).

- Clarification: addition of chemicals which either precipitate dissolved material (Ref. 55), or allow adsorption (Ref. 56), and flocculation (Ref. 57). Aluminum and ferric hydroxides are often used. Organic compounds, often humic acids, have been found to interfere with traditional clarification techniques; however, ozonation has been found to help by converting the organic compounds to more tractable forms (Ref. 58).

- Activated sludge: one of the most common methods of sewage treatment for POTW's. For metal removal, the operator must be aware of some problems. A certain number of metals are essential for growth of the bacteria: K, Ca, M, Fe, Mn, Mo, B, Na, Co and V (Ref. 59). The details of the metal usage are given in Ref. 60. Many of these required metals may be removed by pretreatment - adsorption on clays or cellular material by hydroxide or H_2S. The

bacteria often can adsorb many of the essential and nonessential heavy metals (Ref. 42, 61); however, the chlorine treatment which often follows activated sludge treatment has been found to rerelease the metals in the system (Ref. 62) unless proper pH control is exercised. The heavy metals which circulate through the system can in turn cause deflocculation of the sludge, which can lead to system wash out and failure (Ref. 62). Chelation can also cause problems.

The water can be purified further by more advanced techniques:

- Advanced filtration techniques - These range from interspersal of sand filters and fine screens to the use of a variety of filtration techniques, often depending upon a variety of filter materials for effective removal. (Ref. 64).

- Carbon Adsorption - Metals adsorb on powder, granulated or pelletized carbon. The relatively high cost of this technique has prevented its use in the past. The current rules for discharge, however, have caused increased usage (Ref. 65-67).

- Electrodialysis - A potential is put across the water, the cations migrate to the cathode, the anions to the anode. By alternating cation and anion permeable membranes, successive concentration and dilution occurs (Ref. 68). Recently a high volume technique has been developed which makes the process more viable (Ref. 69).

- Ion exchange - Conventional ion-exchange has involved passing an effluent stream through an exchange resin which substitutes an H^+ or Na^+ ion for cations or OH^- or Cl^- for anions:

$$Ca^{++} + 2\ Rc^-Na^+ \gtrless 2\ Na^+ + (Rc_2^-)\ Ca^{++}.$$

The process has not been used frequently or extensively because of the high cost of regeneration and the problem of waste disposal. A new process, the Sirotherm process, is regenerated by hot water, which lowers the cost and allows for double exchange with the by product of water:

$$Ra^+OH + R_c^-H^+ + Na^+ + Cl \underset{85}{\overset{20}{\rightleftharpoons}} Ra^+Cl^- + RaHa^+ + H_2O. \quad \text{(Ref. 70)}$$

Other techniques have been evolved which allow for selective recovery of particular metals (Refs. 70, 71).

- High gradient magnetic separation - This allows the magnetic properties of the effluent to effect separation. The technique allows a high flow rate and excellent purity (Ref. 72). The technique still is primarily in the developmental stage.

- Reverse Osmosis - (Ultrafiltration) - involves the filtering of the effluent through semipermeable membranes which permit soluable compounds of varying size to pass through them. (Ref. 25).

Many industrial plants designed today utilize all the above techniques, but they are designed to maximize their water and material usage. They are based on the idea of "total plant ultilization", relying on use, recovery (Refs. 70, 71), and recycling of materials and water throughout the plant (Ref. 73). The system therefore not only produces a discharge stream with less waste requiring external treatment, but is also cheaper since it recovers for reuse both water and contaminants.

Another technique currently in practice in Europe is to send all wastes in concentrated form to a central treatment plant, built expressly to handle them (Ref. 74). This means that the industrial users have no waste waters discharge. The detoxification plants at Zofingen and Turgi, Switzerland, then dispose of the sludge as landfill.

Disposal of sludges containing heavy metals accumulated by any of the above processes can present problems. If they are buried or used as soils (Ref. 75), the pollutants can be leached into ground water. Studies are being made to determine the effect, if any, on crops grown in heavy-metal-containing sludges used for soil enrichment (Ref. 75).

b. Control of Non-Point Sources. Non-point sources involve diffuse discharge into surface or ground waters. Air or soil pollution is introduced into surface waters by rainout or setting mechanisms, rain run-off or leaching. Controls must be instituted at the source of air or soil pollution. Systemic and regulatory controls are involved in both cases. Air pollution controls are discussed in the AIR volume of this survey and the 75 references therein. Controls of soil pollution are governed by the EPA and FDA in controlling pesticide, slimicide and fungicide usage in the agricultural business. Similar controls are exercised regarding waste disposal as considered above in Section a in the discussion of sludge disposal.

The results of the current cleanup efforts are somewhat mixed. While the Rhine still suffers from extreme pollution, the Thames has been rejuvenated. In the 1960's all fish life except a few hardy eels had disappeared. In 1977, 91 species had returned including bass, shrimp, and salmon (Ref. 77).

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CONTENTS

*In preparation

II. CONSIDERATIONS INVOLVING SPECIFIC METALS-IN-WATER

Section I of metals in water is a general discussion of metals in the aqueous ecosystem: considering their characteristics, sources, effects, and method of control. Sections III and IV review the general systems of monitoring and the instrumental methods used for determining metals in water. But many metals and metallic compounds have unique characteristics, which require special consideration by the analyst, and so, to some degree, the more important of these metals should be considered separately.

These sections will discuss these considerations for several metals. Each section is divided into two parts, Part I, complete in this up date, will describe the characteristics, sources, effects and controls for each specific metal in the aqueous environment; and in Part II, to be included in the next update, discusses analytical consideration and instrumentation. Much of the information used in the first section will come from Water Quality Criteria Documents (Refs. 1-6). The section and its references are intended as an introduction to the topics. The information in the second section will come largely from the methods manuals (Refs. 7,8) and the current literature.

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CONTENTS

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*In preparation

A. Arsenic

1. Characteristics, Sources, Effects and Controls of Arsenic in Water.

Arsenic compounds were known in antiquity: Hippocrates in the fifth century B. C. recommended the use of arsenic trisulfide for the treatment of skin diseases. Galen and other Roman physicians used arsenic for a variety of conditions including leprosy, tuberculosis, and asthma. During the Middle Ages, arsenic preparations were used extensively by physicians and alchemists (Refs. 1,2). Besides medical uses, arsenic compounds have found use in pesticidies, glass fabrication, metallurgy, medical veterinary applications and poison. Some of these compounds and their beneficial applications are summarized in Table 1.

Environmental interest in arsenic and arsenic compounds stems from their toxicity to humans on ingestion and inflammations caused by skin contact. While beneficial to man in terms of medicinal applications, rodent and pest controls, and manufacturing, residues of arsenic from these uses can be toxic to man, animals, fish and indeed to most living things.

a. Characteristics and Forms of Arsenic in Water. Arsenic (only isotope As^{75} exists in nature) can exist in a variety of inorganic and organic compounds in one of four common oxidation states: 0, +3, +5, -3. Properties of arsenic are listed in Table 2. Arsenic compounds are widely distributed throughout the earth, with an abundance of about 1.5-2 ppm in the earth's crust (Ref. 3). The most common minerals are mispickel ($FeAs_2 \cdot FeS_2$), loellingite ($Fe_{2+x}As_{4-x}$), enargite ($3Cu_2S \cdot As_2S_5$), realgar (AsS), and orpiment (As_2S_3). There are over 150 arsenic bearing minerals. A small amount of the metal occurs in the elemental form.

Arsenic can exist in natural water in the anionic form as either arsenate (+5) or arsenite (+3) inorganic compounds. In fresh waters, it is most often present in the anionic form (Ref. 5, p. 18). Arsenic in ocean water was stated to be present mainly as arsenate (Ref. 6). Table 3 includes reported concentration of arsenic in a variety of waters and sediments (from Ref. 3).

The arsenic content of potable waters rarely exceeds 10 µg/ℓ (Ref. 7). In sea water the concentration is only about 3 µg/ℓ (Ref. 8).

Arsenite (+3) and arsenate (+5) are interconvertible; one form may predominate depending on the pH and oxidizing or reducing conditions of the water. In about 1 M acid solutions, the standard electrode potential for the reaction

$$H_3AsO_4 + 2H^+ + 2e \rightarrow H_3AsO_3 + H_2O$$

Table 1. Uses of arsenic and selected arsenic compounds (Ref. 1)

Compound	Use
Arsenic As	Industrial: hardening copper, lead, alloy mfg of glass Medical: radioactive tracing
Arsenic pentoxide AS_2O_5	Industrial: mfg of colored glass wood preservative Agricultural: fungicide, herbicide, pesticide
Arsenic trioxide As_2O_3	Industrial: mfg of glass, enamels, paints Agricultural: pesticide
Cacodylic acid $(CH_3)_2AsO(OH)$	Agricultural: herbicide

Table 2. Physical Properties of Arsenic (Ref. 4)

Atomic Number	33
Atomic Weight (C^{12} = 12.000)	74.9216
Naturally occurring isotopes, weight, abundance	75, 100%
Common oxidation states	± 3,5
Melting point, °C	817° (28 atm)
Boiling point, °C	613° sublimes
Density (g/m)	5.727
Crystal system	hexagonal-rhomb.- $R\bar{3}m$(166)
Lattice constant	3.760
Heat of fussion cal/g	22.0-uncertain reliability
Capture cross section for thermal neutrons (220 m/sec), b/atom	4.3 ± 0.10
Solubility	insol. hot, cold water sol. HNO_3

Table 3. Concentrations of arsenic in natural waters and sediments (data from Ref. 3., p. 21-23)

Type of Water	Concentration Reported (water) µg/ℓ	Concentration Reported (sediment) µg/ℓ
U.S. Lakes - general	0.0 - 117	
- contaminated	198,000-243,000	
Specific example		
Chautauqua Lake (NY)	3.5 - 35.6	0.5 - 306.0
Lake Superior (MI)	0.1 - 1.6	2.8 - 5.4
U. S. Rivers - general	0.75 - 4.5	
- contaminated	< 10 - 6000	4,470 - 66,700
Specific example		
Sugar Creek	< 10 - 1100	
U. S. Sounds		
Puget Sound	1.5 - 1200	2.9 - 10,000

is + 0.559 volts. Thus, hexavalent chromium, dissolved oxygen, fluorine or chlorine gases oxidize the +3 to +5 form, whereas Sn(II), hydrazine, dissolved SO_2 can reduce the +5 form to +3. In basic solutions it is easier to oxidize the +3 form to +5, see Fig. 1.

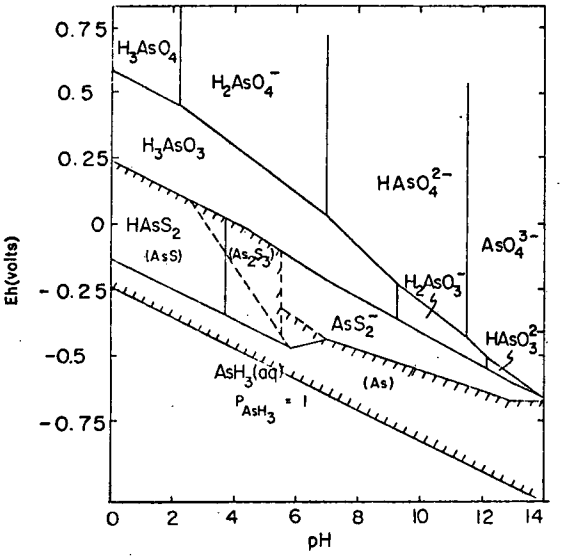

Fig. 1. The Eh-pH diagram for As at 25°C and one atmosphere with total As 10^{-5}mol/ℓ and total sulfur 10^{-3}mol/ℓ. Solid species are enclosed in parentheses in cross-hatched area which indicates solubility less than $10^{-5.9}$. (Reproduced from Ferguson and Gavis, Ref.9, with permission by Pergamon Press, Ltd. copyright 1972).

b. Sources and Pathways of Arsenic in Water. As for any metal, sources of arsenic can be natural or anthropogenic. Natural sources are primarily from erosion or dissolution of naturally occurring minerals; anthropogenic sources are diverse. Arsenic can be introduced directly in water supplies by industrial, municipal and domestic effluents.

Industrial users also are a source of arsenic introduced into water. Currently arsenic may be a constituent in a manufacturer's waste water in the Inorganic Chemicals, Non-Ferrous Metals, and Phosphorous point source categories, as well as in the effluents from some ore mining operations (see Appendix D in the Introduction to this volume). Because arsenic is also used in a variety of industrial processes such as the manufacture of paints, fireworks, glass and cloth (Ref. 8), and as a wood preservative (Table 1), clearly, arsenic compounds may be accidentally released into surface or ground waters by any of these users.

For the past century, arsenic compounds, such as arsenic trioxide (As_2O_3) and pentoxide (As_2O_5) and organo-arsenicals such as cacodylic acid ($(CH_3)_2$ AsOOH) have been used as pesticides and herbicides (Refs.10,11, 12). Once used they may be leached into surface waters during rainfall, or in agricultural (irrigation) runoff, or they may, once dissolved, percolate into aquifers. This process can be particularly insidious, because it can take such a long time. Arsenic used as a pesticide in Minnesota in 1934, was not detected in the ground water until 1972. (Ref. 13). Land disposal of arsenic containing materials is another source. Arsenic waste disposal near Charles City, Iowa has contaminated the Cedar Valley aquifer and currently no large ground water withdrawals are permitted (Ref. 14). Arsenic contamination in detergents is another source of arsenic pollution, which can reach both surface and underground waters (Ref. 15, 16).

Ferguson and Gavis recently published an excellent review of the arsenic cycle in fresh waters (Ref. 9). An inorganic arsenic compound can be degraded to arsine (Ref. 3) or an organic arsine by microbiological action (Ref. 12). Like mercury, arsenic is methylated by certain fungi, yeasts, and bacteria to form gaseous derivatives of arsine. This microbial transformation has not yet been investigated in natural fresh water environments (Ref. 9).

As mentioned previously, sea water contains arsenic in concentrations of about 3 µg/ℓ. Marine animals can concentrate the material and contain arsenic in the range of 5 to 300 µg/kg, and most shell fish, coelenterates, some mollusks, and crustaceans accumulate large quantities. In marine plants, arsenic has been reported at concentrations up to 30,000 µg/ℓ (in brown algae).

Arsenic is also accumulated in the bottom sediments. The concentration of arsenic in sediments is almost always higher than in the water (Table 3). Because it is only slightly soluble, only a small amount of the total arsenic present is released into the water. Long after direct anthropogenic pollution with arsenic ceases, arsenic which has been accumulated in the sediments will be released into the ecosystem.

Arsenic is present in most foods. Many foods such as vegetables and fruit contain naturally occurring arsenic, while shell-fish may contain over 100,000 µg/kg.

c. Effects of Arsenic in Water. Arsenic has detrimental effects throughout the food chain; it is toxic to many species at concentrations ranging from very low to extremely high, depending on chemical form. Its toxicity to man is highly dependent upon form, route

and rate and duration of the exposure (Ref.17). Metallic (elemental) arsenic and arsenious sulfide have low toxicity; on the other hand, gaseous arsine (AsH_3) is extremely toxic. Toxicity of other forms of arsenic, both organic and inorganic, varies between these extremes (Ref. 2, p. 716). Arsenic toxicity is much greater for arsenite, As(III), than arsenate, As(V). Water quality standards do not recognize these distinctions, and always are expressed in terms of total (or dissolved) arsenic concentrations (Refs. 3, 8, and 17).

When arsenic is swallowed, the gastrointestinal tract becomes irritated causing nausea, vomiting, diarrhea, which can result in shock followed by death. Other tissues are affected, possibly including nerves. Chronic poisoning can result in loss of hair, and skin coloration, polyneuritus and kidney and liver damage. Other symptoms of arsenic poisoning include headache, muscular pains, and coma. (Refs. 3, 8, 17).

Consumption of 100 mg usually results in severe poisoning and several researchers report fatalities when 130 - 200 mg have been consumed. As any detective story reader knows, arsenic is a cumulative poison, so that many small doses can be fatal - although a resistance can be acquired. Chronic arsenic poisoning may be apparent only after several years, resulting in eruptions of the skin (sometimes cancerous), or liver or heart damage. (Ref. 18). A number of arsenic compounds are suspected carcinogens. (Biological effects of arsenic compounds on humans are discussed in Ref. 3).

Arsenic in water can have a deleterious effect on animals. Cattle have been poisoned by naturally occurring arsenic in the water supplies of New Zealand. For rats and mice, the 96-hour LC_{50} for As_2O_3 varied from 15.1 to 215 mg/kg. The lethal dose for animals is believed to be about 20 mg per animal pound (Ref. 18).

Fish and other aquatic life have a wide range of tolerances for arsenic; it is acuumulated by mollusks and is highly toxic to them. Concentration factors can be as high as 20,000 (Ref. 9). Both oysters and mussels are also effected by low levels of arsenic. (Ref. 3). The most sensitive species of fish appear to be blue gills and salmon.

The potential pollutional hazard to man is usually from drinking water containing high concentrations of inorganic arsenic, rather than from consuming arsenic containing aquatic organisms, i.e., organic compounds (Ref. 9). Although arsenic is greatly concentrated in aquatic organisms, it is evidently not progressively concentrated along a food chain. In contrast with mercury, arsenic when consumed as an organically bound species in flesh is substantially less toxic. These conclusions have been reiterated by the EPA in the latest criteria document, Ref. 8.

Additional information on effects of arsenic can be found in the four criteria documents (Ref. 8, 14, 16, 17) and the National Academy of Sciences/National Academy of Engineers recommendations, Ref. 18, and the extensive book by the National Academy on Arsenic, Ref. 3.

d. Controls of Arsenic in Water. The introduction of arsenic into the aqueous ecosystem is regulated by industrial and agricultural process controls and by governmental regulatory controls.

(1) Process Controls. Although arsenic is used in a variety of industrial processes, only four industries are currently routinely allowed to discharge arsenic: these are inorganic chemicals, non-ferrous metals, and phosphorous manufacturing and some ore mining operations.

Methods useful for control of the arsenic content of waters include the following:

- its removal by shaking with <8 mesh granulated Si metal allows containing 20.5% al, 12.4%; Ba, 10.6%, 39.0% Si, and 17.5% Fe (Ref. 19) to reduce 25 µg/ℓ as As (and some other metals) to <1 µg/ℓ

- its adsorption onto activated carbon after adjustment to the proper pH. This reduces the levels of As by approximately 50% for As and some other elements (Ref. 20), its absorption onto precipitated aluminum and iron(II) hydroxides (Ref. 21).

Additional information on sources and control of arsenic in water can be found in the Water Section of Chemical Abstracts which is currently published twice each month.

(2) Regulatory Controls. Arsenic in water is regulated in a number of ways as can be seen in Table 4. The water quality criteria (Ref.8) suggest a maximum level of 50 µg/ℓ for human consumption, a level adopted for the National Interim Primary Drinking Water Standards (Ref. 22). A maximum level of 100 µg/ℓ is suggested for irrigation of crops. For marine aquatic life a level of not more than 0.01 × 96 hour LC_{50} for the most sensitive species is recommended; a level of 10 µg/ℓ has been suggested as consistuting minimum risk (Ref. 17).

Table 4. Standards and criteria involving arsenic

Standard or Criterion	Level (μg/ℓ)	(Refs.)
Water quality criterion, human consumption	50	8
Interim primary drinking water std.	50	22
Water quality criterion, irrigation long-term	100	8
Water quality criterion, marine aquatic life	0.01 × 96 hr LC50	17

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CONTENTS

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*In preparation

B. Cadmium

Cadmium is only a minor constituent in unpolluted fresh and saline waters, but may be present in certain waste waters to a greater extent. Freshwaters generally contain less than 1 µg/ℓ and saltwaters about 0.15 µg/ℓ (Ref. 1). In the U. S., the presence of cadmium pollution in surface water was reported by 1954 (Ref. 2) and in Japan as early as 1943 (Ref. 3).

As far as is currently known, cadmium is a non-essential non-beneficial element in biological systems (Ref. 2). It and its compounds are currently on the EPA list of toxic substances, being associated with numerous toxic effects, notably Itái-Itái disease and kidney dysfunction. It is, therefore, a metal which is undesirable in the aqueous ecosystem and it is important to monitor its presence carefully.

1. Characteristics, Sources, Effects and Controls of Cadmium in Water

Cadmium is a soft, white metal with a low melting point. Table 1 shows some of its physical properties. It is readily soluble in acidic solutions, but tends to precipitate under neutral to alkaline conditions.

Cadmium and cadmium compounds have a variety of uses. For example, the metal is used as a constituent of fusible alloys; a neutron shield in nuclear reactors; as a soft solder; in electroplating, as a corrosion protection overcoat for steel; and in nickel-cadmium storage batteries. Cadmium acetate is used to produce iridescent effects on porcelains and pottery; cadmium hydroxide is is used in storage batteries; the yellow-colored cadmium sulfide finds application in coloring glass yellow, in phosphors and in solar energy cells; cadmium succinate has been used as a plant fungicide (Refs. 4, 6).

In three years, domestic production of cadmium which is linked to the zinc industry has remained static at ~ 4.4 million lbs. Consumption in the U. S. was actually down in 1977 from ~12 million lbs. in 1976 to ~ 9 million lbs. in 1977. (Ref. 7).

a. Characteristics and Forms of Cadmium in Water. Cadmium in water exists in

Table 1. Physical properties of cadmium (Refs.4 and 5).

Atomic number	48
Atomic weight (^{12}C = 12.000)	112.41
Naturally occurring isotopes, weight, abundance	106, 1.22% 108, 0.88% 110, 12.39% 111, 12.75% 112, 24.07% 113, 12.26% 114, 28.86% 116, 7.58%
Common oxidation states	2
Melting point, °C	320.9
Boiling point °C	765
Density (g/mℓ)	8.642
Crystal system	hexagonal, close-packed
Lattice constant, Å	a = 2.9727; c = 5.505
Heat of fusion, cal/g	12.9
Capture cross section for thermal neutrons (220 m/sec), b/atom	2450 ± 20
Solubility	insol.-hot, cold water sol.-acids, NH_4SO_4, hot H_2SO_4

the +2 oxidation state. The metal is soluble in mineral acids, but is insoluble in strong bases. Cadmium in water forms soluble complexes with ligands such as ammonia, cyanide, and halides. Soluble cadmium will react to form insoluble precipitates with anions such as carbonate, phosphate, oxalate, arsenate, sulfide, and alkaline hydroxides. Kopp and Kroner found that cadmium in surface waters of the United States exists primarily in the dissolved state, with none found in the suspended state (Ref. 8). This is in contrast to the results reported by Yamagata and Shigamotso in Japan, who reported that cadmium in neutral and alkaline waters was often in the suspended state (Ref. 3).

In 1970, Durum and Hem, using atomic absorption analysis, detected cadmium in 42% of the 727 samples taken of United States surface waters (Ref. 9). The concentrations ranged mostly from 1 to 5µg/ℓ. These samples of water were obtained in three types of locations: public water supplies, U. S. Geological Survey hydrologic benchmark stations, and metropolitan-industrial complex locations. The implication of the data is that the higher concentrations of cadmium in water generally occur in areas of high population density. Cadmium was detected most frequently in the waters of New England and the northeastern United States, with a median concentration of 2 µg/ℓ as can be seen in Table 2. Durum and Hem also found undissolved cadmium in bottom sediments of some of these waters.

The forms of cadmium in water depend on the other constituents in the water, and on the pH. For example, in the presence of some ligands such as NH_3 or CN^-. cadmium forms complexes which are soluble in water above pH 6.7. In the absence of complexing ligands, Cd(II) ions are precipitated about pH 6.7. Cadmium ions react with dissolved carbonate, sulfides, phosphates, or arsenates to form insoluble precipitates and eventually bottom sediments.

Posselt and Weber published a report entitled "Environmental Chemistry of Cadmium in Aqueous Systems" (Ref. 10), which includes models describing the equilibrium solubility of cadmium over a wide range of conditions in both natural and wastewaters.

b. Sources and Pathways of Cadmium in the Aqueous Ecosystem. The most common naturally occurring mineral is greenochite (CdS), which is found associated with zinc and lead. The usual content in ZnS averages 0.3 to 0.4% CdS.

Background levels of dissolved cadmium in fresh waters are probably due to leaching and weathering of naturally occurring ores such as greenochite by rainwater. Wastewaters from electroplating plants, pigment works, textile industries, chemical industries, and drainage water from lead mines can cause concentrations exceeding background levels. McKee and Wolf cite one study in Long Island, N.Y. where ground-water contamination caused by wastes from electroplating industries reached 3.2 mg/ℓ of cadmium. In another case, high cadmium concentrations were reported in Missouri mine waters, where one spring contained 1000 mg/ℓ of cadmium (Ref. 11, page 149).

Cadmium found in polluted rivers and streams often finds its way to neighboring soils. This was the suspected mechanism for contamination of paddy fields in the Jinstu River area in Japan. In Sweden, where a river was reported to have 4 ng/g Cd in its water, neighboring mud was found to contain 80µg/g (dry weight) (Ref. 3). Once cadmium is in the soil, studies in England, Sweden and Japan have found that it is taken up and concentrated by various plants (Ref. 3). Some varieties of shellfish and fish, notably, oysters (Crassostrea Virginica) and salmonids have been found to concentrate cadmium over 1000-fold (Ref. 1, 3, 12). Zaroogian (see Ref. 1) reported that adult oysters, exposed to 10 µg/ℓ

Table 2. Regional summary of cadmium in surface water of the U. S. (adapted from Ref. 8)

Region	Max µg/ℓ	Median µg/ℓ	Not detected %
Northeast	32	2	36
Southeast	90	<1	55
Central	40	<1	55
Southwest	130	<1	65
Northwest	21	<1	78

Cd over a 6 month period, accumulated 18,000 µg/kg of Cd in wet whole meat. This is significantly higher than the threshold value of 13,000-15,000 µg/kg which can cause sickness in humans.

The daily intake of cadmium in man can vary from 4 to 60 µg, depending on the foods chosen. The major sources of cadmium in foods ingested by man appear to be seafords and grains (Ref. 11). At birth, the human body contains only 1 µg of cadmium; this increases to 30 mg at age 50 (Ref. 13).

c. Effects of Cadmium in Water. On being ingested, cadmium tends to concentrate in the liver, kidneys, pancreas, and thyroid of humans and animals. The rate of excretion is extremely low. Although many plant and animal tissues contain about 1000 µg of cadmium per kg of tissue, there is no evidence that cadmium is biologically essential or beneficial (Ref. 11), and it and its compounds are currently on the EPA toxic chemical list.

Cadmium may cause testical tumors, kidney damage, hypertension, arteriosclerosis, growth inhibition, chronic diseases of old age and cancer (Ref. 1). It has been known to cause sickness (i.e. cramps, nausea, vomiting and diarrhea) within hours when consumed in concentrations greater than 13,000 µg/ℓ. Animal studies have shown kidney damage after only short exposures of low levels of cadmium in drinking water, several autopsies of humans who suffered cadmium exposure showed similar results (Ref. 3).

Cadmium has been linked with arteriosclerosis, but the data are generally ambiguous. The effect of cadmium on bone structure is largely secondary. Cadmium itself is not taken into bone; however, the presence of cadmium in the kidneys may upset the calcium-phosphorous balance and can give rise to severe changes in the bone structure (Ref. 3). There is some evidence from animal studies that tumors are formed upon injection of cadmium (in rats); however, the causal relationship between cadmium and cancer in humans has not been positively established (Ref. 3).

Cadmium poisoning can in some cases be mitigated by the presence of zinc or copper (an antagonistic response) and in other cases the two metals seem to have a synergistic effect. The 96 hour LC_{50} for young chinook salmon was 30 µg/ℓ cadmium plus 150 µg/ℓ zinc, a value substantially worse than for each of those metals alone. The NAS and NAE recommended in fact that "in the presence of copper and/or zinc at 1 mg/ℓ or more, there is evidence that the application factor for cadmium should be lower by at least one order of magnitude" for marine aquatic life (Ref. 12). Other workers have found that for plants if the zinc to cadmium ratio is 100 or greater then cadmium will not be concentrated to dangerous levels (Ref. 1).

The acute lethal level of cadmium for fish varies from about 0.01 to about 10 mg/ℓ, depending on diverse factors such as the test animal, the type of water, temperature, and time of exposure. As in humans cadmium acts synergistically with other substances to increase toxicity to fish (Ref. 11).

Hard water is antagonistic to cadmium poisoning in fish; the levels of cadmium considered safe in soft waters are a factor of 3 lower than in hard water. Some species, notably salmonids and cladocerans, are extremely sensitive to cadmium, possibly because they are unable to excrete it, and are only safe in waters which contain cadmium an order of magnitude less concentrated than would be safe for other fish.

(1) Itái-Itái disease. For the past two decades, substantive evidence has built up linking Itái-Itái (Ouch-Ouch) disease to chronic cadmium poisoning. Itái-Itái disease is an extremely painful disease involving renal dysfunction in conjunction with severe pain in the bones (which are embrittled and weakened) eventually involving multiple fractures at the slightest stress (such as coughing). Initially, patients walk with a duck-like gait and eventually are bedridden.

A number of similarities have been found among the victims. They (1) were largelv female with a high number of childbirths, (2) drank river water, (3) probably had vitamin D deficiency and (4) lived in the same area, the Jinstu River Valley of Japan, for more than 40 years and had a fairly low standard of living. Because the Jinstu River has been polluted with cadmium for a long time, cadmium was suspected as a possible causative agent.

Because equally high levels of cadmium have been found in other areas of Japan and Sweden, but with very low incidence of Itái-Itái disease, not all medical authorities accept the causal role of cadmium in the disease. Friberg, et al. (Ref. 3) however, conclude that in this particular area of Japan (Fuchu, Jintsu River Valley) that certain dietary deficiencies, notably calcium and vitamin D linked with high levels of cadmium, can lead to Itái-Itái.

Additional information of cadmium toxicity can be found in the criteria documents, Refs. 1, 2, 9 and 10 and particularly in the two reviews Cadmium in the Environment, by Friberg, Piscator, Nordberg and Kjellstrom (Ref. 3) and Cadmium, the Dissipative Element (Ref. 14).

Table 3. Standards and water quality criteria regulating cadmium in water

Standard or Criterion		Value (µg/ℓ)	Ref.
National Interim Primary Drinking Water Standard		10	2
Domestic Water Supplies (Water Quality Criterion)		10	1
Fresh Water Aquatic Life	Soft water	Hard Water	1
Cladocerans and salmonids	0.4	1.2	
Ohter less sensitive species	4.0	12.0	
Marine Aquatic Life		5.0	1
Agricultural Uses			11
Livestock		50	
Irrigation:			
Continuous use, all soils		10	
Neutral-Alkaline fine texture soils (20 yr period)		50	

d. Methods of Controlling Cadmium in Water

(1) Process Controls. Cadmium can be removed from wastewaters in a number of ways. For example, added sodium sulfides will form the insoluble precipitate CdS (Ref. 14), and neutralization or increasing the alkalinity will also cause precipitation. Cadmium in cyanide electroplating baths is precipitated by the addition of a proprietary peroxygen formulation in the DuPont-Kastone process (Ref. 15).

(2) Regulatory Controls. The current standards and water quality criteria are displayed in Table 3. The recommended water quality criterion for domestic water supplies and the National Interim Primary Drinking Water standard (based largely upon NAS recommendations) is 10 µg/ℓ. The stringency of the standard is in part due to the evidence of poisoning from cadmium contaminated food and beverages, the epidemiologic association of cadmium with Itái-Itái disease and possible association with renal arterial hypertension and finally animal studies (Ref. 2).

The fresh water criteria established by the 1976 EPA study (Ref. 3) are 0.4 and 1.2 µg/ℓ for salmonids and cladocerans in soft and hard water, respectively, and 4.0 and 12.0 µg/ℓ respectively for less sensitive species. At these levels no effects were observed in the various species. (Ref. 1).

The criterion for marine aquatic life, 5 µg/ℓ, is based on the study, which showed that in 6 mos., oysters *(Crassostrea Virginica)* which lived in water containing 10 µg/ℓ cadmium reached levels of cadmium which had been shown to cause sickness. A factor of two was considered to be sufficient to protect the consumers of these oysters (Ref. 1). The National Academy of Sciences stated in Ref. 11 that as no benefits were derived from cadmium in the water, and in view of the unknown effects of cadmium in the ecosystem, the human risk involved in consuming cadmium containing seafood, and the concentration of cadmium by fish and shellfish, "it is suggested that there be no artificial additions of cadmium to the marine environment".

The EPA in 1976 did not revise the NAS/NAE criteria for livestock and irrigation, but suggested that additional research was necessary before the cadmium-zinc-soil plant system was understood.

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CONTENTS

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*In preparation

C. Lead

Lead is a soft blue-gray malleable metal. Although it is only minimally soluble in neutral to alkaline water, its presence in drinking waters has been known to be detrimental since at least Roman times. Its toxic effects, particularly to children, and its numerous uses (providing a wide variety of sources) make it an essential metal to monitor.

Lead ores are plentiful and may be readily refined. It is easy to form and apparently uncorrosive, which may account for its use from earliest times (Ref. 1). The earliest known specimen is a lead statue dating from before 3800 BC, in Abydos in the Dardenelles (Ref. 2). The metal is mentioned in Exodus and other sections of the Old Testament. The Romans called it "plumbum", hence the term plumbing. They used it to make water pipes of all diameters and lengths. It is estimated that the Roman Empire extracted and used six to eight million tons of lead over a period of 400 years.

Lead is currently used for a variety of purposes: for the manufacture of sulfuric acid, in oil refining, as radiation protection, until recently in the gasoline antiknock ingredient tetraethyl lead, in solders, batteries and prints. Lead acetate treated paper is a common method for the detection of sulfide, and lead-arsenic compounds are used as pesticides notably for boll-weevil and gypsy moth. Lead pigments such as lead oxide, lead carbonate and chromate were widely used for years in paints until their toxicity limited their applications. Lead thiosulfate is used in matches and lead sulfide is a glaze (Ref. 3).

In 1968, the United States mined 374.1 thousand short tons of lead, and refined 913.4 thousand short tons. The estimated totals in 1977 were 645 thousand and 1,300 thousand short tons, respectively. The United States consumed a total of 1,450,000 short tons of lead in 1972, compared with 1,309,300 in 1968. (Ref. 4).

Table 1 shows physical and chemical constants of lead.

Additional information on practical uses of lead and lead compounds may be obtained from The Merck Index (Ref. 3), The Encyclopedia of Chemical Technology (Ref. 2), and the Engineering and Mining Journal (Ref. 4).

Table 1. Physical and chemical constants of lead (Ref. 5).

Atomic number	82
Atomic weight	207.19
Common oxidation states	2,4
Melting point, °C	327.5
Boiling point, °C	1740
Density (g/mℓ)	11.3437
Crystal system	face centered cubic Pm3m(225)
Lattice constant	4.9505
Heat of fusion cal/g	5.9
Capture cross section for thermal neutrons (2200 m/sec), b/atom	180 ± 10
Solubility	insol. hot, cold water sol. HNO_3, hot conc. H_2SO_4
Naturally occurring isotopes, weight, abundance	204, 1.48% 206, 23.6% 207, 22.6% 208, 52.3%

1. Characteristics, Sources, Effect and Controls of Lead in Water

a. Characteristics, Forms and Occurrence of Lead in Water. Lead is found dissolved in water as free or complexed Pb(II) or as a suspended solid, but also as Pb(0). The metal is soluble in acids such as nitric and acetic acids; it follows therefore that the salts of these acids are relatively soluble in waters of pH < 6. The lead carbonate, oxide, hydroxide and sulfide are generally insoluble as are any other lead salts in waters and in hard waters, pH > 6. Lead chloride is also readily soluble in solutions containing an excess of chloride ions such as ammonium chloride. On the other hand lead ions react with dissolved carbonate, sulfide, arsenate, chromate, sulfate, phosphate, or hydroxide to form insoluble precipitates and eventually bottom sediments in water streams (Ref. 3). Lead solubility is also dependent upon temperature. For example, lead chloride ($PbCl_2$) is soluble in 93 parts of cold water but only 30 parts of boiling water.

Livingstone reported that U. S. rivers and lakes have median concentrations of about 10 µg/ℓ (Ref. 6), although Durum and Hem in their study reported somewhat less, the median concentrations being from 1-6 µg/ℓ (Ref. 7). Higher levels are generally reported near mine, industry or smelter discharges, or near highways, roads, or streets.

In 1970, Durum and Hem, using atomic absorption analysis, detected lead in 63% of the 727 samples taken of United States surface waters (Ref. 7). As can be seen from Table 2, the concentrations ranged primarily from 1 to 50 µg/ℓ and was most frequently 1-5 µg/ℓ. These samples of water were obtained from three types of locations: public water supplies, U. S. Geological Survey hydrologic benchmark stations, and metropolitan-industrial locations. Lead was detected less frequently in samples collected at benchmark sites than in those from public water supply sources and from streams below metropolitan-industrial areas. Lead had a distinct regional pattern. It occurred most frequently in the well-watered northeast and southeast and coincides with similar patterns in rainfall found by others who found that the highest rates of lead fallout occurred in the northeast, southeast, and eastern part of the central regions of the United States.

b. Sources and Pathways of Lead in Water. Lead in the earth occurs chiefly as sulfides in the mineral galena (PbS), and also as carbonate in cerussite and as a sulfate in anglesite. Lead exists in the earth's crust to the extent of about 15 g/ton or about 0.002%. Background levels of dissolved lead in fresh waters are probably due to leaching and weathering of the naturally occurring minerals.

The dissolving action of water on lead pipes (plumbosolvency) can add lead to water passing through them. This means that water, which was potable in the water distribution unit, may be rendered impotable by action of the water on a home's plumbing. The characteristics of water, soft or hard, that appear to be conducive to plumbosolvency include comparative absence of calcium and magnesium bicarbonates, low pH, high dissolved oxygen, and high nitrate content (Ref. 8).

Until recently a major source of lead pollution in water was rainout, fallout or runoff derived from the tetraethyl lead additive in automobile exhaust (Refs. 9-11). Lead is also introduced into the aqueous environment through precipitation of lead containing dusts

Table 2. Regional summary of lead in surface waters of the U. S. (Adapted from Ref. 7).

Region	Concentration, µg/ℓ		Not detected
	Maximum	Median	%
Northeast	890	6	8
Southeast	44	4	27
Central	84	1	51
Southwest	34	1	61
Northwest	23	1	62

from industries such as coal fired power plants. Lead may be released directly into water supplies in the discharges of the Electroplating Industry, Inorganic Chemicals Manufacturing, Iron and Steel Manufacturing, Non-ferrous Metals manufacturing, Glass Manufacturing, and Ore Mining and Dressing processes (40 CFR 400-60).

Because lead is largely insoluble in neutral to alkaline waters, it is precipitated and accumulated in sediments. Sediment accumulations can then redissolve lead compounds by action of chelating agents such as NTA (Ref. 12).

The pathways by which lead enters the environment from its origin on the earth are still being characterized. Figure 1 gives an ecologic flow chart of the major compartments and pathways of lead transformation in the biosphere. There has been no comprehensive study of its translocation within living systems. However, many parts of the system have been explored. There is not sufficient information on the chemical forms, amounts, and rates of transfer of lead from one compartment of the environment to another to permit treatment of the subject in terms of a complete systems analysis. Neverthless, the available data afford some insight into the movement of lead in the biosphere. Some data come from studies of lead-210, a radionuclide important in tracing the pathways and determining flux rates of lead, as stressed by Burton and Steward (Ref. 13).

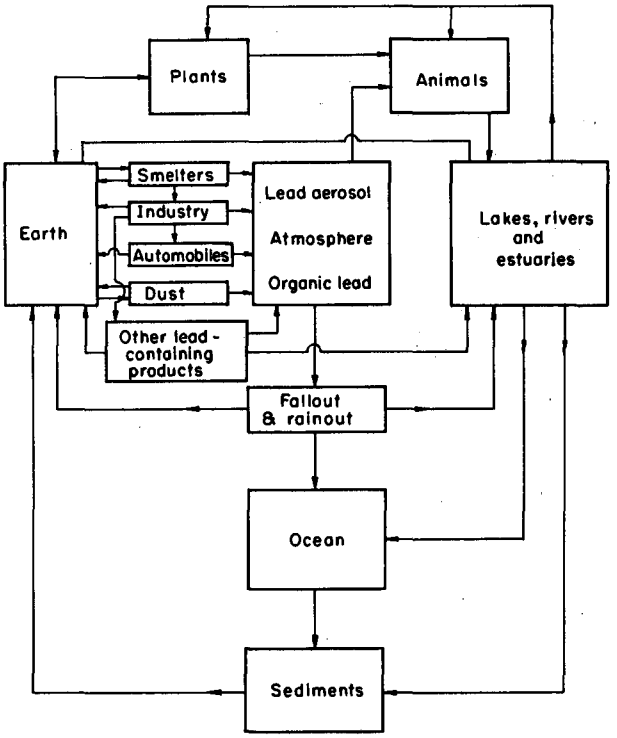

Fig. 1. Ecologic flow chart for lead showing possible cycling pathways and compartments. (XBL 7311-4516)

It is clear that once lead enters the aqueous ecosystem it also enters the food chain by uptake in fish and shellfish (Ref. 14) and plants.

c. Toxic Effects of Lead-in-Water. The mean daily intake of adults in the U.S. is somewhat less than 300 μg (Ref. 15); of this quantity from 10 to 30 μg are found in food and hard water (Ref. 8). The rest must therefore be derived from other sources such as smoking, beverages and the air. Lead has no known nutritional or beneficial aspects in biological systems (Ref. 6).

On being injected, lead can cause anemia, severe intestinal cramps, brain damage causing paralysis in the arms and legs particularly, and kidney damage, resulting in convulsions and coma. Low level chronic lead poisoning results in fatigue, loss of appetite, constipation, flatulence and occasional colic (Ref. 8). Low-level chronic lead poisoning is suspected of causing "impaired neural and motor development" and kidney damage in children (Ref. 6) which often goes unrecognized.

Lead poisoning is actually rarely found in adults but it is particularly dangerous to children who have very low tolerance for it. There are several reasons for this. The gastrointestinal absorption rate for children is 53% vs. 18% in adults. Furthermore, per kg of body weight they consume greater amounts of food and air, thereby taking in greater percentages of lead (Ref. 16). Effects are particularly severe in children under three years of age, and even though some of the symptoms are treatable, brain and kidney damage has so far been found to be largely irreparable.

The major sources of lead for children are paint, dust, canned milk, toothpaste, toys, newsprint ink, air and plumbing (Ref. 16). Of these the most important, seems to be lead based paint, which still remains in older (particularly slum) areas where it is allowed to chip and is therefore readily available to the exploring child. Another potentially dangerous source in the same homes is the plumbing, which can introduce high levels of free lead if the water is soft and acidic. Because of the large variety of sources of lead poisoning and its severe consequences, it is essential to restrict lead intake, where possible, in water and food supplies.

Lead has been implicated in causing hyperactivity, aggressiveness (Ref. 17) and even cancer in rats (Ref. 12), although evidence of carcinogenesis in other larger mammals has not been found.

Table 3. 96 hr LC_{50}'s of lead to several species of fish of various water qualities (adapted from Ref. 6)

Species	Concentration µg/ℓ	Hardness	T°C
Rainbow trout (salmo gairdneri)	471,000 (1,380 free lead)	300	7
Rainbow trout (salmo gairdneri)	3,750	43-45	14.7
Coho salmon	800	17-26	10
Sticklebacks	100	—	—
Mosquito Fish	>56,000,000	—	18-20
Bluegills	23,800	20	25
Bluegills	442,000	360	25

Freshwater and marine life are both effected strongly by lead. Table 3 shows the 96 hr $LC_{50's}$ for several freshwater species. The table suggests that the hardness of the water is an important factor in lead toxicity perhaps because lead in precipitated form is less readily consumed. Marine organisms, notably the oyster, concentrate lead in their flesh. Oysters exposed to a variety of concentrations of lead have concentration factors of ~1000.

Additional information on the toxic effects of lead can be found in the criteria documents presented by McKee and Wolf (Ref. 8), the EPA (Ref. 6) and the NAS/NAE (Ref. 15). The justification for the National Interim Primary Drinking Water Standards (Ref. 16) and the NAS study, Airborne Lead in Perspective (Ref. 18) are also informative.

d. Controls of Lead in Water.

(1) Process Controls. Lead wastes are commonly removed by conventional methods: chemical precipitation, cementation, electrodeposition, reverse osmosis or ion exchange (Ref. 19). Westinghouse reported in 1972 success using trisodiumphosphate ($TSP=Na_3PO_4$) to precipitate its lead wastes. Using this technique they were able to achieve levels of 50 µg/ℓ in the waste fluid which was then mixed with other plant effluent and discharged (Ref. 20).

Lead may also be easily precipitated at pH >6 - using $CaCO_3$ or other agents- and then collected. As a method for removal of the last few mg/ℓ of lead, activated carbon or electrodeposition are promising techniques (Ref. 19).

(2) Regulatory Controls. The currently applicable (or latest) water equality criteria and standards are listed in Table 4.

In establishing the drinking water standards a variety of factors were considered, namely (1) drinking water is only one of several paths by which lead enters the body, others being food, air, smoke, other beverages, etc., and (2) that the tolerance for lead in a child is substantially less than for an adult, and while some of the symptoms of lead poisoning can be reversed by the use of chelating agents, there is no evidence that once brain damage has occurred, that it can be reversed (Ref. 21).

In establishing the drinking water standards, the severity of the problem was taken into account:

"It should be reemphasized that the major risk of lead in water is to small children. There is a serious problem with excess lead in children; it is well documented. It can lead to lead poisoning. Lead poisoning does cause death and morbidity in children... With the widespread prevalence of undue exposure to lead in children, its serious sequelae, and studies suggesting increased lead absorption in children (chronic brain or kidney damage, as well as acute brain damage); it would seem wise to limit the lead in water to as low a level as practicable" (Ref. 16). The level chosen was 50 µg/ℓ.

Table 4. National water criteria and standards for lead.

Control	Standard or criterion (μg/ℓ)	Ref.
National Interim Primary Drinking Water Std.	50	16
Domestic water supply	50	6
Freshwater aquatic life	0.01×96 hr LC_{50}[a]	6
Marine aquatic life	insufficient data	6
Agricultural Uses		
Livestock	50	15
Irrigation	insufficient evidence of accumulation to warrant a criterion	6

[a]Using the receiving or comparable water as a diluent, and soluble lead measurements using an 0.45 μm filter, for sensitive freshwater species.

The water quality criterion recommended by the EPA in 1976 for freshwater aquatic life was 0.01 times the 96 hour LC_{50} for sensitive species. Because so many factors influence lead toxicity (pH, hardness, organics present, and temperature among them), a recommendation which was based on the toxicity experienced in the particular water source was deemed the most satisfactory method of determining the appropriate level. From Table 3, it is easy to determine criteria. For rainbow trout in hard water at 7°C, the criterion would be 4,710 μg/ℓ, but in soft water at ~15°C, it would be 3.75 μg/ℓ. For sticklebacks the criterion would be 1 μg/ℓ-- and so on.

It is interesting that despite the well documented evidence that marine shellfish are sensitive to the presence of lead and have concentration factors of ~1000, the EPA has not reissued the marine aquatic life criterion. Presumably when more data are available they will issue one.

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CONTENTS

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*In preparation

D. Mercury

1. Characteristics, Sources, Effect and Control of Mercury in Water

Mercury is an element which is present throughout the aqueous environment, but is not known to be biologically essential or beneficial. It and its compounds are on the EPA list of toxic substances. It is therefore an important metal to monitor.

Mercury (or quicksilver) is a shiny liquid at room temperature. This unique property, which makes it valuable for numerous uses, has also given it is magnical and possibly sinister reputation. Mercury has been used since the medieval period - alchemists were fascinated by it - and its toxic effects have long been known. In fact, according to Goldwater (Ref. 1), the first attempt to close a factory to prevent mercury poisoning was in Finale, Italy in 1700.

Somehow in the 1900's the dual nature of mercury - incredibly beneficial to industry, science, and agriculture but deadly - was ignored, if not forgotten. Then in the mid 1950's an outbreak of disease in Minamata, Japan, was reported. It was associated with mercury compounds from a plastics factory whose effluent was discharged untreated into the bay. Similar outbreaks were reported in Pakistan, Sweden, and Guatemal. By 1969 experts throughout the world were concentrating great effort to understand mercury poisoning, its sources, paths, effects and most important methods of controlling it. A major body of literature was generated in the process and several reviews from this period was included in Refs. 1-15.

Mercury is rarely found in elemental form in the environment; most often, it is found as cinnabar (HgS) (Ref. 16) and other similar minerals. Some of its properties are listed in Table 1. Mercury and mercury compounds are used for a variety of purposes. Some of those include embalming, disinfection, electroplating, preserving, ink manufacturing ($HgCl_2$) and in herbicides (phenylmercuric acetate), fungicides and medicines (organomercury compounds) (Ref. 16). Table 2 includes a number of the uses for mercury and mercuric compounds.

a. Characteristics, Forms and Concentrations of Mercury in Water. Mercury can occur in three oxidation states: 0, +1

Table 1. Physical and chemical properties of mercury (Ref. 17)

Atomic number	80
Atomic weight	200.59
Naturally occurring isotopes, weight abundance	196, 0.146% 198, 10.02% 199, 16.84% 200, 23.13% 201, 13.13% 202, 29.80% 204, 6.85%
Common oxidation states	1,2
Melting point, °C	-38.87
Boiling point, °C	356.58
Density (g/mℓ)	13.5939
Crystal system	N/A at R.T.
Heat of fusion, cal/g	2.7
Capture cross section for thermal neutrons	375 ± 5
Solubility	insol. hot, cold water insol. dilute HCl, sol. HNO_3

Table 2. Sources and uses of mercury (Refs. 4, 12)

Source	%	Major Compound Released (Ref. 4)
Electrical Industry	20%	Metallic mercury, Hg°, inorg. mer.
Chlor-Alkali Industry	20%	Metallic Hg°, inorganic Hg^{2+}
Paints	10%	Phenyl mercury, $C_6H_5Hg^+$
Industrial Control Equipment	10%	Metallic mercury, Hg°
Pulp and Paper Industry		
Catalysis (Chem. Mfg.)		
Agriculture		Methyl mercury, $CH_3\ Hg^+$ Methylethyl mercury, $CH_3C_2H_4Hg^+$
General Laboratory Uses		
Pharmaceuticals		

(mercurous compounds) and +2 (mercuric compounds). In oxygen containing atmospheres the 0 and +2 state are by far the more stable, and in nature mercury is more likely to occur in either of these states. Compounds may be inorganic, such as $HgCl_2$ or HgS, or organic, i.e.g., methyl mercury. Mercury compounds can be dissolved, absorbed onto sediments or be suspended in natural waters. While the inorganic forms are more likely to be introduced into the aqueous ecosystem, micro-organisms, plants, fish and shells are able to transform the inorganic compounds into organic ones (Ref. 18). In fish and shellfish, mercury exists primarily as methyl mercury (Refs. 12, 19).

In 1970, unpolluted U. S. waters generally contained less than 0.1 µg/ℓ, (Ref. 20), although the EPA criteria document (Ref. 21) reports levels from 0.03 to 0.2 µg/ℓ. In mining, industrial and agricultural areas the levels in both sediments and waters tend to be higher. Gardner, in 1975 (Ref. 22), reported 33.5 µg/ℓ in the oceans of the northern hemisphere, vs. 0.0112 µg/ℓ in the southern hemisphere.

Levels of mercury in sediments near points of discharge may be significantly higher than background levels. Since 1970, substantial decreases in discharges of mercury have taken place, and this eventually may be reflected by lower levels in sediments near discharge points. Sediment immediately downstream of a chloralkali plant in Saskatoon (Canada) was reported in 1971 to contain 1800 ppm of mercury (Ref. 9). Sediment in Lake Ontario near Hamilton Harbor contained 692 ppm of mercury (Ref. 9). The content of mercury in some water samples in the same area ranged from 0.99 - 10.4 µg/ℓ (Ref. 23).

b. Sources and Paths of Mercury in the Aqueous Environment. Mercury is introduced into the aqueous environment by both natural and anthropogenic sources. Natural sources include the leaching or dissolution of mercurials occurring in rocks or soils (Ref. 24), microorganisms acting on naturally occurring mercurials in (Ref. 25) bottom sediments, and the results of geothermal and volanic erruptions (Ref. 26).

Concentrations resulting from background contributions exceed guidelines in some cases. Tuna and swordfish caught in unpolluted waters near Malaya and Africa had mercury concentrations exceeding the Food and Drug Administration guidelines of 0.5 ppm (Ref. 1). The air above ore deposits may contain as much as 20 µg/m^3 of mercury (Ref. 5), much higher than the Environmental Protection Agency's recent suggestion of 1 µg/m^3 maximum for public, long-term average exposures (Ref. 27).

However, the major sources of mercury pollution do appear to result from man's activity - industrial effluents to the air, soil and waters and agricultural runoff. A study of fish preserved in museums has shown a marked increase in mercury concentrations over those reported in 1920 (Ref. 28), as have levels in the Greenland Ice cap (Ref. 29).* These increases are attributed to enhancement of mercury concentrations over natural levels by man's activity.

As a result of man's activities, mercury concentrations can be elevated above background levels, unsafe conditions created, and

*This last evidence has been disputed by Ref. 30.

Table 3. Mercury levels found in U. S. foods (Ref. 36)

	% Samples with mercury level minimum detection limit below mdl of technique used in test	Mercury Range (ppb)
Flour	89	<3 - 6
Milk, whole	72	<4 - 9
Potatoes	42	<1 - 15
Beef	39	<2 - 7
Chicken	38	<1 - 7
Shrimp	0	<5 - 43
Liver	50	<2 - 8
Eggs	91	<2 - 5

natural hazards enhanced. Liquid wastes can induce high levels of mercury in local waters and wildlife. Perch caught upstream from a pulp and paper mill outfall contained from 0.18 to 0.70 ppm mercury; those caught downstream from the outfall contained 1.90 to 3.02 ppm mercury (Ref. 4). Whitefish, pike and walleye were found to contain 0.10-9.00 ppm of mercury (Ref. 31). Mercury discharged into Minamata Bay in Japan was taken up by fish and entered the human food chain. The result was the death of 46 people directly due to eating the contaminated fish (Ref. 32-35). Other foods more commonly ingested than fish in the United States do not appear similarly contaminated with mercury, as shown by the data in Table 3 (Ref. 36). However, uncontrolled plant emissions into air and water can result in the surrounding ambient air containing average mercury concentrations over 1 $\mu g/m^3$ (Ref. 4).

One major source of anthropogenic mercury is the direct discharge of industrial waste into navigable waters. Until recently they included direct discharges from a variety of industries, e.g. the electrical industry, pulp and paper, chemical (including plastics) manufacturers, the chlor-alkali industry and so on. The mercury compounds discharged by these various industries are given in Table 2.

Prior to July 1970, 50 plants were dumping 130 kg (287 lb) of mercury per day into U. S. waterways; by September 1970, this was reduced to 18 kg (40 lb) (Ref. 4). In 1978 the EPA guidelines concerning best practicable control technology currently available, BPTCA (see Table 4), allowed the discharge of 0.28 g of Hg per kg of product in one day and 0.14 g per day over a 30 day period in the chlor-alkali industry, and in the ore mining industry permits 2 $\mu g/\ell$ in one day (1 $\mu g/\ell$ per day over

Table 4. 1978 allowed mercury discharges (40 CFR 415, 440, July 1, 1977).

Point Source Category	Subcategory	Discharge (BPTCA) units 1 day	30 day/av	
415 Inorganic Chemicals	Chlorine and sodium or potassium hydroxide (chlor-alkali)	0.28	0.14	µg/kg prod.
440 Ore Mining and Dressing	Base and precious metals	2	1	µg/ℓ
	Mercury ore	2	1	µg/ℓ

30 days). Discharges of mercury are not currently permitted from any of the other industries mentioned in Table 2. The discharges of mercury from agricultural runoff are more difficult to control except by reduced usage of mercury compounds as fungicides, herbicides, pesticides, or as disinfectants for seeds. Possibly as a reaction to the widespread incidence of poisoning resulting from the consumption of mercurial-treated seeds, or foods that have been contaminated by those seeds, this usage at least has declined. As a result mercury contamination in runoff should eventually drop (Refs. 7, 11 and 37).

Mercury is also introduced into the aqueous ecosystems from rainout surrounding industries such as coal-fired power plants (Refs. 37, 38). And of course, bottom sediments which have been polluted through man's activities rerelease the chemical. (Ref.39).

Thirdly, because of the mobility of mercury, discussed below, discharged mercury does not remain localized. Through natural cycles, it slowly disperses and extends itself into much broader regions to remain almost indefinitely.

Once mercury has entered the aqueous ecosystem, it permeates it. In fact increased loading of mercury may not show significantly in the water, but may appear in increased levels in the sediments and suspended particulates, and in the biota (Ref. 24). By 1969 Jensen and Jernelov (Ref. 18) had shown that microorganisms could transform inorganic mercurcy to methyl mercury. In 1973 and 1974, Bisogni and Lawrence (Ref. 40) and Wood (Ref. 41) and others (Ref. 42) have shown that in natural waters, inorganic mercury is possibly converted to methyl mercury; in fact the various forms of mercury, Hg°, Hg^{+}, Hg^{2+}, CH_3Hg, and $(CH_3)_2Hg$ may achieve a steady-state condition. Because of this evidence, the EPA has concluded that the most reasonable water quality criterion is one for total mercury (Ref. 21).

Mercury has pathways to virtually all parts of the aqueous system. It is accumulated by plants by surface adsorption, is taken up by fish and shellfish and concentrated (Refs. 4, 18, 19, 22, 25, 43, 44). McKim, as reported by the EPA, found that in a period of one year, some species of fish showed concentration factors of 27,800 (Ref. 21). Since most of the mercury in fish and shellfish is methyl mercury (Ref. 19), a form which is highly toxic to man, levels which are toxic to man can accumulate in fish and shellfish from relatively low levels of mercury in water.

c. Effects of Mercury in Water. Mercury compounds are toxic at very low levels to most species in contact with the aqueous environment - invertebrates, plants, fish, shellfish and mammals, including man. In man, the symptoms encountered depend on the form of mercury, the manner of contact and whether the contact or ingestion is acute or chronic.

In general, inorganic forms are less toxic than organic, mercurous (Hg^{+1}) forms being less toxic than mercuric. Goldwater (Ref. 1) states that mercury as the metal can be swallowed without harm. Glass blowers working with glass which has contained mercury(0) report serious headache, presumably from breathing the substance. Other researchers (Ref. 1) report irritation of the lung, chills and fever, coughing, tremors and irritability associated with inhaled mercury (0). Inorganic mercuric salts are reported to be lethal to man in doses of 20 mg to 3.0 g. Symptoms of acute inorganic mercury poisoning are intestinal cramps, vomiting, ulcerative hemorrhagic colitus, hepatitis, circulatory collapse, inflammation of the kidney and the pharynx (Ref. 21). Chronic inorganic mercury poisoning is associated with headaches, giddiness, skin discoloration and reduction of perception. More severe effects include tremors, salivation, restlessness and hysteria (Ref. 45).

The symptoms associated with organic mercurial poisoning are those commonly associated with Minamata disease: illness, weakening of the muscles, loss of vision, irreversible neurological damage, paralysis, coma and death (Ref. 1). Organic methyl mercury is readily absorbed by the intestine - up to 95% - as compared to inorganic mercury compounds of which only 2% are absorbed - rendering it far more toxic (Ref. 45). Even more dangerous is its attack on unborn fetuses. A mother can consume levels of methyl mercury which do not appear to effect her directly, but are concentrated (apparently) in the fetus and can lead to brain damage and blindness in the child.

There are two major effects of mercury in fish and shellfish: (1) toxicity and (2) bioaccumulation. As has been mentioned above in the section on paths in the environment, many species concentrate methyl mercury - the maximum concentration factor being 27,800, as reported by McKim for brook trout (Ref. 21). The trout involved contained greater than 0.5 µg/gm mercury - in fish which were raised in waters containing from 0.018 to 0.030 µg/ℓ - in 20-48 weeks.

Toxic symptoms have been reported for brook trout raised in water containing 2.9 µg/ℓ, although no effects were noticed at 0.29 µg/ℓ. Flathead minnows are somewhat more sensitive, since all in a test group died after 3 mos at 0.41 µg/ℓ, 92% died at 0.23 µg/ℓ and spawning was inhibited at 0.12 µg/ℓ. No toxic effects were noted at 0.07 µg/ℓ. Daphia magna suffered impaired growth at 0.04 µg/ℓ (Ref.21). Mercury compounds also have been reported to inhibit growth of freshwater algae (Ref. 46).

Marine species have been effected at 1.0 µg/ℓ and accumulation is roughly similar (Ref. 21) to accumulation reported for freshwater species.

d. Controls of Mercury in Water

(1) Process Controls. Mercury may be removed from process waters by a number of techniques. These include precipitation with sulfide (S^{2-}), by ion exchange or sorption on wool, activated carbon, and chemically modified cellulose derivatives. (Refs. 47, 48).

(2) Regulatory Controls The standards and water quality criteria for mercury are extremely stringent, as can be seen in Table 5. The level of 2 µg/ℓ for drinking water and domestic water supplies will permit only 4 µg Hg in the estimated daily intake (Ref. 46). The recommended upper limit for total daily intake is 30 µg/70 kg/day which provides a safety factor of 10 for adults and slightly less for children based on a lowest toxic effects level of 300 µg/70 kg/day.

The level of 0.05 µg/ℓ for freshwater aquatic life and wildlife was determined by dividing the FDA limit of 500 µg/ℓ by a concentration factor of 10,000. This should provide adequate protection for the freshwater species (except Daphnia magna) and the consumers thereof. (The limit of 10 µg/ℓ for livestock water is also to protect consumers). The marine aquatic life level is 1/10 the lowest reported concentration to effect marine species. The FDA value of 500 µg/kg of fish would permit the consumption of 60 grams of fish per day which is a fairly low level of consumption for some low income families whose main protein source is fish.

Table 5. Standards and water quality criteria for mercury in the aqueous ecosystem

Standard or Criterion	Level (µg/ℓ)	Ref.
Nation Interim Primary Drinking Water Standard	2	21
Water Quality Criterion - Domestic Water Supplies	2	21
Water Quality Criterion - Freshwater Aquatic Life and Wildlife	0.05	21
Water Quality Criterion Marine Aquatic Life	0.10	21
Mercury in Edible Fish (FDA)	0.5 mg/kg	21
Agricultural Uses - Livestock	10	43

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CONTENTS

III. MONITORING SYSTEMS

A system for monitoring metallic pollutants involves the entire process used in determining the amount of a metal or metal species present in the aquatic environment. The process may include many steps from the initial decision to proceed: sampling, sample preservation, pre-measurement treatment, measurement, sample disposal, data analysis and reporting. Before deciding upon a monitoring system the analyst must determine:

a) the metals which must be detected, and whether the analyses are for total, dissolved or particulate species
b) the frequency and number of analyses to be performed
c) the required sensitivity
d) the accuracy necessary
e) any additional information sought (oxidation state, coordination, etc).

Additional considerations are the availability of instrumentation, and the number and skill of the lab personnel. Once the requirements have been established, one must choose the most suitable among the types of systems available.

A. Systems Approaches

The analyst setting up a system to determine metals in water has a choice of several types of systems. He must determine whether he will use "direct" or "surrogate" analysis. "Direct" analysis implies that the analytical steps from sampling through data reporting are performed on the body of water in question or samples of that body. In "surrogate" analyses the analytical procedure is applied to a substance which in some way represents the body of water, but is not the water itself.

The analyst must decide whether he will use continuous or intermittent monitoring and if the analysis will be performed at the site or in a laboratory. He must decide if the operations will be performed and controlled manually or if some form of automation will be used.

1. Direct Versus Surrogate Analysis

Systems for monitoring metals usually involve direct analysis, often chemical or instrumental, of the water in question for its metallic constitutents. The instruments and systems used for analysis of metal in water are discussed to a great extent in the remainder of the section. (Metals-in-Water: IV, Instrumentation.)

Recently, there has been an emphasis placed upon the use of "surrogates;" that is, analyzing other substances such as sediments from the body of water in question, or shellfish living in it, which have been affected by metallic pollutants therefore providing an indication of the amount of the metal present in the water. Several surrogate systems have been suggested.

One system involves the analysis of different species of biota for the presence of metals which they have accumulated (Refs.1-9). The mussel has been suggested as a particularly advantageous species as it is sedentary, ubiquitous, and easily obtained, and is a known concentrator of heavy metals. The literature contains numerous references to metal concentrations in mussels all over the world - lead and mercury in Port Philip Bay mussels (Refs. 10,11), mercury in Canadian, Californian and European mussels (Refs. 12-15), and so on. Many other species have also been suggested, such as sand flatheads (Ref. 2), oysters, clams and their shells (Refs. 16-20), as have various forms of vegetation (Refs. 3, 21), mammals (Refs. 4, 9, 22, 23), fish (Refs. 24-28) and organisms (Refs. 29-31). The references mentioned here are only a sampling of the literature on surrogate species available. Interested readers may use them as an introduction to the literature.

The advantage of using the surrogate for analysis is that it allows the monitoring laboratory to determine chronic concentrations which are present. The biological systems are far less affected by daily fluctuations of low metal levels, but do reflect chronic levels of metals polluting the water around them; in effect they serve as integrating devices.

The study of the effect of pollutants on species in the water under consideration has also been suggested (Refs. 5,6) but systems to do this are less well developed. Sublethal physical effects such as incidence of tumors, birth defects, rate of respiration, lowering of growth rates, and lowering of birth rate may be indicative of the particular concentration or combinations of concentrations of metallic pollutants present. Behavior modification, such as avoidance of a certain area, or sluggish movement, may also allow the analyst to predict the amount of pollutant present. So far the data necessary to make such predictions are not extensive enough for practical usage.

A major research effort is under way using the presence of metallic pollutants in sediments as a monitoring system throughout the world (Refs. 7, 8, 32, 33, 34) - from Michigan to Egypt. Sedimentation studies serve a dual purpose – the results serve as a pollution monitor and provide information regarding the sediments as a possible source of the metallic species. Careful analysis of sediment layers allows the analyst to develop a history of the metallic pollution of an area.

Analysis of the water in question, i.e. direct analysis, allows the monitoring analyst to measure quickly and directly the variable he most often wants to know – the concentration of the metallic pollutant – be it dissolved, suspended or total. A disadvantage to direct measurement is that unless the water supply is continuously monitored, (see Section 2, Continuous vs Sampled Monitoring) a known, regular monitoring schedule may produce biased results. "Surrogate" systems, on the other hand, are by nature continuous integrating monitors, allowing the analyst to study the long term effects of the concentrations of metals which are present in the water. Determination of concentrations from surrogates can present a complex problem, introducing a variety of unknowns such as concentration factors or dose-response relationships. These unknowns add a greater degree of uncertainty to an already complex situation.

2. Continuous Versus Intermittent Monitoring

When data taking is not interrupted it is defined as being continuous. If data are recorded only periodically it is referred to as intermittent. For example, an uninterrupted chart record of temperature is continuous, a reading every hour is intermittent.

Metal analyses are rarely performed continuously; the instrumentation, personnel and data analysis requirements would be exceedingly costly as compared to the benefits of such monitoring.

3. Laboratory Versus Field Analysis

Laboratory monitoring systems involve sampling on-site (either taking a "grab" sample or separating a stream of water from the body being monitored), sample preservation, transportation to the lab and analysis there. Field monitoring systems allow for analysis on-site, either continuous or intermittent.

Field systems are advantageous in that they require little if any sample preservation and only a short time lapse between sampling and analysis; this protects the sample from decomposition, loss through adsorption onto the container walls, and contamination through leaching from container walls.

Field monitors to be effective must be designed to operate under environmental conditions which may be expected in the field. Laboratory systems allow for more complex systems, often more elaborate instrumentation, and more controlled conditions for both the sample and the analysis.

4. Manual Versus Computerized or Automated Systems

A "manual" analytical lab involves an analyst who obtains samples of the water to be analyzed (or sets up instrumentation for continuous monitoring if that is the chosen system), performs the pretreatment steps, the measurements, reduces the data and reports the results to the appropriate authority.

Computerized systems (or hybrid systems) use a processor to control one or more of the steps enumerated above. The Central Laboratory of the United States Geological Survey, Denver, uses a computer to determine work schedules, process data and generate reports in order to handle the 40,000 samples it processes each year (Ref. 35). Almost any system or part of a system can be automated. Currently, the ASTM (American Society for Testing Materials) Committee E-31 is working on a set of standards which a laboratory will be able to use to set up computerized systems (Ref. 36).

Most laboratories currently use minicomputers or calculators (built-in or desktop) for data processing, and many instrument manufacturers are including microprocessors in their instruments automatically (Ref. 37). A dedicated or connected microprocessor allows the instrument to perform many functions, thereby introducing greater reliability by removing human variability. Many instruments, notably the atomic absorption spectrometers, have a calculator (microprocessor) available as an accessory or an integral part of the instrument system. This, of course, simplifies data analysis since results can be printed out for the analyst, or punched as data or connected to another computer system for further analysis. It not only reduces the possibility of human error in calculation, or data reporting, but is also much faster. Figure 1 shows the variety of outputs available from a single water quality monitoring instrument.

In fact, inclusion of a microprocessor in instrumentation for determining metals in water is no longer the exception but is becoming the rule. The particular system which has been integrated into or is available as an accessory for an instrument is discussed in the instrument notes (Section IV). The reader is also referred to the "Data Analysis" section of the Introduction to this volume (to be published Winter, 1979).

B. Steps in a Monitoring System as Applied to Metals in Water

1. Direct Monitoring

There are four major steps in determining the concentration of metals in water: sampling (including sample preservation and

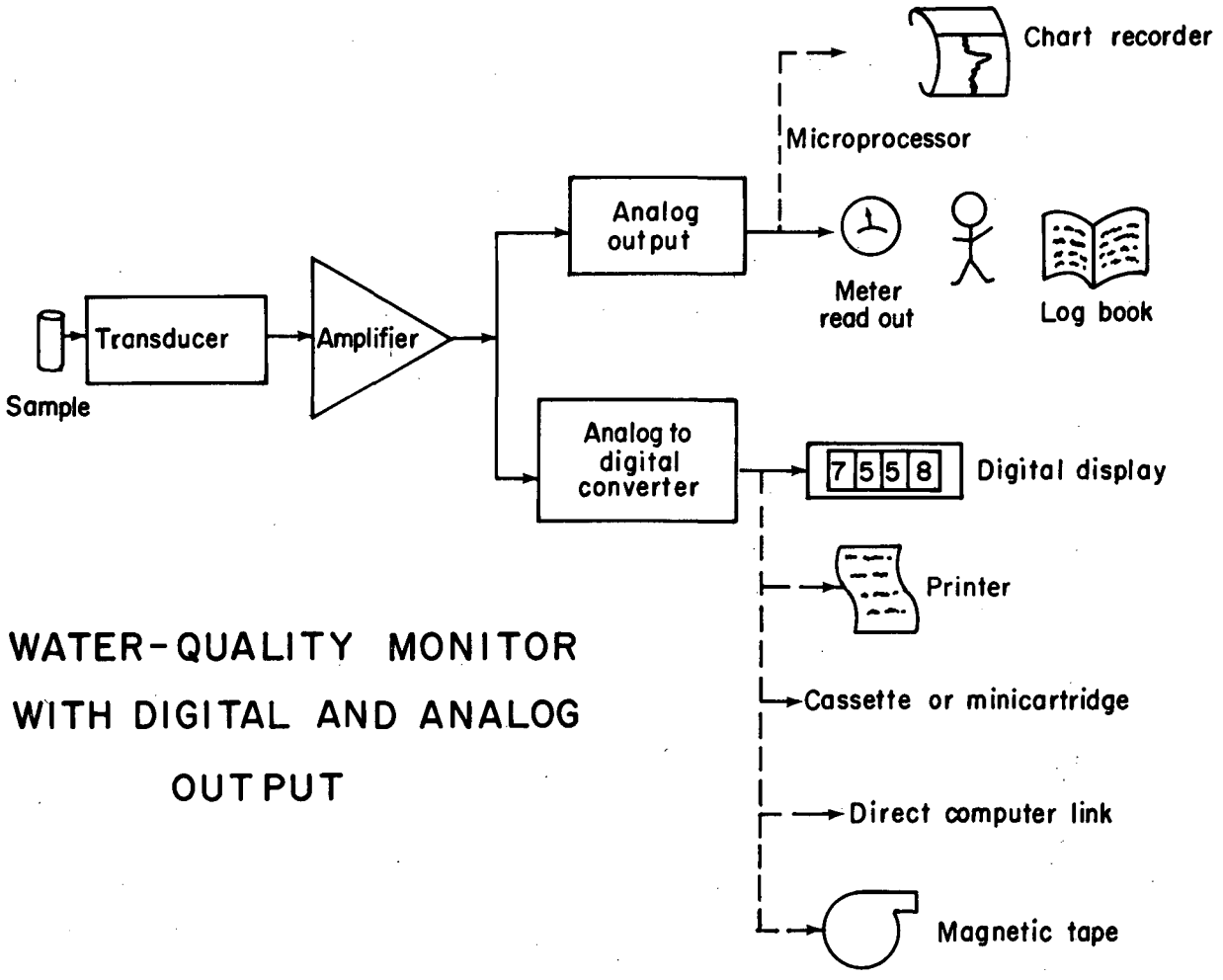

Fig. 1. Water quality monitor with output available from many digital and analog instruments (adapted from Ref. 38). (XBL 7810-11544)

preparation), calibration, measurement, and data analysis. For a discussion of calibration and data analysis, see the Introduction to this volume. (The discussion on sampling is being prepared). These steps as they apply to metals-in-water are discussed below. If the technique is applicable only to a certain metal or instrument, it will be found in Section IV, Instrumentation Techniques, or II, considerations involving Specific Metals in Water.

a. Sampling. Careful sample collection, preservation and preparation is essential for analysis of metals in water. Sampling for analysis of metals in water is difficult because of such factors as low concentrations of the metal in question and difficulty of obtaining a representative sample. Samples should be large enough to allow detection of metals present. They should be carefully identified. The USGS suggests that for surface water samples the identification should include:

- Precise location of sampling point: name of water body, location of station or site, point of collection.
- Date and time of collection
- Depth of collection (guage height and water discharge)
- Temperature of the water
- Name of collector
- Weather and other natural or man-made factors that may assist in interpretation.

For ground water, they suggest including in addition to the above information:

- Depth, diameter, and normal yield of well
- Length of casing and positioning of screens
- Water bearing formation
- Water level
- Appearance of water at time of collection.

The analyst must be careful to obtain a representative sample from the body of water in question. For most monitoring of this type, there are at least two types of samples necessary: end-of-pipe samples to determine discharge concentrations and samples representing ambient concentrations.

Samples to determine end-of-pipe concentration must be taken frequently enough to be representative of the total outflow of a plant.

Samples which are to represent the ambient concentrations of metals in a body of water must be even more carefully considered. In any body of water, the sampling should be far enough away from the point of discharge and mixing zone so that it is representative of the ambient concentration. The analyst must be aware of current fluctuations within the body of water: both regular currents, such as tidal changes, and irregular currents, such as rain runoff or wind-induced current. The analyst must be aware of possible bias introduced into monitoring data by cyclical fluctuations (Ref. 39). These can be natural fluctuations such as tidal patterns or biological cycles, or they can be cycles involved with industrial processes.

Since metallic pollutants can be dissolved, suspended or actually sedimental, the analyst must decide upon the optimum depth for taking the sample. The analyst must also be aware of variations in the sediment-water mixing region so that spurious solids are not introduced in the portions taken.

Sample storage is an important concern. Containers must be meticulously cleaned; procedures to do so can take over two weeks (Ref. 40). The container itself should be constructed of material which does not permit adsorption of metal ions from the sample on to the container walls. Standard Methods (Ref. 41) suggests glass, polyethylene or teflon-lined containers--although even these have been found to attract metals from solutions of very low (nanogram/ℓ) concentration (Ref. 52). It is also possible for the sample solution to leach impurities from the container walls, so the construction material must be chosen carefully, and the possibility of leached metal ions should be remembered at all times (Ref. 40). If the sample is to be filtered, filtration should take place as soon as possible to prevent settling out, further precipitation or redissolution of the metals in the sample.

The possibility of sample contamination is so great in trace metal analysis that a "clean room" (a room carefully constructed and ventilated to prevent dust and other contamination from the room itself) is advisable. A dust particle can introduce subnanogram levels of impurities, which can introduce serious errors if one is analyzing ultratrace quantities of metals.

The EPA's "Methods for Chemical Analysis of Water and Waste Water" recommends the addition of hydrochloric or nitric acid to a pH of 3.5 as a preservative. The importance of preservation is illustrated by the results of a study of mercury loss from creek water (Ref. 43) during storage. Losses as high as 60% were reported from unpreserved samples after only minutes of storage under standard ambient laboratory conditions in a polyethylene bottle. However, unless care is taken, strong acids used for preservatives can introduce impurities to the sample by leaching metals from container walls or by dissolving solids which might be collected on a filter (Ref. 44).

Sample preparation depends upon the analytical technique which is to be used and the metals which are the suspected pollutants. It may be necessary to concentrate or dilute a sample, to filter it, to adjust the pH or ionic strength, to remove possible interfering ions or chelates, or to convert the metal ion to a form more amenable to measurement.

Concentration techniques can range from simple evaporation to use of ion exchange resins (Ref. 41), and solvent or chelate extraction techniques (Refs. 41, 45, 46). Various chelates such as dithiocarbates, substituted phenanthrolines and amines are often used as extracting chelates. Table 3 in Section IV shows various metals and chelating agents commonly used for atomic absorption. Copper, gold or silver grids and 0.45μm membrane filters are recommended for collection and thereby concentration of suspended solids for analysis. It is important to recognize the possibility of dissolved metal adsorbing to the filter. Silver wire is used for the collection or concentration of soluble mercury compounds, but not for suspended mercury (Ref. 47). Many of the same techniques used for concentration, notably ion exchange and extraction, can also be used to remove interfering ions.

An important consideration is whether the measurement taken is to determine the dissolved, suspended or total metals present. For convenience and regulatory purposes dissolved metals have been defined as those which will

pass through a 0.45μm filter, even though a solution such as those containing iron oxides, which has been filtered using such a filter still scatters light and appears to have particulates suspended in it. Since toxicity has been associated with all three states (dissolved, suspended or total), it is frequently necessary to determine more than one.

Sample filtration is therefore an important step in water analysis. As in any additional analytical procedure the possibility of introducing errors is high. There is a possibility of smaller particles being trapped on the filter or of larger particles being eroded and passing through or even of large particles passing through a flaw in the filter. In an open filtration system the possibility of dust contamination is extremely high. It is also possible that impurities might be leached from the filter or the filtration apparatus.

Other sample preparation techniques can involve converting from organic to inorganic forms of a metal as is done with arsenic (Ref. 41) or conversion to a particular oxidation state (total chromium is determined by initially converting all Cr(III) or Cr(VI)). Some metals are converted to more volatile forms to allow use of gas chromatography (Ref. 48). Biological or highly chelated forms of metals can be treated with perchloric acid to allow more rapid oxidation in graphite furnaces prior to measurement using atomic absorption (Ref. 49). Sample preparation techniques can, of course, introduce impurities or interfere with a measurement so the analyst should try to keep this part of the procedure to a minimum.

A further problem for metal analyses is "speciation". This involves preserving intact and then separating the various species of metals present in a solution. For example (as is mentioned above) mercury can be present in a body of water in many oxidation states - mercury (0), mercury (I) or mercury (II); it can be inorganic or organic. Although currently most monitoring which is performed to fulfill government regulations does not require the identification of the forms of mercury present in the water sample, most analysts recognize that certain mercury species are more dangerous to man than others, so many labs are already monitoring the ratios of organic to inorganic mercury, conversion rates between the forms and so on.

Several methods of analysis and separation are used for speciation; most common are chromatographic techniques and anodic stripping voltammetry (discussed in Section IVC - Developing and On-Going Techniques). Two chromatographic techniques are currently used for speciation of metal compounds: gas chromatographic (GC) procedures, i.e., GC followed by a variety of detection techniques including GC-MS, and high performance liquid chromatography (HPLC) (Refs. 51, 52) and thin layer chromatography (Ref. 52). ESCA, electron specroscopy for chemical analysis, can also be applied (Ref. 50), but is only rarely used as a quantitative tool for trace water analysis.

Descriptions of the detailed operations of sampling currently recommended for use by analysis laboratories are found in Standard Methods, 14th Ed. (Ref. 41) and Methods for Chemical Analysis of Water and Wastes (Ref. 53). The subject is also discussed in McKee and Wolf, (Ref. 54), Mancy (Ref. 55) and in Water Quality Criteria (Ref. 56).

b. Calibration and Standardization. Calibration and standardization is essential to all facets of monitoring systems used for determining metals in water. Before calibrating the system it is necessary to determine the probable sources of error in an analysis, decide whether the error is likely to be random or systematic, and then calibrate or standarize the system to remove or minimize these possible errors.

The instruments used for measuring quantities of metals, particularly trace amounts, must be calibrated regularly checking against a primary standard. This is done by making measurements of known substances or when this is not possible an electrical signal is used to simulate the transducer output, thereby standardizing the output. For example, ultraviolet spectrophotometers may be calibrated for wavelength by the measurement of the known emission spectrum of an elemental discharge lamp (often mercury). Calibration for the intensity of the signal of most absorption spectrometers is usually achieved by measuring the absorption of various solutions of known concentration and then plotting a calibration curve. Frequent calibration of both wavelength and intensity of absorption is necessary to insure the instrument's integrity. A study performed in the early days of spectroscopy revealed that out of ten spectrometers tested, only five were working properly, three were defective and two were inaccurate (Ref. 57).

It has been determined that in any water analysis, particularly one involved in determining trace substances such as metals, major sources of error are in the premeasurement steps: sampling, preservation, and pretreatment. Thus it is necessary to standardize the entire system, that is, determine and assure its accuracy and precision. Two methods are commonly used, analysis of standard solutions and analysis of spiked solutions (Ref. 58, 59).

Table 1. Results of an interlaboratory study conducted by the Quality Assurance and Laboratory Evaluation Branch of Methods Development and Quality Assurance Research Laboratory (MDQARL). (Adapted from Ref. 53).

Number of Labs	True value µg/ℓ Manganese	Mean value µg/ℓ Manganese	Standard dev. µg/ℓ	Accuracy as % bias
77	426	432	70	1.5
78	469	474	97	1.2
71	84	86	26	2.1
70	106	104	31	-2.1
55	11	21	27	93
55	17	21	20	22

The six test solutions contained Al, Cd, Cr, Fe, Mn, Pb, and Zn in natural water.

• The Use of Standard Solutions (Ref. 58). The EPA manual for quality assurance suggests the use of eight standards throughout the concentration range expected and multiple determination. Standard solutions containing a variety of metal ions (including interfering ions) commonly present in water can be obtained from many commercial sources (See Introduction, this volume, Calibration, Table 2) and in some cases from the EPA Analytical Q.C. Laboratory, National Environmental Research Center, Cincinnati, Ohio. A water analysis lab can then analyze these solutions using the entire analytical system to establish the accuracy and precision of their methods. The results of a laboratory comparison for the recommended method for manganese is shown in Table 1. The test involved analysis of six "unknown" solutions containing aluminum, cadmium, chromium, iron, manganese, lead, and zinc in natural water. The results indicate that for a certain range of concentrations of manganese the laboratory system produced meaningful results and a mean concentration close to the true value, but that in many cases there was a high standard deviation, in one case, 128%.

• Method of Standard Additions. For standardization of the accuracy of the method employed, using the actual water to be analyzed, the laboratory may wish to use the method of standard additions. To determine the accuracy of the system for determining the accuracy of a particular analyte metal, an amount of that metal should be added to a series of solutions whose concentrations have already been determined. If, for example, one has determined the concentrations of chromium in two samples as 0.06 µg/ℓ and 0.82 µg/ℓ, then an additional amount of Cr is added and the concentration redetermined. The second concentration is then divided by the calculated concentration. The EPA recommends adding a sufficient amount to double the lower concentration and to raise the chromium concentration to within 75% of the recommended upper limit for the procedure (Ref. 58).

A general discussion of calibration methods is included in the Introduction to this volume. Calibration for atomic absorption and UV-vis spectroscopy is discussed in greater detail in Section IVA and IVB.

2. Surrogate Methods

As in "direct" monitoring procedures, there are four major steps in any system: sampling, calibration and standardization, measurement, and data analysis and reporting.

Sampling sample pretreatment and calibration procedures for surrogate analysis are substantially different than those for water. Since surrogate analysis is not a routine monitoring technique these procedures have been considered beyond the scope of this text, but the interested reader may consult the BIO volume of this series for consideration of biological sampling, such as freeze drying, and to the references which cover biological surrogate techniques for an introduction to the literature. General Techniques for Bioassay can be found in Standard Methods, Ref. 41. For sediment studies, the reader is referred to Refs. 7 and 8.

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CONTENTS

IV. METALS-IN-WATER INSTRUMENTATION

Prior to 1940, most metals were analyzed using volumetric or gravimetric procedures. Since then, instrumental methods have achieved greater prominence because of increased sensitivity, selectivity, capability of simultaneous analysis, amenability to automation with resultant lower cost per sample, and decrease in sample processing time.

Determination of the concentration of metals in a body of water can usually be accomplished by analyzing the water directly rather than observing the effects upon species in the water. The measurement can be made in situ, on a continuous but separated stream, or by analysis of grab samples. The determination may be performed in the field or in an analytical lab. Direct measurement performed on the water itself is currently the most common method of determining concentrations of metals in water, and the instrumentation used for performing these analyses is the topic of most of this section of Metals in Water.

The metal content of water may also be determined qualitatively and semiquantitatively by analyzing "surrogate" species. This topic is currently beyond the scope of this volume.

Table 1. Detection Limits of Selected Instrumental Methods for Monitoring Metals in Water.[a]

Instrumental Method	Minimum Detection Limits µg/ℓ[b]
Polarography, linear	100
Polarography, square wave	10
Sweep voltammetry	10
Molecular absorption	1
Spark source mass spectrometry	1
Polarography, pulse	1
Atomic absorption, flame	1
X-ray fluorescence	1
Atomic emission, flame	0.01
Atomic emission, plasma	0.01
Atomic fluorescence	0.01
Molecular luminescence	0.001[c]
Neutron activation	0.001[c]
Atomic absorption	0.001
Anodic stripping voltammetry	0.001

[a] For any method, the detection limit will vary according to the particular metal.

[b] Order of magnitude.

[c] For these methods, the sample must be taken to dryness or preconcentrated, so that any detection limit is very relative. These values represent minimum detection limits which have actually been reported.

Table 2. Techniques for Determining Metals in Water, According to 40 CFR 136 (Ref. 1).

Metal	Symbol	Form Monitored[a]		40 CFR 136 Description of the Recommended Instrumental Technique.[b]	Recommended Instrumental Technique from the Methods Manuals				
		Total	Dissolved		Standard Methods[c]	EPA Manual[d]	ASTM[e]	USGS[f]	Other[g]
Aluminum	Al			Digestion → AA, colorimetric	Both	AA	—	AA	—
Antimony	Sb			Digestion → AA	—	AA	—	—	—
Arsenic	As			Digestion → AA, colorimetric	Both	Both	—	Both	—
Barium	Ba			Digestion → AA	AA	AA	—	AA	—
Beryllium	Be			Digestion → AA, colorimetric	Both	AA	—	AA	—
Boron	B			Colorimetric	Col.	Col.	—	—	—
Cadmium	Cd			Digestion → AA, colorimetric	Both	AA	AA	AA	AA
Calcium	Ca			Digestion → AA	AA	AA	AA	AA	
Chromium	Cr			Digestion → AA	AA	AA	AA	AA	AA
Chromium(VI)	Cr(VI)			Extraction→ AA, colorimetric	Col.	Both	—	Both	—
Cobalt	Co			Digestion → AA	AA	AA	AA	AA	AA
Copper	Cu			Digestion → AA, colorimetric	Both	AA	Both	AA	AA
Gold	Au		No	Aqua regia → AA	—	EPA[h]	—	—	—
Iridium	Ir		No	Aqua regia → AA	—	EPA	—	—	—
Iron	Fe			Digestion → AA, colorimetric	Both	AA	Both	AA	AA
Lead	Pb			Digestion → AA, colorimetric	Both	AA	AA	AA	AA
Magnesium	Mg			Digestion → AA	AA	AA	AA	AA	AA
Manganese	Mn			Digestion → AA, colorimetric(2)	All	AA	AA	AA	AA
Mercury	Hg			Flameless AA	AA	AA	AA	AA	—
Molybdenum	Mo			Digestion → AA	—	AA	AA	—	—
Nickel	Ni			Digestion → AA, colorimetric	Both	AA	AA	AA	—
Osmium	Os		No	Aqua regia →AA	—	EPA	—	—	—
Palladium	Pd		No	Aqua regia →AA	—	EPA	—	—	—
Platinum	Pt		No	Aqua regia →AA	—	EPA	—	—	—
Potassium	K			Digestion → AA, colorimetric, or Flame Photometric	F.Ph./Col.	AA	F.Ph.	AA	AA
Rhodium	Rh		No	Aqua regia →AA	—	EPA	—	—	—
Ruthenium	Ru		No	Aqua regia →AA	—	EPA	—	—	—
Selenium	Se			Digestion → AA	AA	AA	—	—	—
Silica	SiO_2	No		0.45 μ Filtration →colorimetric	Col.	Col.	Col.	Col.	—
Silver	Ag			Digestion → AA, colorimetric	Both	AA	—	AA	AA
Sodium	Na			Digestion → AA, flame photometric	Fl.Ph.	AA	Fl.Ph.	AA	AA
Thallium	Tl			Digestion → AA	—	AA	—	—	—
Tin	Sn			Digestion → AA	—	AA	—	—	—
Titanium	Ti			Digestion → AA	—	AA	—	—	—
Vanadium	V			Digestion → AA, colorimetric	Both	AA	Col.	Col.	Col.
Zinc	Zn			Digestion → AA, colorimetric	Both	AA	AA	AA	AA

Footnotes for Table 2

a. If there is a blank in either of these columns then there are recommended techniques for determining both the total metal and the dissolved metal. The dissolved metal is defined as the quantity of metal which passes through a 0.45μ filter. A "no" in either column means that this variable is not to be determined, or no method is recommended for its determination.

b. Only instrumental techniques are indicated. "Digestion → AA, colorimetric" is short form for "Digestion followed by atomic absorption, or by colorimetric." These appeared in Federal Register, 41, 52780-52786 (12-1-76) and were amended in Fed. Reg., 42, 3306 (1-18-77).

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g. References for "Other" found in Fed. Reg., 41, 52780 (12-1-76).

h. "EPA" refers to a special procedure supplied by the EPA.

Many instrumental techniques are available for measuring the metal content of water. Many of them are summarized in order of increasing sensitivity in Table 1. In principle, all these methods can be used on a particular sample by bringing the metal concentration within the sensitivity limits by appropriate pretreatment such as dilution, concentration or precipitation.

For determination of metals in water for both analytical and monitoring purposes, two instrumental methods, atomic absorption (AA) and UV-visible absorption, (colorimetry) are recommended by the Environmental Protection Agency in "Guidelines Establishing Test Procedures for the Analysis of Pollutants" (40 CFR 136, Ref. 1). These "standard methods" are those which are legally acceptable for monitoring labs under the jurisdiction of the EPA. Alternative methods can be used if approved by Methods Development and Quality Assurance Research Lab., Cincinnati, OH. (MDQARL) or the regional EPA administrator. The procedure for having alternative methods approved is outlined in the Introduction to this volume. The "Guidelines" refer to techniques described in Refs. 2-8. The two manuals which will most commonly be referred to are Ref. 2, the EPA Manual, and Ref. 3, Standard Methods, 14th ed.

Table 2 is a listing of the metals for which regulations exist and the Standard Methods suggested for their analysis. The recommended techniques include flame and flameless atomic absorption, and colorimetry. Included in Table 3 are such important experimental parameters as the suggested gas combinations for flame AA, and the wavelength at which the measurement is made for flame or flameless AA. The suggested complexing agent and measurement wavelength are listed for the colorimetric techniques. Atomic absorption techniques, both flame and flameless, are acceptable for all "metals" except boron and silica. In the past, flame methods have been used more frequently. (As was explained in the Introduction to the Metals-in-Water Section, several elements such as silicon and boron and their compounds, which are not generally considered metals, but are often determined using UV-vis techniques and are therefore considered in the Metals-in-Water section). Flameless techniques are achieving greater prominence and it is understood that the 15th edition of Standard Methods will include a broader discussion of these techniques (Ref. 9).

Colorimetric and molecular spectrophotometric techniques are acceptable for many metals. Flame photometric and automated tech-

Table 3. Selected Experimental Parameters Recommended by 40 CFR 136 (Ref. 1).

	Atomic Absorption or Flame Photometric, Experimental Conditions			Colorimetric, Experimental Conditions	
Metal	Fuel	Oxidant/ Support	Wavelength (nm)	Complexing Agent	Wavelength (nm)
Aluminum	C_2H_2	N_2O	309.3	Eriochrome Cyanine R	535
Antimony	C_2H_2	Air	217.6	—	—
Arsenic	H_2	Argon	193.7	Silver Dithiocarbamate	535
Barium	C_2H_2	N_2O	553.6	—	—
Beryllium	C_2H_2	N_2O	234.9	Aluminon	515.5
Boron	—	—	—	Curcumin	540
Cadmium	C_2H_2	Air	228.8	Dithizone	515
Calcium	C_2H_2	Air	422.7	—	—
Chromium	C_2H_2	Air	357.9	Diphenylcarbazide	540
Chromium(VI)	C_2H_2	Air	357.9	Diphenylcarbazide	540
Cobalt	C_2H_2	Air	240.7	—	—
Copper	C_2H_2	Air	324.7	Neocuproine	457
Gold	C_2H_2	Air	242.8	—	—
Iridium	C_2H_2	Air	264.0	—	—
Iron	C_2H_2	Air	248.3	Phenanthroline	510
Lead	C_2H_2	Air	283.3	Dithizone	520
Magnesium	C_2H_2	Air	285.2	—	—
Manganese	C_2H_2	Air	279.5	Persulfate/Periodate	525/525
Mercury	—	—	253.7	—	—
Molybdenum	C_2H_2	N_2O	313.3	—	—
Nickel	C_2H_2	Air	232.0	Heptoxime	445
Osmium	C_2H_2	N_2O	290.9	—	—
Palladium	C_2H_2	Air	247.6	—	—
Platinum	C_2H_2	Air	265.9	—	—
Potassium	C_2H_2	Air	766.5/768	Cobaltinitrite	425
Rhodium	C_2H_2	Air	343.5	—	—
Ruthenium	C_2H_2	Air	349.9	—	—
Selenium	H_2	Argon	196.0	—	—
Silica	—	—	—	Molybdosilicate	410
Silver	C_2H_2	Air	328.1	Dithizone	620
Sodium	C_2H_2	Air	589.6/589	—	—
Thallium	C_2H_2	Air	276.8	—	—
Tin	C_2H_2	Air	286.3	—	—
Titanium	C_2H_2	N_2O	365.3	—	—
Vanadium	C_2H_2	N_2O	318.4	Gallic Acid	415
Zinc	C_2H_2	Air	213.9	Dithizone	535

niques are suggested for only a few metals: potassium, sodium, calcium, and hardness ($[Ca^{++}] + [Mg^{++}]$).

This section (IV) will discuss in detail and provide instrument notes for the instrumentation used in the standard methods: atomic spectroscopy (IVA) and UV-visible absorption (colorimetric) (IVB) techniques. Principles of operation and a brief description of the experimental techniques will be provided for the techniques in Section C, Developing and On-Going Techniques. This section provides information on neutron activation, x-ray fluorescence, and electrochemical techniques. For ease in finding specific material, an outline of each of the five major divisions will be presented at the beginning of each section.

Many texts offer good discussions of the instrumental techniques used for determining metals in water. The interested reader is referred to Refs. 10-13.

CONTENTS

A. Atomic Spectroscopy (Refs. 14-19)

When a metal atom in the gas phase is exposed to an energy source, its electrons may be excited (raised to higher energy levels):

$$M + \text{energy} \rightarrow M^*.$$

Excitations may result from a variety of mechanisms - interactions with photons, or collisions with electrons or other atoms.

An excited metal atom can then return to a lower state by a variety of processes, both luminescent and radiationless:

$$M^* \rightarrow M + \text{energy } (h\nu \text{ or collisional})$$

h = Planck's Constant

ν = frequency of light.

If the excitation or decay mechanism involves absorption or emission of photons by the metal atom, then the frequency of the absorbed or emitted light is characteristic of the particular metal. The amount of the light absorbed or emitted is proportional to the number of atoms being excited.

Three optical atomic spectroscopic techniques have been developed using these principles: atomic emission (AES), atomic absorption (AAS), and atomic fluorescence (AFS) spectroscopy. The three techniques are intimately related. For atomic emission spectrometry the metal or metal ion is atomized and excited in a flame or flameless energy source (AC spark, DC arc or RF plasma).

During atomization, the number of atoms, N_j, excited to any energy state, j, is given by;

$$N_j = No(P_j/P_o)\ \exp(-E_j/KT)$$

where No is the number of atoms in the ground state, P_j and P_o are the statistical weights of the excited and ground states, and T is the absolute temperature of the vapor. Walsh (Ref. 14) has calculated the ratio N_j/No for the most populated energy states of several elements in the temperature range encountered in atomization systems (2000°K - 4000°K), and found that the vast majority of atoms of most species are at the ground state.

Atomic absorption and fluorescence spectrometry involve atomization in a flame or flameless device, then excitation using an outside light source such as a hollow cathode lamp, electrodeless discharge lamp or a continuum source. Figure 1 illustrates the basic apparatus used for atomic emission, atomic absorption, and atomic fluorescence spectroscopy.

Atomic absorption (AAS) is based on the fact that the ground state atoms will absorb radiation of a frequency specific to a particular atomic structure. The radiation is supplied by a light source constructed of the metal of interest.

Atomic fluorescence (AFS) is similar to atomic absorption in that an external light source is required to excite the populated ground state atoms. The difference is that the resulting fluorescence of the excited atoms is measured rather than the absorbance of the light source. The three techniques are discussed in greater detail in the next sections: IV-A-1, Atomic Absorption; IV-A-2 Atomic Emission; IV-A-3 Atomic Fluorescence; and IV-A-4 Atomic Spectrometry - A Summary.

1. Atomic Absorption Spectroscopy

a. Principles of Operation. An atomic absorption spectrophotometer measures the light transmitted through a metal vapor. If the energy of the light transmitted through the vapor (the incident beam) corresponds to

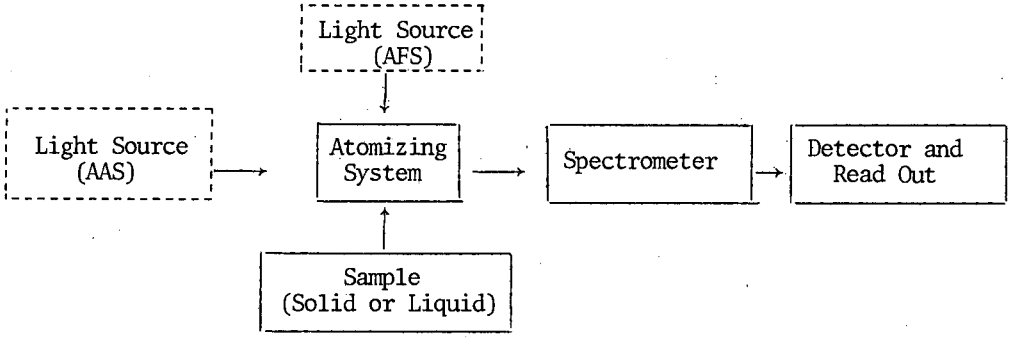


Fig. 1. Basic apparatus for analytical atomic spectroscopy (reproduced from Kirkbright and Sargent Ref. 15, with permission by Academic Press Inc, (London) Ltd., copyright 1974). (Note: There is no external excitation source for AES).

the difference in energy levels in the metal atom, then light may be absorbed:

$$M \xrightarrow{h\nu} M^* \quad \text{if}$$

$$\nu_{M-M^*} = \frac{E_{M^*} - E_M}{h} \qquad (1)$$

E = Energy of an electronic state
M = Metal in the ground state
M* = Metal in an excited state

Since the energy of light absorbed corresponds to the known energy level separations of metals, it is theoretically possible to perform a qualitative analysis on a solution containing unknown metals. Theoretically, the intensity of the absorbed light at a single wavelength is related to the number of metal atoms present by the relation:

$$I = I_0 e^{-k_\nu l} \qquad (2)$$

I = Intensity of transmitted beam
I_0 = Intensity of incident beam
k_ν = Absorption coefficient (per unit length) at the frequency, M-M*
l = Pathlength through the material to be analyzed (absorption cell)

which allows the analyst to use AAS for quantitative determination. The absorption coefficient, k_ν, is related to the transition probability between the states involved, the concentration of metal atoms in the absorption cell and the frequency of the incident beam by a complex integral expression. If the light of the excitation source has a broad range or continuum of frequencies, the theoretical relationship between the number of atoms in the cell and the intensity of the transmitted beam can be solved only by making approximations which can introduce significant errors. Of course, the measurement of k_ν requires the use of a spectrometer which can resolve the profile of the absorption line (Ref. 15).

The theoretical problem becomes much simpler if a sharp line excitation source is used. Walsh suggested that the theoretical and experimental considerations of the relationship between the intensity of the transmitted beam and the concentration of metal atoms are simplified if the frequency of the incident beam ν_{M-M^*} is at the peak of the absorption band (Ref. 14). With this simplification the absorption coefficient may be considered a constant and the relationship between $k_\nu l$ and the number of metal atoms in the beam becomes linear (Ref. 14) and is given in Eq. 3. (The exact derivation of this expression may also be found in Ref. 15):

$$k_\nu l = C N_j \qquad (3)$$

C = A series of constants
N_j = Number of metal atoms in the ground state in the absorption cell.

Referring to Eq. (2) and substituting Eq. (3) the quantity CN_j is related to the quantity I_0/I by the expression:

$$\log I_0/I = CN_j \log e = 0.4343\ CN_j. \qquad (4)$$

The expression, $\log I_0/I$, is an easily measured quantity called the absorbance (A)

$$A = \log I_0/I \qquad (5)$$

which in theory is linear over a wide range of concentrations.

When the pollutant metals are known, the theory thus predicts a simple experiment, which is the basis for the design of most commercial instruments available today. A solution containing the metal to be analyzed (the analyte) is vaporized and the metal atomized. The metal is excited by light at the frequency of the metal absorption band. The excitation source usually is a hollow cathode lamp or electrodeless discharge lamp (EDL) which radiates the emission spectrum of the analyte metal. Most hollow cathode lamps and EDL's contain only a single metal; a few contain two or three metals. This means that using the Walsh technique of monochromatic excitation, it is necessary to have a separate excitation source for each metal to be analyzed.

Actually in performing a quantitative analysis, the metal concentration is not determined from the first order theory given above, but from a calibration curve. This is necessary since the plot of the concentration of metal atoms in the absorption cell versus the absorbance is not linear over as wide a concentration range as is predicted by the simple theory. Important factors causing a deviation from the theory are the finite band width of the emission line, differences in width relative to that of the absorption lines, broadening and frequency shifts of the absorption line, due to pressure and the effect of hyperfine structure, variable ground and excited state populations and association and dissociation of analyte atoms with other atoms in the absorption cell (matrix effects) (Ref. 15). Some of these factors are discussed further in the following section, Experimental Techniques.

b. Experimental Techniques. An atomic absorption spectrophotometer (see Fig. 1 for a schematic drawing of the basic apparatus) has several major components: the light source, the atomizing system, the monochromator and optical system, and the detector system and

peripheral electronics. (Refs. 14, 20). The actual optical and electronic systems range widely from the simple to the highly sophisticated. Atomic absorption instruments are now able to solve many problems encountered by the analyst. The various system components are discussed below.

(1) Light sources. The light source in an AA instrument provides the radiation which the analyte absorbs. Most commerically available instruments are based on the Walsh technique and use a source emitting the spectral lines of a particular metal(s) ("line sources").

Line sources should produce high intensity radiation which is both uniform over the sample volume and constant in time. Such sources produce higher signal to noise levels which lowers the detection limit and improves the precision. The emission lines should be free from interference (from filler gas spectral lines or lamp impurities) and the line profile should be narrow and regular. For practical reasons, the lamps should require little maintenance and have a long life.

Commercial AA instruments today use primarily two types of line sources: hollow cathode lamps and electrodeless discharge lamps. Both are often marketed by the manufacturer of the instrument, though not always manufactured by him. In the Instrument Notes (Section IV) the hollow cathode lamps sold by the manufacturer are listed as "Accessory A"; if electrodeless discharge lamps are available, they are listed as "Accessory B".

a. Hollow Cathode Lamps. First described by Paschen (Ref. 19), a hollow cathode lamp consists of a sealed glass tube containing an anode, a cathode composed of the analyte metal, and an inert filler gas (neon or argon) at a low pressure (1-5 torr). A schematic diagram is shown in Fig. 2. When the current flows between the cathode and anode, metal atoms are sputtered from the cathode. Collisions with the neon or argon ions cause a proportion of the metal atoms to become excited and emit their characteristic radiation (Ref. 21).

The intensity of emission can be controlled by adjusting the lamp current. The current should be as small as will give the necessary instrument sensitivity. In any event, it should not exceed the maximum specified by the manufacturer. The lower the current the longer the life of the lamp will be. An old lamp may become noisy and unstable giving poor results. For further general information about these lamps see Refs. 15 and 16.

b. Electrodeless Discharge Lamps. These high intensity line sources may be used for both AAS and AFS work. A small sealed pyrex or quartz bulb containing a volatile compound of the analyte metal and an inert gas at a pressure of about 1 torr is placed in a microwave or radiofrequency field. A low-pressure plasma is set up and is sustained by the high frequency field. The metal compound evaporates and dissociates. The plasma excites the metal atoms causing its spectrum to be emitted (Ref. 16). The construction and power supply needs for these lamps are discussed in detail in Ref. 15.

While the line spectrum produced by an EDL is both narrow and of high intensity, there was a problem in the past with reproducibility, stability, and interference by inert gas lines. Browner et al. (Ref. 16) reported that by controlling the lamp temperature, the reproducibility and stability of the spectrum improved considerably (Ref. 16). Many instrument manufacturers distribute or make electrodeless discharge lamps; for certain elements (As, Se, P) EDL's provide improved sensitivity and lower detection

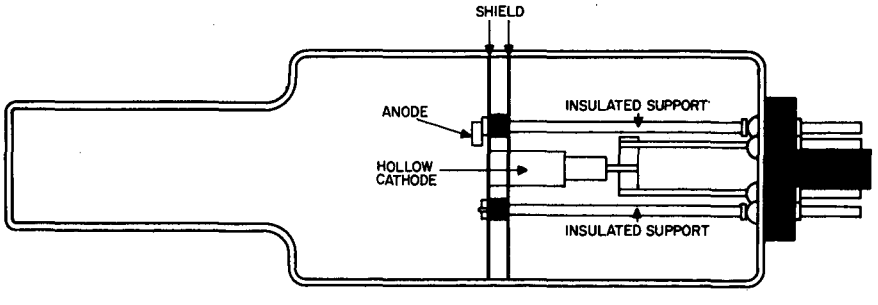


Fig. 2. Commercial hollow cathode lamp with simple disc electrode (reproduced from Kirkbright and Sargent, Ref. 15, with permission by Academic Press, Inc.,(London) Ltd., copyright 1974).

Table 4. Comparison of Lower Detection Limits Reported Using Atomic Spectrometric Techniques[a]

Metal		Atomic Absorption		Atomic Emission			Atomic Fluorescence
	Sym-bol	Flame[b] Manufacturer's Range	Flameless[c] Manufacturer's Range	Flame Emission[d]	Plasma Sources RF Plasma[e]	DC Plasma[f]	Literature Values[g]
		µg/ℓ(ppb)	µg/ℓ(ppb)	µg/ℓ(ppb)	Manuf.Range µg/ℓ(ppb)	Manuf.Range µg/ℓ(ppb)	µg/ℓ(ppb)
Aluminum	Al	20-50	0.004-0.05	10	8-15	1	100
Antimony	Sb	60-100(6)[h]	0.08-0.2	—	30-60	—	50
Arsenic	As	100-400(0.1-1)[h]	0.06-0.1	—	20-330	—	100
Barium	Ba	15-30	0.04-1.0	2	0.02-5	1.0	—
Beryllium	Be	1-5	0.001-0.2	40,000	0.3-8	0.5	10
Boron	B	2000-9000	—	—	5	2.5	—
Cadmium	Cd	1-2	0.003-0.01	2,000	1-3,4	2.0	0.001-1
Calcium	Ca	1-2	0.4	0.1	0.09-4	1.0	1
Chromium	Cr	3-8	0.005-0.100	5	1.8-6	4.0	40-50
Cobalt	Co	3-20	0.03-0.400	50	2-5	2.0	5
Copper	Cu	2-5	0.008-0.100	10	0.45-3	1.0	0.05-2
Gold	Au	9-30	0.010-0.05	500	5-30	—	5
Iridium	Ir	1200	—	—	70-100	—	—
Iron	Fe	3-10	0.003-0.02	50	0.45-3	10.0	3-20
Lead	Pb	10-30	0.05	200	20-50	20.0	10
Magnesium	Mg	0.1-0.5	0.007	5	0.07-20	1.0	0.2-3
Manganese	Mn	1.5-8	0.01	5	1.2 — 3	1.0	5-6
Mercury	Hg	200-1000(0.1-0.5)[i]	0.—	—	13-200	—	0.2
Molybdenum	Mo	10-40	0.06-0.5	100	5-22	5.0	500
Nickel	Ni	7-20	0.025-1.0	30	6-19	10.0	3-30
Osmium	Os	200	—	—	200	—	—
Palladium	Pd	20-25	0.2	50	40	—	40
Platinum	Pt	50-100	0.450	2,000	30	—	300
Potassium	K	1-5	0.100	—	100-260	—	—
Rhodium	Rh	6-10	—	—	20-30	—	3000
Ruthenium	Ru	80-200	—	—	60-5,000	—	—
Selenium	Se	100-350(0.2-1)[h]	0.1-0.5	—	20-93	—	40
Silicon	Si	20-230	0.3-0.8	—	10-30	10.0	600
Silver	Ag	2-3	0.005	20	4-15	1.0	0.1-0.7
Sodium	Na	0.3-1	0.004	—	1-75	1.0	—
Thallium	Tl	20-70	0.05	20	75-1000	—	8
Tin	Sn	20-200	0.06-1.0	300	6-70	—	20-50
Titanium	Ti	50-150	0.03-20	200	0.5-5	—	—
Vanadium	V	20-160	0.15-5	10	1.3-5	5.0	70
Zinc	Zn	0.6-3	0.002-0.001	—	2-10	2.0	0.0003-5

Footnotes for Table IV-4

a. Detection limits are quoted by the manufacturers in a variety of units: ppb, ppm, µg/mℓ, µg/ℓ, mg/ℓ and $g \times 10^{-12}$. These are all easily interconverted: ppb = µg/ℓ
ppm = µg/mℓ, mg/ℓ
ppb = ppm$\times 10^{+3}$ (1000 ppb = 1 ppm)
$g \times 10^{-12}$ is an absolute measure which may be converted to ppb by dividing the absolute figure in 10^{-12}g by the sample size in µℓ

$$\mu g/\ell = \frac{g \times 10^{-12}}{\text{sample size in } \mu\ell}$$

For ease in comparison of figures all detection limits in this section are in ppb or µg/ℓ.

b. For flame atomic absorption detection limits, instruments included were:

Manufacturer	Models	Inst. Note Number
Fisher, Jarrell-Ash	Dial-Atom III, 810, 850	1, 2, 3
Hitachi	170/10, 170/30, 170/50	1, 2
Instrumentation Lab.	151, 251, 351, 751	1, 2, 3
Perkin Elmer	103, 107, 272, 373, 460, 603	1, 2, 3, 4, 5
Pye-Unicam	190/191, 1900/1950, SP2900	1, 2, 3
Varian	175,375	1, 2

c. For flameless atomic absorption detection limits, instruments included were:

Manufacturer	Model	Inst. Note Number
Fisher, Jarrell-Ash	FLA-100	C
Hitachi	GA-2	C
Instrumentation Lab.	IL 152, IL 252, IL 352, IL 555 CTF	4, C
Perkin Elmer	HGA-2100, HGA-76B,	C, D
Varian	CRA-90	C

d. Reference 16, p. 134

e. For RF Plasma detection limits, instruments included were:

Manufacturer	Model
Applied Research Labs.	Inductively-Coupled RF Plasma Quantometer (ICPQ)
Fisher, Jarrell-Ash	Plasma AtomComp (ICAP)
Labtest Equipment Co.	Model V-25 ICP, Model ICP 2100

f. For DC Plasma detections, instruments included were:

Manufacturer	Model
Spectrametrics	SpectraSpan III, IV

g. Reference 16, p. 177

h. Hydride generator.

i. Cold vapor technique.

limits than obtained with hollow cathode lamps.

c. Continuum Sources. The use of a continuum source, while more difficult to handle theoretically, eliminates some of the major limitations on current AA techniques; the need for a separate line source for each element to be determined and the concurrent inability to detect unexpected elements. Work is currently proceeding at O'Haver's laboratory to produce an instrument which will be capable of determining up to 20 elements simultaneously, which would be a significant innovation. (Ref. 22).

The experimental problem associated with a continuum source is that it is difficult to obtain sufficient intensity with a noise level low enough to achieve necessary detection limits. Recently, researchers have obtained fair detection limits by using extremely stable sources, which lower the noise level. Others have used high resolution monochromators to reduce the noise level and subsequently, the detection limit loss from scattered light falling on the detector.

(2) The Atomization System. The main function of the atomizer is to thermally reduce the analytes to atoms which are capable of absorbing radiation from the light source. The atomizer for use with flame AAS also serves to deliver the sample, in the form of a fine aerosol mist to the flame, whereas the flameless atomizer requires direct injection of the sample into the atomizing chamber. Although the EPA designates flameless methods as acceptable, Standard Methods (Ref. 3) only refers to them briefly. The instrument manufacturers are now producing accessories for flameless techniques which have good detection limits and reproducibility for most elements and hence this method is becoming more popular. The detection limits for both flame and flameless techniques, for a variety of metals, are summarized in Table 4.

(a) Flame Techniques. Two types of atomizers, or burners, for flame AAS are currently in use: the total consumption burner and the pre-mix burner. In total consumption burners, the aspirated sample and flame gases are kept separate, being mixed in the flame. The resultant flame is turbulent. In pre-mix burners which are the most commonly marketed today, the sample and flame gases are thoroughly mixed before reaching the flame. The resultant flame is "laminar." In general, laminar flames are less "noisy" than turbulent flames.

The atomizing system for pre-mix burners has four basic components: (1) a gas control system, (2) a nebulizer, (3) a mixing chamber, and (4) a burner head; see Fig. 3.

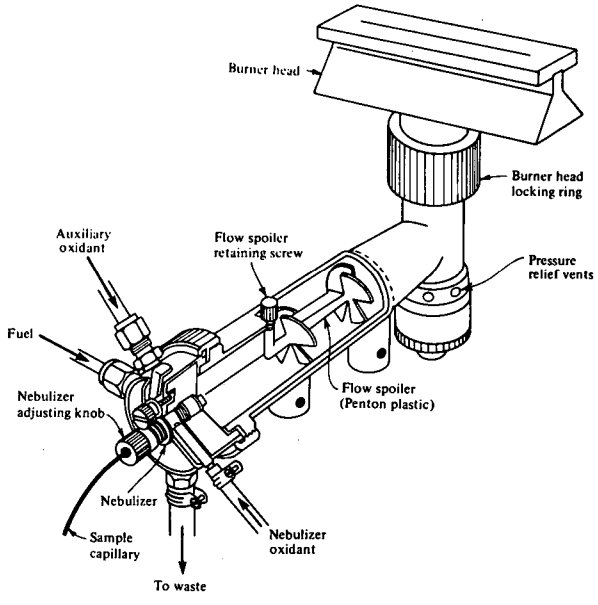


Fig. 3. A slot burner and expansion chamber (reproduced with permission by and courtesy of Perkin-Elmer Corp., Ref. 11).

Two gases are necessary: a fuel and an oxidant. Usually acetylene is used as the fuel and air as the oxidant. The temperature of the air-acetylene flame is approximately 2300°C. For elements which form refractory oxides, the nitrous oxide-acetylene flame (2900°C) is used. Other gas mixtures, such as air-hydrogen, argon-hydrogen and air-propane are used when specific chemical or spectral problems are encountered. The optimum flame recommended by the EPA for each metal is listed in Table 3.

There is a great variety of gas control systems in commercial instruments. The simplest provide inlets which allow for the use of an air-acetylene (C_2H_2) flame. Most modern instruments provide built-in pressure regulators and flow meters as well as accessibility for up to five gases. Many provide a T-valve for switching to nitrous oxide. T-valves currently available have a safety interlock to prevent an undesired switch-over.

The nebulizer serves to aspirate the sample through a capillary by one of the gases used in the flame. The resulting fine aerosol mist enters the mixing chamber where it is mixed with the fuel and oxidant gases before entering the burner head where the metals are atomized.

Nebulizers may be of two types, the venturi type that draws the liquid into a moving gas stream by a pressure difference (shown in Fig. 3), and the ultrasonic type

that relies on high frequency acoustic energy to form minute droplets at the surface of the liquid (Refs. 23, 24). Ultrasonic nebulizers produce smaller droplet size that increases sensitivity through (1) increased atomization efficiency and (2) increased aerosol density. However, because of added expense, this technique has not yet been widely adopted.

The combustion zone, or cell path, is determined by the burner head. Burner heads for an air-acetylene flame normally have a single slot of 10cm in length by 0.38-0.60mm in width. Burner heads for a nitrous oxide-acetylene flame also have a single slot, but with a shorter length (5cm) to prevent flash backs. "Flashbacks" occur when the flame gas mixture ignites in the mixing chamber causing the mixing chamber to explode. They occur when the gas velocity is not appropriate for the mixture. In the past, they have frequently occurred when the usual air-C_2H_2 mixture is changed to N_2O-C_2H_2. If the same burner head is used for N_2O-C_2H_2 mixtures as for air-C_2H_2 the flow rate is too slow and flash backs are a danger. The shorter slot on the nitrous oxide-acelylene burner head compensates for the burning velocity.

Three-slot (Boling) burner heads are used when increased sensitivity is required. Increased sensitivity results from the fact that the three slot burner head provides a wider flame environment over that for the single slot burner head with the result that more of the hollow cathode radiation passes through the atomic vapor.

Nebulizers, premix chambers and burner heads are constructed of a variety of materials. For determining metals in fresh waters, the standard stainless steel capillary nebulizer and burner head with a corrosive resistant premix chamber are adequate. If the analyst must work with water with high salt concentration, such as brines or estuarine waters, or highly corrosive industrial wastes, he may need to consider obtaining a corrosion resistant nebulizer.

b. Flameless Techniques. Numerous flameless AA atomizers have been marketed over the past few years. Furnaces, filaments, cathodes and several other devices have been used to atomize metals in water. The most common is the graphite furnace (Jarrell-Ash, Perkin-Elmer, Instrumentation Laboratories and Hitachi) and the carbon rod atomizer (Varian). For a comparison of the two atomizers see Fig. 4.

The graphite furnace is based on early furnace designs developed by King and L'Vov (Ref. 19). Examples of both furnaces are shown in Fig. 4.

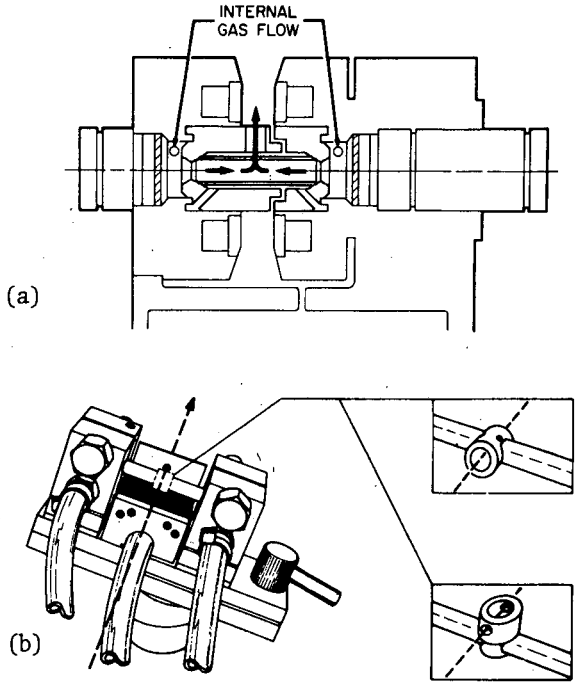


Fig. 4. Heated graphite atomizers,
(a) schematic diagram of the Perkin-Elmer HGA-2100 (reproduced with permission by Perkin-Elmer Corp., Ref. 25 and
(b) schematic diagram of the Varian CRA-90 (reproduced with permission by Varian, copyright 1972).

A liquid sample containing the analyte is pipetted into the graphite heater through an access hole in the tube. Graphite tubes will accept up to 100 µl of solution, while carbon rods accept up to 20 µl. In early experiments, one of the major sources of error was the difficulty in reproducing the exact size and location of the sample in the furnace (Ref. 16), a problem which has been largely solved with the introduction of automatic sampling equipment. There are also provisions for placing solid samples in the tube, but care must be taken to ensure homogeneity of the solid sample.

Once the sample is dispensed into the graphite tube, a program button is activated, and the power supply automatically heats the tube according to the preset conditions. Absorbance peaks are rapid, and must be displaced on a strip chart recorder.

Contamination is more serious with flameless AAS than with flame AAS because of the lower metal concentrations that are detected. Ideally, clean room facilities should be available for sample preparation.

The graphite tube is electrically heated by means of a power supply which delivers a high current (up to 500 amps) through the tube. The current to the tube is controlled by three rheostats on the power supply to allow for setting of drying, charring and atomizing temperatures. Atomization temperature can be increased to as high as 3000°C on most instruments. There are also controls to set the individual times for the temperature settings. Typically, the temperature and time settings are determined experimentally for the analyte and the matrix in which it exists.

An inert gas, nitrogen or argon, continually purges the graphite tube to remove vapors during drying and charring cycles, and to protect the graphite tube and analyte from air oxidation. The flow of inert gas can be varied and can be interrupted during atomization to increase the residence time of atoms in the tube and hence further increase the sensitivity. However, continuous purging of the tube during atomization extends the lifetime of the graphite and improves the linearity range.

Flameless AAS produces "smoke" during the heating cycles which absorbs a broad continuum of radiation leading to erroneously high absorbance readings; therefore it is advisable to use background correction. Two types are commonly used continuum source and Zeeman field background correction. They are discussed in section (6) below.

Another possible source of error is "matrix effects" which occur when a metal or the substance it is in, are not atomized by the furnace with the same efficiency as in the standard. The processes controlling the atomization of metals in the graphite tube are not generally appreciated (Refs. 27-29). The effects of the sample matrix elements and the carbon environment on the analyte metal must be thoroughly documented for each sample type and individual metal before routine anlysis can proceed.

This can be accomplished by two methods: analyse a "known" with the same sample matrix or add a known amount of analyte to the unknown and determine the recovery. (This is the method of standard additions). The added analyte must be in the same form as that contained in the unknown sample. If the above conditions are met and the measurement agrees with the known value, the analyst may assume that the method being used is valid for that sample type. Meeting the conditions of "same sample matrix" or "same analyte form" is very difficult and the ingenuity displayed in solving this problem makes a statement about the value of the analyst. If the above procedures are ignored, it is possible to spend many hours obaining values that have no validity.

Another problem encountered when using the graphite furnace is the formation of several fairly stable metal carbide complexes which substantially reduce the signal. In order to prevent this, tantalum ribbons have been used for flameless atomization. The sample is placed directly on the ribbon. It then undergoes a similar heating process as has been outlined for the graphite furnace. One disadvantage of the ribbon type atomization device is that there may be greater matrix effects than with a graphite furnace. This phenomenon is attributable to the temperature drop which occurs upon vaporization of the samples (Ref. 16).

There are a number of other flameless atomizers being marketed which are limited to certain metals or matrix types. Among these atomizers are the tantalum boat, the tantalum strip atomizer (mentioned above) and the Delves cup. They are restricted to the more volatile elements (Cd, Pb, Zn) and are used mainly for analyses of these metals in biological samples.

An attachment is also available for mercury analyses in which the mercury in solution is chemically reduced to mercury vapors and passed through a cold vapor sample chamber.

Special flameless attachments are available for arsenic and selenium analyses in which their hydrides are formed. The gaseous hydrides are passed into an argon-hydrogen entrained air flame where absorbance of the hollow cathode radiation is measured.

Despite several obvious sources of error or possibly difficulty, flameless AAS represents a major advance in trace metal analyses and should be seriously considered by all water analyses laboratories.

Flameless techniques, in general, have a higher sensitivity (up to 1000x) and lower noise levels than standard flame techniques. (Table 4 compares the limits of detection for several metals under flame and flamelesss conditions). This is a result of two factors. First, in flame AAS, less than 10% of the sample is atomized. Most of the sample is condensed from the aerosol mist after nebulization and, consequently, never reaches the flame. In flameless AAS, the entire sample is atomized. Second, the atomized vapor remains in the graphite tube longer than it does in the flame.

c. Automated Sampling and Sample Preparation. It is possible to automate much of the sampling process in AA. Automation can range from an automatic sipper, an apparatus which sequentially sips a quantity of sample from test tubes on a rotating turntable containing the sample solution, to the auto-analyzer which takes raw water samples,

adds pretreatment chemicals, mixes the solution and feeds the mixture to the aspirator.

One example of automation of a metal-in-water analyzer is the coupling of a module of a Technicon Auto Analyzer to an atomic absorption instrument (Refs. 30-32). Fishman and Erdman (Ref. 32) used a Technicon sample and proportioning pump in series with a Perkin Elmer 303 AA. The absorption of samples containing copper, lithium manganese, potassium, sodium, iron and zinc in the ppm-ppb range were determined using the sampler directly. Calcium, magnesium and strontium were pretreated by the addition of lanthanum chloride suppressant reagent, thoroughly mixed in the solution, and the resulting solution was fed to the aspirator. The results for both measurements were registered on a strip chart recorder. Depending on the metal, 30 to 60 samples can be analyzed per hour. Analytical data obtained by using this system were fully as accurate as data obtained using manual preparation and aspiration.

Atomic absorption usually measures one metal at one time, sometimes two, so that a new lamp must be inserted for each metal. This required 5-10 minutes. Clearly there is a disadvantage in automatic AA measurement of more than one metal per solution.

Automation is particularly appropriate for laboratories analyzing any number of samples for the same metal or when repeating a measurement several times. In flameless AA, auto-injectors have increased the precision of measurements considerably, since they are able to repetitively inject an exact amount of solution into the same position in the furnace.

Automated sampling and chemical pretreatment is of most use when the spectrometer signals are interfaced to a computer. In this way, standards and check samples can be regularly inserted in the sample tray and the resulting confidence limits can be reported.

Automation in general saves considerable operator, and turnaround time, reducing the cost of each analysis. When operating properly, they only require sampling and instrument set-up, and periodic checks. However, automated techniques are only of value if the sample matrix does not change appreciably. Interferences causing incorrect determinations will not, in general, be noticed unless samples are run by independent methods.

3. Optical Systems

In atomic absorption instruments, the optical system includes all components which control the beam of light as it passes from the light source, through (or by) the sample, into the monochromator and to the detector. Section (a) below will discuss the monochromator, which selects a narrow band of light from the interval of incoming light. Section (b) will discuss the optical paths which are used in atomic absorption instrumentation. The optical path refers to the routing of the light beam from the source until it finally impinges upon the detector.

a. Monochromators. The function of the monochromator is to direct only a narrow bandwidth of light at the exit slit at one time. Monochromators can work at set wavelengths or they can scan. They work by dispersing different wavelengths at different angles, by use of a prism or diffraction grating. The path of light through the monochromator depends upon the particular mounting of the optics within it.

Prisms. A prism relies on the principle of changing index of refraction with wavelength to disperse incoming light into its spectrum. It must have a high optical transparency for the region of interest. (Prisms are often made of quartz because this material has a wide wavelength bandpass - from the far ultraviolet (UV) to the near infrared). The prism should also be relatively insensitive to humidity. Calcium floride, sodium chloride, potassium bromide and cesium iodide are also used in the infrared regions of the spectrum but are difficult to maintain. They can be hard to clean and tend to be attacked by even small amounts of dampness, unless heated or purged with dry air.

The major disadvantages to prisms are their sensitivity to temperature and humidity, their high cost, and their non-linear and lower dispersion when compared to gratings. They are rarely used in atomic absorption instruments.

Gratings. A diffraction grating disperses the light impinging upon it, by presenting a surface with regularly spaced lines to the beam of light. The phase relationship between the various wavelets of the diffracted light causes different wavelengths to travel in different directions. Figure 5 shows a beam of light impinging upon a grating with an angle of incidence, α. A wavelength of light, λ, is diffracted at the angle of diffraction, β. Only when the grating relationship:

$$m\lambda = d(\sin\alpha \pm \sin\beta) \qquad (6)$$

(where m = the order of diffraction, an integer) holds will the wavelets be in phase and reinforce each other. At a single order for each angle, β, only a single wavelength of light will be in phase; all other wavelengths in the same order will exhibit destructive interference at that angle.

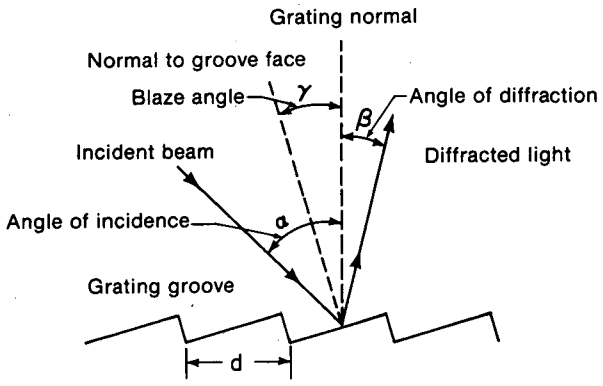


Fig. 5. Diagram showing the relationship between the angle of incidence, angle of diffraction and the blaze angle
α = angle of incidence with respect to a normal to the grating
β = angle of diffraction with respect to a normal to the grating
γ = blaze angle
d = grating constant of distance between successive grooves
(adapted from Ref. 11). (XBL 7810-11543)

The diffracted light is most intense when the angle of diffraction is equal to the angle of reflectance from the groove face, γ (see Fig. 5). As can be seen from the figure, this angle is the angle between a normal to the groove face and a normal to the grating. It is common to report that a grating was blazed at 500 nm, which means that the grating was ruled with the groove faces at an angle which maximizes the intensity of the light diffracted at 500 nm.

The angular or linear distance between diffracted wavelengths is called the dispersion. The angular dispersion is the differential of Eq. (6):

$$\frac{d\beta}{d\lambda} = \frac{m}{d \cos \beta} . \qquad (7)$$

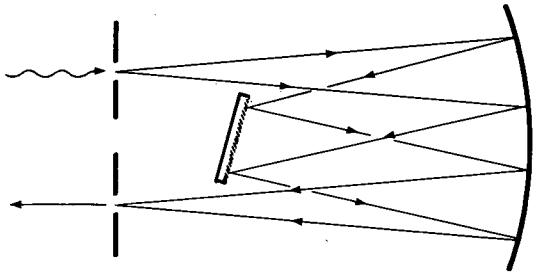
To determine the linear dispersion, dl, that is the linear distance between wavelengths, the angular dispersion, $d\beta/\lambda d$, is multiplied by the focal length of the grating, f:

$$\frac{dl}{d\lambda} = \frac{mf}{d \cos \beta} . \qquad (8)$$

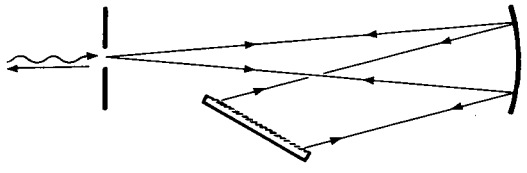
Most monochromators used in commercial instruments utilize a diffraction grating as the dispersive element. The grating is more commonly used today because of its greater dispersive power and flexibility. On the practical side, they are easier to replicate, are less sensitive to temperature and humidity and are often cheaper.

Mounts. Three types of monochromator mounts are commonly used in commercial systems: The Littrow mount used in many of the Perkin-Elmer Instruments; the Czerny-Turner mount, which is used by the higher resolution Varian instruments, and the Ebert mount which is used by Instrumentation Lab, Varian and some Perkin-Elmer instruments. All three mounts are diagrammed in Fig. 6. The Littrow system uses the same entrance and exit slit for the beam, which is diffracted from a planar

a. EBERT MOUNT



b. LITTROW MOUNT



c. CZERNY-TURNER MOUNT

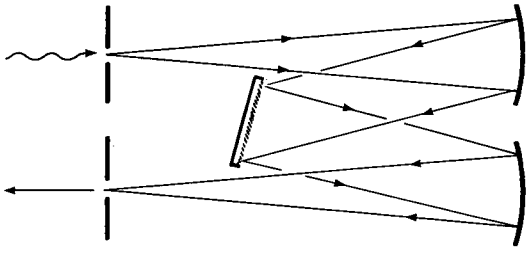


Fig. 6. Diffraction grating mounts.
(a) Ebert (adapted from Ref. 33).
(b) Littrow mount (reproduced from Kirkbright and Sargent, Ref. 15 with permission by Academic Press, Inc. (London) Ltd., copyright 1974). (c) Czerny-Turner mount (reproduced from Kirkbright and Sargent, Ref. 15, with permission by Academic Press, Inc., (London) Ltd., copyright 1974).

grating. The Czerny-Turner uses two separate slits, allowing the experimenter a greater degree of flexibility. The Ebert mount uses a single concave mirror and planar grating to diffract the beam, a separate entrance and exit slit.

There are several requirements for any dispersive device used for routine analyses of metals in water. These are (1) good stability and reproducibility in the wavelength-setting mechanism; (2) good stability and reproducibility in the slit-setting mechanism; (3) an adjustable slit to determine optimum operating conditions; (4) an accurate and simple wavelength calibration technique, and (5) sufficient resolution to distinguish between adjacent absorption bands. Requirements (1) and (2) prevent drift during measurement and increase reliability of measurements. Requirement (4) - the need for accurate and simple calibration to be checked frequently - can not be emphasized enough. Wavelength calibration optimizing the energy on a particular peak, is an essential part of instrument operation.

Requirement (5) - the resolution is often determined by knowing the reciprocal linear dispersion and the slit width, which describes the theoretical resolution. Actual resolution generally runs 70% of theoretical because gratings are not perfect. (Ref. 34). Atomic absorption instruments of high resolution should be used if elements with complex spectra are to be determined (i.e., Fe, U, rare earths).

b. Optical Paths. Despite the variety of instrumentation available, there are two major types of optical paths used, single and double beam. The two systems are illustrated in Figs. 7 and 8.

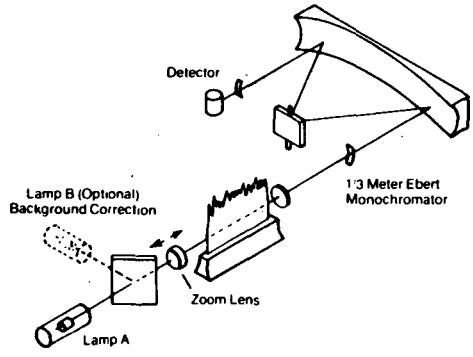


Fig. 7. A single beam atomic absorption spectrophotometer, Instrumentation Laboratories, Model IL 151, optical diagram (reproduced from the manufacturer's brochure, Ref. 35, with permission by Instrumentation Laboratories).

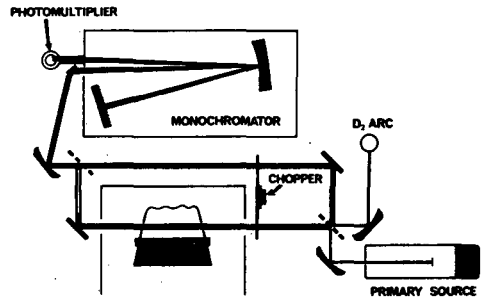


Fig. 8. A single beam atomic absorption spectrophotometer, Instrumentation Laboratories, Model IL 151, optical diagram (reproduced from the manufacturer's brochure, Ref. 35, with permission by Instrumentation Laboratories).

A single beam spectrophotometer (Fig. 7) involves a collimating device which passes the light through the sample to another device which focuses the light on the entrance slit of the monochromator. The monochromator disperses the beam of light into its component wavelengths permitting only the selected bandwidth to pass through the exit slit and impinge upon the detector. The absorbance measured is the absolute absorbance whereas the double beam system measures relative absorbance.

A double beam spectrophotometer chops or splits the single source beam, allowing alternating pulses of a beam of light to bypass the sample area. The sample and reference beams are then passed through the monochromator and the exit slits to the detector. The detector then measures the absorbance of the sample beam relative to the reference beam. This provides an automatic correction for variation of lamp intensity, photomultiplier sensitivity, and electronic gain.

Two methods are used for generating the two beams of light and analyzing the resulting impulses on the detector. The most common involves a mechanical chopper with a half mirror surface which produces alternating pulses in the sample and reference areas. It can develop phasing problems but is a satisfactory method and widely used. After the beams have passed the sample and reference area the beams are recombined, passed through the monochromator and exit slits onto a single detector, whose electronics responds to both the sample and reference beam, and compares the two.

The second method uses a quartz beam splitter, which splits the beam in two and then after they have passed through the sample and reference areas focuses the dual beams on matched monochromators and detectors. The electronics then compares the output of both de-

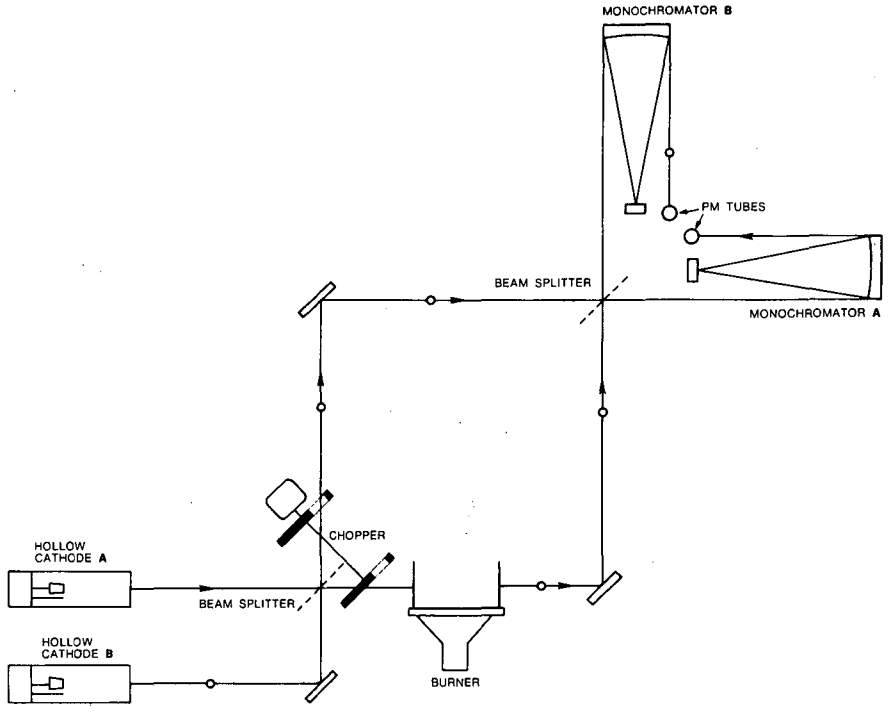


Fig. 9. A dual channel, double beam atomic absorption spectrophotometer, Jarrell-Ash Model 810 (reproduced from manufacturer's brochure, Ref. 33, with permission by Jarrell-Ash Division, Fisher Scientific Co.).

tectors. The difficulty with this system is that only very rarely (if ever) are two photomultipliers truly matched throughout their entire range.

An elaboration of the double beam spectrophotometer is the dual-beam - dual-channel spectrophotometer (Fig. 9). This instrument has dual beams as well as dual monochromators which allow the operator to work in several modes. Two metals in the same sample may be measured simultaneously. One channel can be used for AA the other for AE. The second channel may be used to subtract the background correction, (A-B) or to monitor an internal standard (A/B). (Ref. 33).

The optics of either single or double beam instruments can be mirror-or lens-based. Most commercial instruments use mirrors, since they are cheaper. There is no need to correct for chromatic aberrations in mirrors; they are usable over a wider range in the uv and visible, and involve less light loss through absorption, reflection, or material defects.

4. Detector and Readout Systems. The detector and readout system in an AA instrument takes the resultant beam of light and translates it into a signal which the analyst can interpret in terms of the concentration of a solution. The detector for most AA spectrophotometers is a photomultiplier tube (PMT). A photomultiplier is a photoelectric device that converts very low intensity light beams into measurable electrical signals. It consists of a photocathode and multiplier section and an anode. Electron multiplication relies on the principle that when some metals are irradiated by photons of sufficient energy, electrons are emitted. By using six to 14 cascaded metal dynodes very large (10^7) current gains are possible. (See Fig. 10 for a schematic diagram of the amplification process.) The resultant current is then processed (for a detailed discussion of signal processing techniques for atomic absorption, see Ref. 15).

The current produced by the detector is an analog signal which is used to drive a chart recorder or a meter. The meter is usually calibrated to read in absorbance units. The analyst uses the data received to create a calibration curve and to determine the concentrations of unknown solutions. If a chart recorder is used, the height of an absorption peak may be read or the whole peak can be scanned. If a peak is scanned, the area under the curve is integrated; many instruments have a peak integration mode built into the circuity, saving the operator this tedious calculation.

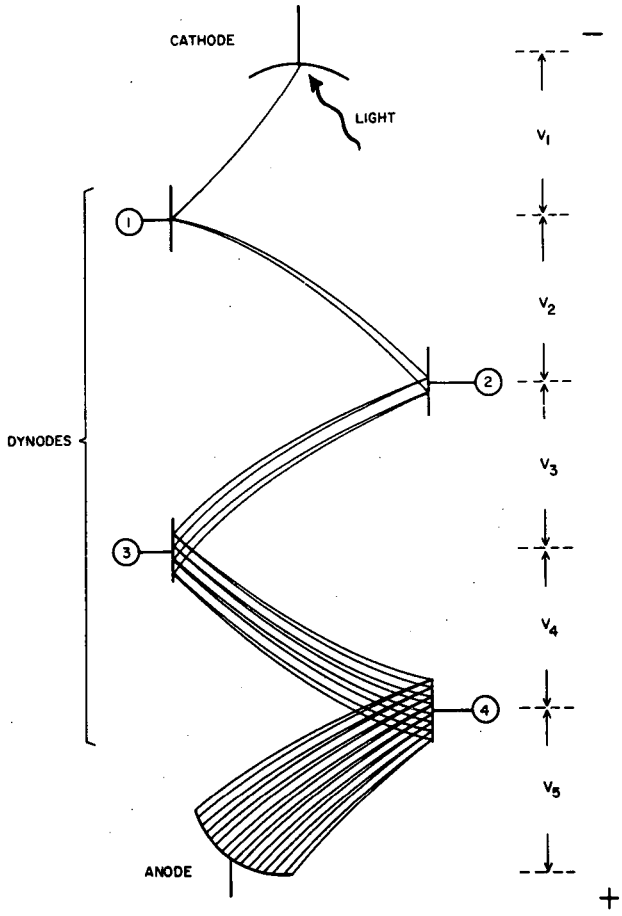


Fig. 10. Schematic representation of a photomultiplier tube (reproduced from Kirkbright and Sargent, Ref. 15, with permission by Academic Press, Inc. (London) Ltd., copyright 1974).

Most instruments, which provide a digital signal, rely on a analog to digital converter. The digital signal can be used with a digital readout meter or teletype unit with a dedicated or remote computer for a variety of computational analyses.

Double beam signals require somewhat more sophisticated electronics. These electronics amplify and separate the input into a reference mode and sample mode. The ratios of the signals are then obtained, the output being a signal which has compensated for source variation.

5. Sources of Error

In atomic absorption spectroscopy, there are two general sources of error which may be encountered: interferences and error which are introduced by instrument malfunction or operator error. Interferences are those errors which result because of differences in behavior between the sample and the standard during the atomization process. Interferences can be encountered even if the monitoring system is functioning as it is supposed to. Errors which are introduced by malfunction of the instrument or operator error may occur anywhere in the procedure, in calibration, sampling, instrument operation or in data reduction. Interferences and methods used to compensate for them are discussed in section (a) below. Of the errors introduced by instrument malfunction or operator error, only those associated with instrument operation are discussed below in section (b). Errors introduced in the calibration, sampling or data reduction portions of the monitoring system are discussed in those portions of the introduction to this volume ("Sampling and Data Reduction" are still in preparation) or in Ref. 2 and 3.

It should be noted that operator errors and instrument errors may overlap: failure to properly align the source lamp with the background corrector lamp (instrument error) will lead to incorrect background correction (interference).

2. Interferences. Three types of interferences may be encountered using atomic absorption spectroscopy: physical, chemical and spectral.

Physical interferences are influences on the absorption signal by the physical characteristics of the test absorption and the physics of the process of atomization and nebulization. These may include some matrix effects, ionization effects and also scattering effects. These interferences apply to both flame and flameless AAS, although the magnitude of the interference may differ between flame and flameless analysis.

One type of matrix (matrix interferences) also known as viscosity or bulk interference, is well documented for both flame and flameless AA analyses (Ref. 37). This interference occurs when the physical characteristics (temperature, viscosity, density, surface tension and composition) of the sample and stanstandard solutions differ considerably. This can happen when the sample solution contains a higher concentration of dissolved salts or compounds than the standards; when different solvents are used for samples and standards; or, when the sample and standards are at different temperatures. Matrix interferences encountered in flame AAS usually arise from differences in aspiration rates between the samples and standards. In most cases, preparing the standard in the same matrix as the sample will eliminate the interferences. However, when the samples contain high or variable concentrations of dissolved salts (estuarine waters, brines or marine waters),

preparation of identical standards is ineffective or impractical, and dilution or extraction of the samples to reduce the salt concentration is often necessary.

In flameless AAS, matrix interferences cause a difference in the rate of analyte volatilization during atomization. For the more volatile elements, matrix interferences may be eliminated through selective volatilization in which the analyte is atomized at a temperature below that at which the matrix elements volatilize. However, occlusion of the analyte by the bulk matrix salts may preclude the usefulness of this approach.

As with flame AA, most matrix interferences associated with flameless AA can be eliminated through dilution or extraction of the sample. Before resorting to dilution or extraction as a routine procedure, the analyst should consider carefully the contamination problems inherent in any chemical procedure.

Laboratories which routinely analyze fresh water samples with low concentrations of dissolved or suspended solids will rarely experience this physical interference. Laboratories working with brines, estuarine waters, or waters with high concentrations of dissolved or suspended solids, may have considerable trouble with it.

A second type of matrix effect occurs when the analyte metal is not released in atom form by the complex matrix in which it occurs. If the test solution has a high concentration of dissolved solids the analyte may be occluded in particles which are formed upon evaporation in the flame. If these particles are not atomized (and they sometimes are not) then the absorption signal may be reduced. These problems can be minimized by control of the rate of aspiration and careful use of the nebulizer. If the size of the particles formed is minimized, then the possibility of occlusion is less, since with smaller particles there is a greater probability of complete atomization. (Ref. 15).

A similar problem can be encountered when analyzing biological samples along with a complex background absorption which requires correction. This problem is considered below under spectral interferences.

Incomplete atomization (which might be considered an instrument malfunction or operator error) can also introduce a severe scatter problem which reduces the absorption signal, introducing a considerable error, which is difficult to correct.

The chemical composition of the flame or furnace can be used to maximize atomization. The fuel/oxidant ratio of the flame can effect its reducing power. Graphite furnaces are good reducing agents which can attack many compounds, but also can form highly stable carbides. For metals that form stable carbides a flame technique or a tantalum furnace may be more effective in preventing matrix effects. (Ref. 15) Physical interferences and matrix effects are considered in greater detail in both References 15 and 37.

Ionization interferences occur when an electron is removed from a neutral atom giving a positively charged species which decreases the analyte atom population in the atomizer. This phenomenon is more typical of flame AA than flameless AA. An example is the ionization of sodium or potassium in the flame. Ionization interference can generally be overcome by adding an excess of an easily ionizable element to the samples and standards prior to analyses.

Chemical interferences reduce the absorption signal by reducing the number of metal atoms that are present in the absorption path through chemical reactions. The analyte metal may react with other species in solution, either before or after atomization, to form compounds which are not volatile or not atomized by the flame or furnace. If this occurs, the signal is reduced. An example of chemical interference is the reduction of the calcium signal in the presence of phosphate or sulfate.

In flame AA, chemical interferences which exist in the air-acetylene flame may be eliminated by using the higher temperature nitrous oxide-acetylene flame. For example, phosphorous forms a stable compound with calcium in the air-acetylene flame, whereas this compound is destroyed in the nitrous oxide-acetylene flame.

Chemical interferences may also be reduced by extraction of either the analyte metal or the interfering species, or by the use of releasing and protective agents. Releasing agents preferentially combine with the interfering species. Lanthanum is often used to protect the calcium species in the presence of phosphate or sulfate (Ref. 11). Protective chelating agents preferentially combine with the analyte species forming complexes which are more easily vaporized. 8-hydroxyquinoline and EDTA (ethylenediamine tetracetic acid) are both used extensively.

A more complex interference occurs in the vapor phase if the interfering species in some way effects the equilibria between the excited and ground states of the analyte atom. This problem is usually insignificant under normal operating conditions. (Ref. 15).

In flameless AA, matrix modification is the addition of a chemical designed to alter the matrix salts prior to analyte atomization.

An example of this technique is the addition of NH_4NO_3 to sea water in the furnace prior to charring. The NH_4NO_3 reacts with the interfering NaCl salt forming the volatile products NH_4Cl and $NaNO_3$ which are removed prior to atomization of the less volatile analyte. Conversely, more volatile analytes, e.g., selenium, can be stabilized with nickel to form nickel selenide allowing matrix salts to be volatilized prior to the atomization of selenium.

Chemical interferences may also be removed by extraction of the sample prior to analyses. When a number of transition series metals are to be analyzed in brackish waters, it is usually best to carry out an extraction on the waters to remove the bulk salt interferences and isolate the transition metals.

Chemical interferences are of concern in any water laboratory. They are a constant problem, and the analyst must attempt to predict the probable chemical composition of the sample. If results are suspicious, he may wish to perform a qualitative analysis of the sample to ascertain if an interfering species, not previously expected, is present. A periodic qualitative analysis of a sample solution for possibly interfering metals would be a valuable procedure in any event, since an analyst may not necessarily recognize results as spurious, if the interference effect is small.

Spectral interferences are caused by factors that influence the spectrum observed in an AA instrument. These may be spectral overlap, flame emission, undesired source emission or background molecular absorption. They may be encountered in any water laboratory.

Spectral overlap can occur if atomic or molecular-resonance lines of materials vaporized from the sample coincide with the resonant line of interest of the analyte. The problem arises because "sharp line" sources are not in fact lines but have finite width. Several effects have been shown to broaden the absorbance line (Ref. 15):

Natural broadening - caused by the finite lifetime of the atom in the excited state.

Doppler broadening - caused by thermal motion of atoms.

Lorentz and Holtzmark broadening - caused by the collision of absorbing atoms with metal atoms of the same kind (Holtzmark) or different kind (Lorentz). Also called pressure broadening.

Stark and Zeeman broadening - results from the splitting of electronic levels in the presence of strong, non-uniform electric fields (Stark) or strong magnetic fields (Zeeman).

Quenching broadening - broadening due to radiationless transition, usually of minor importance.

Self-absorption broadening - result of absorption of light emitted by excited state atoms in the source of light.

Hyperfine effects - due to the presence of several overlapping spectral lines within a single line producing a non-uniform profile.

The mathematical relationships between these effects and the line width are further elucidated in Ref. 15. Finite or broadened source lines cause non-linearity of calibration curves.

In practice, spectral interference is encountered when several metals in the sample have lines which are close to those of the analyte metal. For example, manganese absorbs at 403.1, 403.3 and 403.5 nm, gallium at 403.3Å, potassium at 404.4 and 404.7 and and to 405.8 nm (Ref. 11). The problem of spectral overlap is best solved by extraction of the analyte or the interfering species or by observation at another spectral line.

Broad band background interferences can originate from two sources. Metals (other than the analyte) and other species in solution or in the absorption cell can form molecular species which have a broad band absorbance masking the absorbance of interest. Or emission from the flame can occur at the same frequency as the analyte line of interest to produce a high noise level. Deuterium arc continuum sources and Zeeman AA have been used to correct for these types of interference. Both techniques are discussed in Section (6) below.

b. Operator Errors and Instrument Malfunction (Ref. 31). An atomic absorption instrument is a sophisticated piece of equipment. The most effective method for eliminating operation or instrument malfunction errors is to have a skilled, trained operator. Such a person will allow fewer operator mistakes to occur and will be more likely to note instrument malfunctions early, and may be able to correct most if not all of them.

The correct procedure for using each particular instrument will be different and is beyond the scope of this volume. The manufacturers provide manuals with their instruments and often have training courses for the person who is to operate their instrument. Both should be used.

Most AA instruments require minor adjustments when they are used. Therefore whenever an AA is turned on, it should be checked to be sure it is operating properly.

Manufacturers publish sensitivity specifications which must be met when the instrument is functioning properly. Sensitivity is usually defined as the concentration of a metal which will produce a signal of 1% absorption (0.0044 absorbance units). When the sensitivity specification is not met, the operator should recheck the optimization of all the parameters, for flame and flameless AA this means checking lamp alignments and current settings, slit width, atomizer alignment, filter selection, wavelength selection, expansion and damping selections, and recorder mv range. For flame AA, this means checking the nebulizer flow rate and fuel to oxidant ratios. For flameless AA, this means checking the condition of the graphite tubes and cones, and drying, charring and atomizing temperatures. If after all this is done, and the sensitivity specification is still not met, the problem may still be as simple as installing a new hollow cathode lamp.

Incrustation of the nebulizer, capillary or burner head can lead to a reduced signal. Corrosion of these components can increase the rate of aspiration and increase the signal. This problem can be alleviated by frequent cleaning of the nebulizer and burner head, and replacement of damaged parts.

The operator should thoroughly read the manufacturer's operation manual and attend a training course on the particular instrument. Training courses are usually free when a new instrument is purchased. Above all the operator must think through a trouble shooting regime. The repair of instrument malfunctions is best left up to the manufacturer's service engineers. Service contracts can be purchased from the manufacturer to cover repairs as they are needed. However, it is up to the operator to determine if an instrument malfunction is the fault of the instrument or the fault of the operator.

6. Background Correction. Background absorption may occur if the analyte solution contains species that absorb or scatter over a large wavelength region; some flames also naturally absorb some radiation. Background correction can be of great importance in the analysis of waters with a high saline content.

Continuum Source Background Correction. Several commercial instruments use a continuum source deuterium lamp as a background correction device. A chopper mirror is used to send alternating deuterium and source radiation through the sample. The flame and interfering species will absorb the continuum source and lamp equally, at least within experimental limitations. Absorption of the continuum by the analyte will be negligible. This is true because the bandpass of the monochromator is much larger than the line width of the resonant line. The electronic system then subtracts the deuterium signal from the sample signal.

Zeeman Background Corrections. The application of a strong magnetic field to an atomic metal vapor causes the splitting of degenerate energy levels. This fact has been applied in two different ways to correct for background absorptions. In the first method, the sample chamber is placed in a magnetic field; in the second, the field is applied to the source.

A schematic of such an instrument using the first method (Ref. 38) is shown in Fig. 11. The incident beam of light, before passing through the sample chamber, is chopped by a rotating polarizer into pulses of light that are polarized alternatively parallel ($P_{\parallel}$) and perpendicular ($P_{\perp}$) to the magnetic field ($P_{\perp}$). The magnetic field splits the electronic line into its Zeeman components, a π line that occurs at the same frequency as the original absorbance band, and two σ lines which are shifted to wavelengths slightly greater than and less than the original absorption line. The π component can only absorb light that is polarized parallel to the magnetic field; the $\pm\gamma$ bands can only absorb light perpendicular to the field. When $P_{\parallel}$ passes through the chamber it may be absorbed by both analyte and background, as is illustrated in Fig. 12. When $P_{\perp}$ passes through the chamber, the beam is only absorbed by material producing the background absorbtion, since the magnetic field has almost no effect on this material (Fig. 12). $P_{\parallel}$ may be used as a sample beam and $P_{\perp}$ as the reference beam. The signals from the two beams are then subtracted to correct for background absorption.

The other method of Zeeman correction involves the Zeeman hyperfine splitting of the light source (Ref. 40). This spectrophotometer is diagrammed in Fig. 13. The electronic line profile of the excitation source is split into its perpendicular π and $\pm\sigma$ components. The π band is used to monitor the analyte plus background absorbance and the $\pm\sigma$ bands may be used to monitor the background absorption. The plane of polarization of the π and σ components is rotated using a variable phase retardation plate and then passed through a linear polarizer, which allows light of one and then the other component to impinge upon the detector. The electronics then substracts the two signals to obtain the analyte signal. Spectrophotometers using this configuration are not generally available in stock models, but may be more available in the future. The technique is especially useful in determining Hg in biological samples, which is important

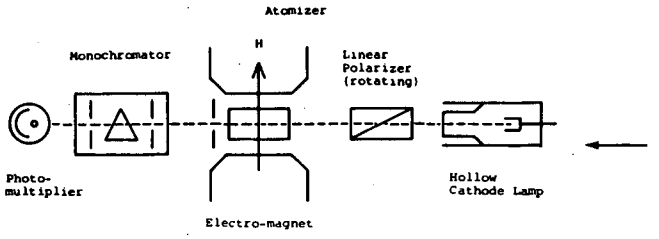


Fig. 11. Schematic design of the Hitachi 170-70 Zeeman corrected atomic absorption spectrophotometer (reproduced from Koizumi and Yasuda, Ref. 38, with permission by Pergamon Press, Inc., copyright 1976).

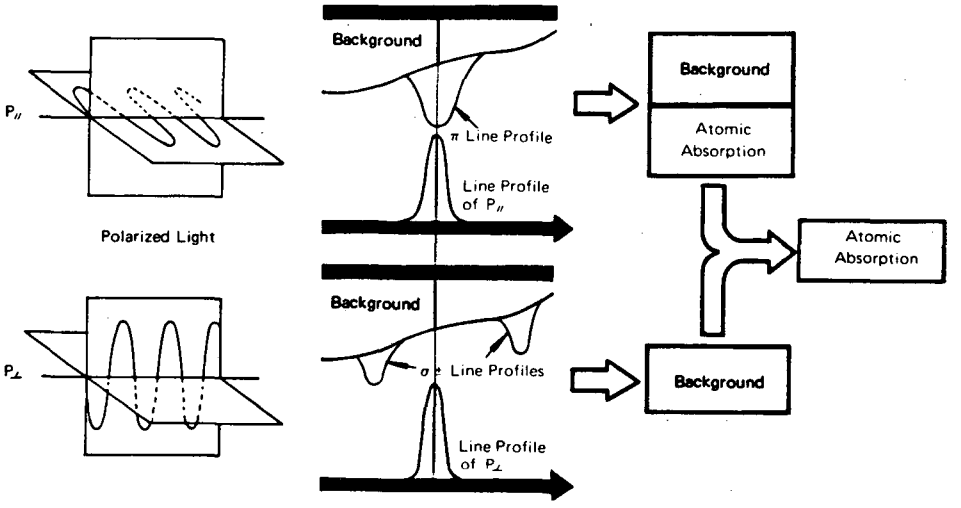


Fig. 12. Schematic representation of Zeeman effect atomic absorption spectrometry (reproduced from the manufacturer's bulletin, with permission by Nissei Sangyo Instruments – Hitachi, Ref. 39, n.d.)

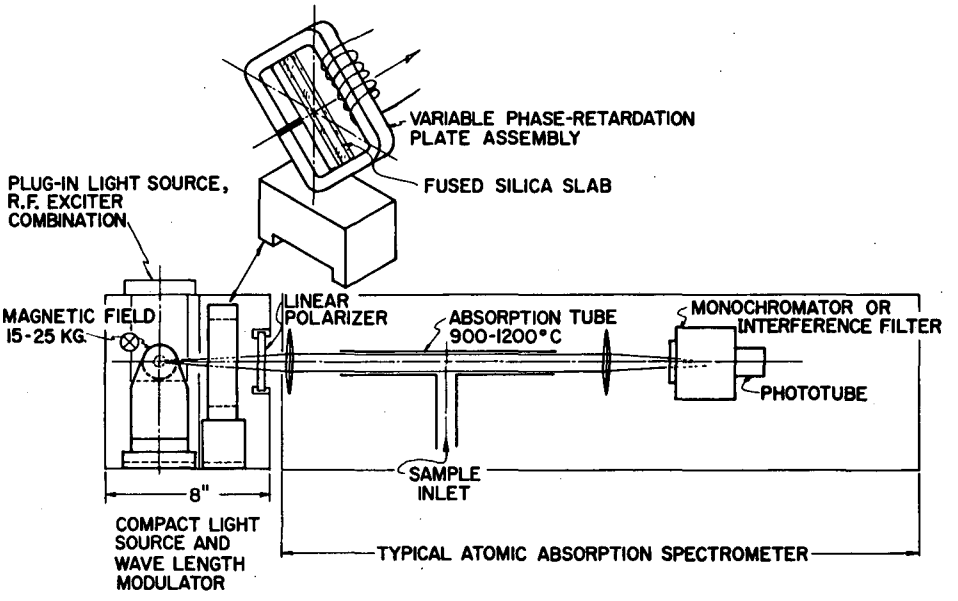


Fig. 13. Schematic design of atomic absorption instrument for isotope Zeeman atomic absorption (IZAA) spectroscopy (reproduced from Hadeishi and McLaughlin, Ref. 40. Courtesy of the authors).

for current biological monitoring. It has recently been developed to determine the same metals that are determined on traditional atomic absorption.

Instrumentally, the technique is able to perform a background correction without the use of the complicated optics associated with double beam instruments. It is presently being used with a large volume furnace that allows different methods to be utilized to reduce molecular formation in the analyte.

7. AA Instrumentation: A Summary

Most AA instruments, commercially produced, rely on the Walsh technique of monochromatic excitation, using hollow cathode lamps and EDL's as excitation sources. The analyst has several choices of instrument parameters:

(a) Flame atomizer, flameless atomizer or both
(b) Single beam or double beam optics
(c) Simple or elaborate data reduction electronics.

(a) Atomizers. Flame techniques are well established, are sometimes not sensitive enough to determine some metals at the levels required for drinking water analysis without preconcentration, and are often the least expensive option. Flameless techniques have excellent sensitivities and detection limits. With the development of automated sampling, reproducibility is good, and the operator can be saved much tedium. The methods used are not as well established, so initially, it may be necessary to have a more highly qualified person to establish a routine procedure for analysis.

Most instruments can function in both modes if an optional flameless attachment is purchased. Although this option is more costly, it allows the analyst considerable flexibility.

If the analyst chooses flame techniques, there is a choice of a variety of burner head materials, which should be chosen based on the nature of the metals, and water to be analyzed. Almost invariably, the atomizing system will consist of a pneumatic nebulizer, a premix chamber and a burner head. The position of the burners is usually adjustable. Some manufacturers provide indicators on all three dimensional adjustments to allow reproduction of the exact position. Others only provide indicators in one or two directions.

In working with water with a high salt content (brines, estuarine waters), corrosive industrial wastes or waters with a large concentration of suspended solids, the analyst should be certain that the atomization system can be easily removed, cleaned and replaced reproducibly.

In using a flameless method, the analyst must decide between the various carbon techniques and the tantalum filament method. The graphite furnace is furnished by most manufacturers and is used for determining most metals. The tantalum technique might be more acceptable if many of the metals to be tested form highly stable carbides.

(b). Optics. AA instruments using a single beam light path are usually easier to operate and less expensive than instruments using a double beam. The optical system is less complicated and does not require the delicate alignment required by double beam instruments.

Double beam instruments are able to perform a simultaneous deuterium arc background correction, and some can be operated to measure two-elements simultaneously. Obtaining a background correction using a single beam AA requires recording a separate background spectrum and subtracting the data or using more sophisticated techniques such as Zeeman AA.

(c) Data Reduction. Data reduction capability available in AA instruments varies widely; from simple meter readout of the absorbance to dedicated computer readout of the concentration. Simple meter readout is least expensive, but requires hand reduction by an analyst. The analyst remains aware of each piece of data generated and the status of the instrument. At the other extreme are instruments which include a dedicated computer or calculator which reads the absorbance values of the standards, constructs the calibration curve, and performs a curvature correction. Some models read the absorbance, calculate the concentration of the unknown solution and print out a laboratory report form. For a laboratory which must process many samples daily, considerable operator and analyst time can be saved by using such a system. These options add considerable expense so that the time saved must be balanced with the expense incurred. A less obvious disadvantage to an instrument with a dedicated computer is the possibility of the operator becoming less aware of its operating status.

2. Atomic Emission Spectrometry

a. Principles of Operation. An atomic emission spectrophotometer measures the light emitted from a metal vapor which has been excited to a higher electronic state. If a metal atom receives sufficient energy, electrons will be excited to higher energy levels:

$$M + \text{energy} \rightarrow M^{*}.$$

The atom can then reemit the energy as light,

$$M^* \rightarrow M + h\nu$$

and return to lower energy levels. The light which is emitted is characteristic of the metals in the vapor. The intensity of the radiated light is proportional to the concentration of excited atoms.

In actual practice, the concentration of a metal in a sample solution is not determined from first principles. As in AAS, the instrument must be calibrated by measuring the emission of a series of standards of known concentration.

b. Experimental Techniques. The solution containing an analyte metal must be atomized and excited to energy levels above the ground state. When the excited electrons fall back to the ground state, the light which is emitted is passed through a monochromator and onto a detector. There are, therefore, three major components in the AE spectrometer: the excitation source/atomizing system, the spectrometer (the dispersive device and optics) and the detection-readout system.

Two types of emission spectrometers are currently in use: conventional flame emission spectrometers and AE spectrometers using a higher energy source. Flame emission spectrometers often use many of the same components and instruments used for AAS. The components are described in section 1b, Atomic Absorption Spectrometry, Experimental Techniques: the instruments appear in the instrument notes for AA spectrometers.

AE spectrometers using a higher energy source, usually a plasma source, either RF, inductively-coupled (ICP) or dc, are also used. Although they can be used with a monochromator, as are conventional AE instruments, they typically use a polychromator (see below).

(1) Excitation Sources. The source of excitation for the conventional AA/AE spectrometer, the flame, system has been discussed in Section 1b.) However, the need for a higher excitation energy source has led to the development of several other sources; inductively-coupled RF argon plasmas (ICPs), DC plasmas, and the laser microprobe.

An inductively coupled RF plasma provides an excellent atomization system and excitation source for AES. The plasma, a gas with a considerable percentage (ca.10%) of its particles ionized, may be induced by an RF field. This field transfers energy into the plasma by accelerating cations in one direction and electrons in the other. The field then reverses and the directions of the ⊕ and ⊖ particles are reversed. As the field alternates, collisions occur, causing greater thermal excitation thus maintaining the plasma. Temperatures can reach 9,000-10,000°K.

The sample is injected into the plasma. Since the temperature is so high, atomization is nearly complete. Chemical interferences are minimal, however the plasma temperature can be effected by sample composition. Atoms have a long residence time in the plasma, leading to greater efficiency of volatilization, a higher probability of excitation and more emission thus enhancing the sensitivity. Table 4 lists the detection limits observed using an RF torch. Applied Research Labs, Fisher-Jarrell-Ash, and Labtest Equipment manufacture atomic emission spectrometers using RF argon plasma torches.

A dc plasma is another high energy excitation source used for atomic emission. A dc plasma is started by arcing a high voltage spark from cathode to anode. Once started, the plasma can be maintained using a low voltage (Ref. 41). The advantages to the dc plasma are the same as those for RF plasma: enchanced sensitivity resulting from more complete volatilization and long residence time in the flame. Spectrametrics for their SpectraSpan III and IV use dc plasma torches; minimum detection limits can be found in Table 4.

(2) Optical Systems. Atomic emission spectrometers can use monochromators and polychromators. Conventional AA/AE instruments use monochromators: the dispersive element moves, allowing the detector to "see" a single frequency at a time. Although this arrangement allows the instrument to determine the concentration of only one or two metals at one time, it enables the analyst to use the same instrument for different elements by changing the wavelength. The gratings and optical design of the conventional AA/AE instruments were discussed in Section 1b above.

Emission spectrometers using a high intensity source, such as an ICP or dc plasma, often use polychromators. The dispersive element is fixed; defining slits and detectors are then placed to monitor frequencies representative of the metals of interest. In this way, it is possible to monitor many metals simultaneously; commercial instruments can typically look at greater than ten metals in one determination and up to 60.

Polychromators require the use of high resolution, highly dispersive grating. The Resolution (R) is a function of the number of lines on the grating, N, and the particular order, m involved,

$$R = mN. \qquad (9)$$

Resolution is also a function of diffraction angle, β, and the width of the defining slit, the aperture of the system (W) and other factors (Ref. 36):

$$R = \frac{2W}{\lambda} \sin \beta.$$

As was mentioned in Section 1b(3) (a) on AAS monochromators, the linear dispersion, that is the actual distance between two diffracted wavelengths of light is $(d\ell/d\lambda) = (mf/d \cos \beta)$ where ℓ is a unit of distance, m is the order, f is the focal length of the grating, d is the groove spacing, and β is the diffraction angle.

High resolution can be achieved by increasing the order used (m), the number of grooves/mm (N), and the total number of grooves. High dispersion can be achieved by increased grooves/mm (N), use of higher orders (m), and use of long focal length gratings (f).

Conventionally, high resolution, high dispersion gratings with long focal lengths use high line density. Applied Research Labs uses a grating ruled with 1080 lines/mm, with a focal length of one meter for its Model ICPQ. The line spacing is not remarkable, but the focal length of one meter is between two and four times longer than the focal length of gratings found in conventional AA monochromators.

An echelle ("ladder" in French) grating uses a high blaze angle, low groove density, and high orders of diffraction to attain high resolution (Ref. 42). The spacing of each step is much larger than the wavelength of the light it is diffracting, and therefore many orders overlap. These overlapping orders are usually separated with a prism placed with its dispersion perpendicular to that of the grating (41, 43, 44). The prism selects a narrow band of wavelengths, so that there will not be interference from other orders. Figure 14 gives the schematic design of a spectrometer using an echelle grating, the SpectraSpan III, made by Spectrametrics. In uses an echelle grating that is ruled with 79 lines/mm (Ref. 41) and a 0.75 m focal length. The orders used are often higher than 100.

To achieve maximum detection limits and high sensitivity for monitoring metals in water, stray light and scatter must be kept to a minimum. This can be achieved by using extremely high quality nearly perfectly spaced conventional gratings and by using higher orders. Labtest Equipment Company uses holographic gratings in its Model ICP-2100. Gratings which are ruled using a holograph are, ideally, nearly perfectly spaced, reducing stray light, scatter and ghosts.

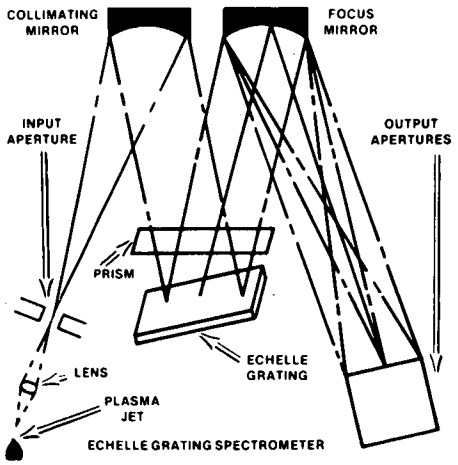


Fig. 14. Schematic design of the Spectrametrics SpectraSpan III (reproduced from the manufacturer's bulletin, Ref. 44 with permission by Spectrametrics, n.d.)

(3) Detection and Readout Systems. The majority of the instruments using an ICP or dc plasma source have the capability to determine several elements simultaneously. The spectrometer system therefore breaks the emission spectrum into a series of lines and detectors; usually photomultiplier tubes (PMTs) are placed at the optimum position for detecting light emitted by the metals of interest. In some spectrographs, the arc formed by the detectors describes the Rowland circle, defined by the focal point for each dispersed wavelength. A typical arrangement is shown in Fig. 15, illustrating the optical system used by the Applied Research Labs ICPQ. Similar arrangements are found in the Labtest Equipment ICP-2100 and the Jarrell-Ash ICAP.

The output of instruments using echelle gratings and a prism presorter is in a 2 dimensional x-y array (Fig. 16). Detectors are placed at the optimum positions to observe the frequencies representative of the metals of interest.

Because the readout consists of simultaneous determinations of a large number of elements, (frequently as many as 30), and because of the large amount of data handling this entails (calibration, zeroing, background correction, and computation of concentrations), the output of the PMTs are fed directly into a computer.

(4) AE Instrumentation: A Summary. Two types of atomic emission instruments are used commonly for monitoring metals in water: conventional AA/AE instruments and AE instruments using a plasma source. Conventional AA/AE instruments use the flame as an excitation source, and a monochromator

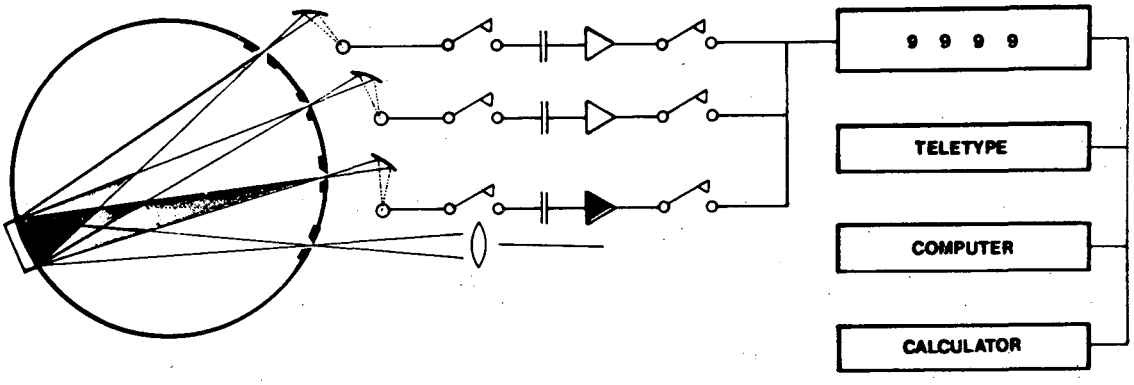


Fig. 15. Schematic design of the polychromator used in the Applied Research Labs., ICPQ (reproduced from the manufacturer's bulletin, with permission by Applied Research Laboratories, Ref. 45, n.d.)

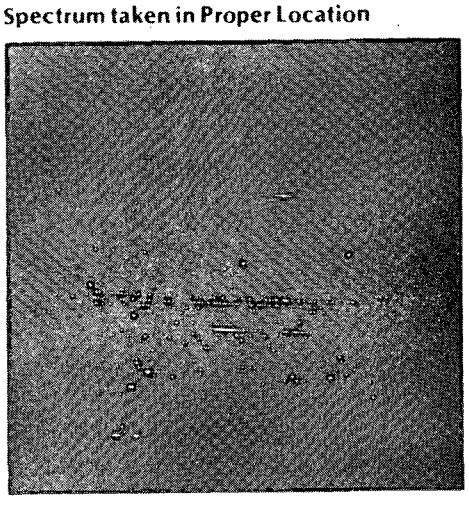


Fig. 16. The spectrum produced in the Spectra-Span III spectrometer which uses an echelle grating in conjunction with a prism to sort the orders. (Reproduced from the manufacturer's bulletin, with permission by Spectrametrics, Ref. 44, n.d.)

which monitors a single metal at a time. Because no light sources other than the atomizer are necessary for AES, it is quite possible to perform qualitative as well as quantitative analyses, a flexibility which may become important to even the smallest water monitoring lab. A new pollution source could introduce metals to a body of water which were not previously anticipated and may not be reported to the lab. Routine qualitative analyses would alert the lab of their presence.

Conventional AA/AE instruments are of only moderate size and expense and usually may be used for AA as well as AE. A dedicated computer will perform similar calculations for both modes. Spectrometers using a plasma source often employ a polychromator which has the option of monitoring many metals simultaneously. Some commercial instruments, the SpectraSpan IV for example, monitor only a single element at one time, or have a scanning monochromator as an option.

Although AE is not the method recommended in 40 CFR 136 for determining most metals-in-water, one ICP, the Jarrell-Ash ICAP, has been approved as an alternative method by the EPA for Region V (Chicago) and is used for monitoring the waters of that region (Ref. 46). (See Introduction to this volume for alternative method approval - an alternative method must be approved for each user, not each instrument).

Because separate light sources for each element are not necessary, it is possible to perform simultaneous multielement determinations, which can save considerable operator time. The use of a plasma torch as an excitation source is claimed to reduce the matrix effects encountered in lower energy flames. Matrix effects are encountered (Ref. 43) but the software provided with most of the instruments helps to compensate for them.

One of the greatest disadvantages encountered with instruments using plasma sources, dedicated computers, and large capacities for simultaneous multielement determinations, is the cost. They vary in price from $14,000 for a basic instrument which can only perform sequential quantitative analysis to greater than $50,000 for an instrument able to determine 40 metals simultaneously. A second problem is the size; all but the SpectraSpan III and IV require considerable

space-often an entire room. Finally, they are complex, sophisticated instruments, which require the attention of skilled personal.

3. Atomic Fluorescence Spectrometry

a. Principles of Operation. An atomic fluorescence spectrometer measures the light emitted by an atom which has previously been excited by an outside source. The technique involves both atomic absorption and emission. Light from a high intensity source impinges upon a vapor containing the analyte atoms. If the energy of the light (photons) corresponds to the difference in energy of the electronic states of the metal, (i.e. $h\nu$ = energy difference) the light may be absorbed:

$$M \xrightarrow{h\nu} M^*.$$

The energy which was absorbed will then be released:

$$M^* \longrightarrow M + \text{energy}.$$

The energy is released as radiative energy (light) i.e., luminescence, or by non-radiative processes, such as collisional transfers.

In AFS, if a metal is illuminated by a line source, it will usually luminesce at a frequency level lower or equal to that of the excitation source. Occasionally there can be a two step excitation in which case the emission can be at a higher frequency.

When a metal atom is irradiated, several processes can occur which are illustrated in Fig. 17. An electron in the atom may be excited directly (17a) or in a stepwise fashion

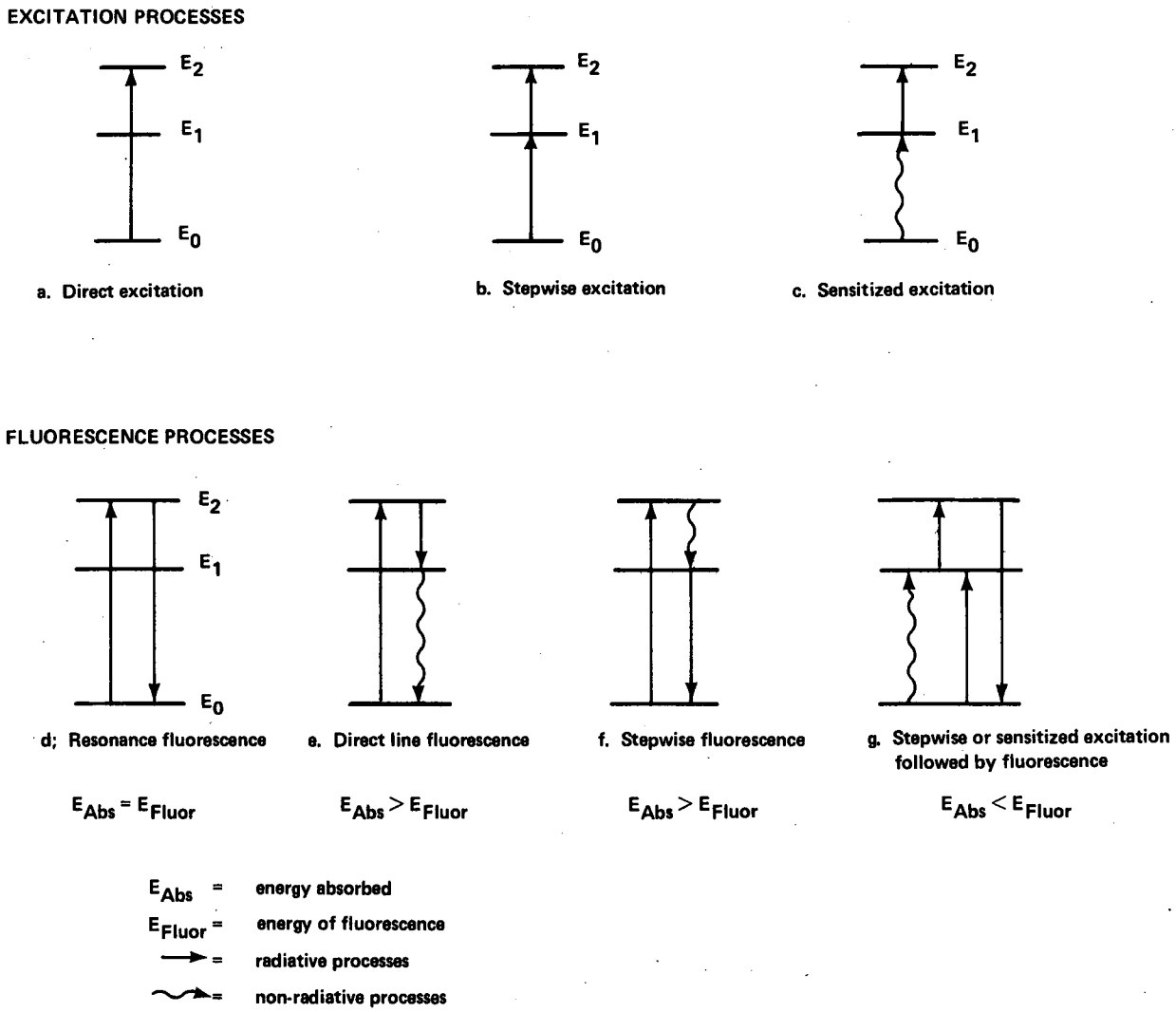


Fig. 17. Electronic transitions observed in atomic fluorescence spectroscopy (adapted from Ref. 15).

(17b) to the level E_2. Stepwise or sensitized excitation involves the absorption of two photons to reach an energy level which is equal to the sum of the energy of the two sources. It may then undergo resonance fluorescence (17c), direct line fluorescence (17d) or stepwise fluorescence (17e). Or, of course, the electron may decay entirely by non-radiative processes (not shown). As Fig. 17d shows, resonance fluorescence involves the reradiation of light of the same energy as that absorbed from the excitation source. This is a very commonly observed type of fluorescence. Another common process, direct line fluorescence, occurs when there are allowed transitions to energy levels between the level that the electron is occupying and the ground state (Fig. 17e). The atom luminesces as it decays to an intermediate level. The energy of the fluorescence line will be of lower energy and longer wavelength than that of the excitation source. Stepwise fluorescence (Fig. 17f) occurs when the first transition from an excited state involves non-radiative transfer of energy. If a radiative transition is allowed between the state the electron occupies and the ground state, fluorescence can occur. The energy of the line will be at lower energy and longer wavelength than that of the source. If an electron, which has been excited by sensitized or stepwise excitation, decays to the ground state, the energy of the fluorescence may be higher than that of either of the excitation sources.

The relationship between the intensity of the fluorescence line and the concentration of the analyte metal atom is complex. Many factors other than analyte concentration can effect the measured intensity of the fluorescence of an aerosol. The fluorescence quantum efficiency (the number of fluorescing atoms per quantum of light hitting each atom) depends upon the number of quenching molecules in the atomization system, which collisionally deactivate an excited species. The quenching molecule may itself become excited or it may dissociate. Scattering of light from particles in the aerosol also effects the measured intensity. (The derived relationship between the intensity of measured fluorescence and analyte metal concentration is described in Ref. 47). Because of the complexity of the theoretical relationship, determinations are usually made by calibrating the instrument using solutions of known concentration.

b. Experimental Techniques. The techniques used are very similar to those used for conventional AA and AE, using a slightly different configuration which is illustrated in Fig. 1. The solution containing an analyte metal atom is atomized and excited to higher energy levels using an outside source for excitation. When the absorbed energy is reemitted light is given off in all directions. The detector is placed in a position perpendicular to the atomizer-source axis. It is therefore able to detect the fluorescence without detecting the source radiation, which minimizes the background and enhances the signal to noise ratio.

The instrumentation involved is often an adaptation of the techniques discussed above for atomic emission and atomic absorption. The systems components are the excitation source, the atomizing system, the monochromator and the detector. Since this technique is not yet considered a "Standard Method", it will be discussed only briefly in this section. The interested reader is referred to Refs. 15, 16 and 47 and the references contained therein for a more complete discussion.

(1) The Atomization System. The atomization should be designed to atomize the analyte material efficiently to reduce sensitivity loss (non-atomized analyte will not fluoresce). It should have a low background emission, since the technique is primarily an emission technique. Finally, it should have a low concentration of quenching molecules to prevent loss of sensitivity caused by a low quantum efficiency (Ref. 16).

Both flames and furnaces have been successfully used as atomization systems. Furnaces appear to be advantageous for use in AFS since they provide much less background radiation. They also provide more complete atomization, reducing matrix effects and scatter, and fewer gaseous molecules to quench fluorescence.

(2) The Excitation Source. (Ref. 16). Since conventional hollow cathode lamps are often not of high enough intensity, several other sources have been tried. Special high intensity hollow cathode lamps have been constructed using a pulsed current or an auxiliary electrical discharge. Metal vapor lamps, sealed arc discharge lamps and electrodeless discharge lamps have also been tried. Recently experiments have been made using tunable-dye lasers as excitation sources. These lamps are of extremely high intensity, but cost is still excessive for routine work. Experimentation has also been undertaken with a continuum light source. A continuum source requires only a single excitation lamp, but currently the sources available are not of high enough intensity to produce acceptable detection limits.

(3) Dispersive Devices. (Ref. 16). If a line source is used then only very simple dispersive devices are necessary. Any spectrometer used for atomic absorption or emission would be more than adequate. It has even been demonstrated that this sort of system can work without a monochromator.

4. Summary

a. Comparison and Evaluation of Atomic Spectrometric Techniques. Atomic absorption, emission and fluorescence spectrometry are all techniques used for determination of metals in water, based on the principle that light emitted or absorbed occurs at lines characteristic of the metal involved, and the amount of light absorbed or emitted by a given metal vapor is in some way proportional to the number of absorbing or emitting atoms. All three techniques are very sensitive for a wide variety of metals. Minimum detection limits are compared in Table 4 which illustrates the variation in the detection limits from metal to metal and instrument to instrument.

Atomic spectrometric techniques are not useful for elucidating the form in which the metal appears. For example, using AAS it is not possible to distinguish between the concentration of Cr(VI) and that of total chromium. Standard Methods (Ref. 3) recommends the extraction of Cr(VI), followed by AA determination). Atomic techniques cannot distinguish between inorganic or organic forms of a metal. For example, AAS is not used to determine whether the mercury in a sample is $HgCl_2$ (inorganic) or methyl mercury (organic).

Each of the techniques has advantages and disadvantages for use in monitoring metals in water. They are reviewed below.

(1) Atomic Absorption Spectrometery. Atomic absorption spectroscopy is by far the most widely used technique for monitoring metals in water. It is recommended by 40 CFR 136, for use by monitoring laboratories for determination of most metals. Because this technique is widely used, many manufacturers and experimentalists have spent a great deal of time developing the techniques and the instruments used. Instruments currently available are relatively easy to use and readily automated. Many have options for background correction using single and double-beam techniques. Microprocessor-controlled instruments perform much of the tedious calibration and zeroing procedure, and may even perform instrument diagnostics. Most important, a single AA instrument is able to determine most of the metals a monitoring laboratory might need to detect.

Many of the disadvantages of atomic absorption are associated with the use of sharp line excitation sources. Since a separate source is needed for each metal, it is difficult to perform qualitative analyses. Instruments are rarely designed to allow for determinations of more than one metal at a time, and purchasing a line source for a variety of metals is expensive and frequent changing of lamps is time consuming. AA instruments need to be recalibrated frequently since calibration curves are rarely linear over large concentration ranges and are effected by sample matrix.

(2) Atomic Emission Spectroscopy. This technique is less widely used than AAS, and is recommended by the EPA for only a few methods. Because many conventional AA instruments can operate in an emission mode, it is not necessary to purchase a separate instrument if the laboratory already has or will be purchasing an AA. Since no spectral line sources other than the flame are necessary, it is possible to perform qualitative analyses with AES using a scanning monochromator.

AES using plasma sources and polychromators are able to determine quantitatively many elements simultaneously. Minimum detection limits are sufficiently low in many cases. While it is not possible to perform qualitative analyses with a polychromator, (since a detector is positioned to monitor each specific metals) many instruments can be used with a scanning monochromator or what ARL calls a scanning polychromator, which diffracts successive wavelengths of emitted light onto a single detector or multiple detectors.

The disadvantages of AES are largely technical. Operators must be skilled in order to obtain reproducible results. (This same statement can and should be made for any techniques.) The intensity of the line is dependent upon the temperature of the plasma. It is necessary to have a high resolution dispersive element in order to avoid spectral interferences (Ref. 15), which can add to the cost of the instrument. Additional expense is incurred with systems using a polychromator because of many detectors and the sophisticated data readout and analysis systems necessary. Even with the best of systems, the detection limits achieved in some cases are not low enough to effectively monitor some trace metals without some preconcentration.

(3) Atomic Fluorescence Spectroscopy. AFS is less frequently used in water monitoring laboratories than either AAS or AES. Nevertheless, the technique has advantages. The equipment employed can be simple. Only a high energy excitation source is necessary to increase sensitivity. Normally, high intensity, sharp-line sources are used in which case no dispersive elements is required. However, continuum sources and broad-line sources can be used. In this case a dispersive element is required.

The technique can be costly if line sources are used in determining a wide variety of metals. Quenching caused by molecules in the atom cell and scattering caused by unatomized particles can reduce sensitivity considerably.

b. Comparison of Instruments. It is a difficult task to compare a large number of complex instruments, particularly when a wide variety of options are offered. The reader must consider the analysis which must be made and the instrument which best suits his needs. He should also consider the cost of the instrument, the reputation of the manufacturer involved, and the service, delivery, and training available. In preparing the instrument notes on atomic spectroscopy instruments, an attempt has been made to provide as much of the same information in the same units as possible for each instrument. This was not always possible. Where information was unobtainable the instrument note has a blank. Some of the manufacturers provided additional information which was included wherever possible.

5. Description of Instrument Notes. For atomic absorption instruments, the information included is:

a. Section - in the Mnemonic, H20-MET, Notes, AAS or Notes, AES.
b. Manufacturer and Note Designation - usually an abbreviated form of the manufacturer's name, for example, the Jarrell-Ash Division of Fisher Scientific Company is abbreviated, "Fisher, Jarrell-Ash". This designation is in the mnemonic. Following the manufacturer's name is the number of the instrument note. A manufacturer may make several instruments under several designations; they appear in increasing numerical order. Several instruments may appear in one note. Accessories are labeled by letter: hollow cathode lamps appear as accessory A, electrodeless discharge lamps as accessory B, graphite furnaces as accessory C; others follow in alphabetical order. If a company does not market electrodeless discharge lamps, no acessory B appears.
c. Date and Page - The data is the date on which the manufacturer mailed the instrument notes he had reviewed. If for some reason the manufacturer did not return the notes, the date is that of the last contact with him.
d. Type of Instrument, and Model name - for example:
   Atomic Absorption Spectrophotometer
   Perkin - Elmer Model 460
e. Class - The note will designate whether the instrument is primarily used in the laboratory, under controlled conditions, or in the field, that is, able to withstand a possibly hostile environment.
f. Description - A brief description of the instrument, noting its major distinguishing features.
g. Modes of Operation - identifies which techniques can be applied, (i.e. AAS, AES or AFS.)
h. Lower Limit of Detection - supplied by the manufacturer.
i. Multielement Capability - The number of elements detectable and the number detectable simultaneously.
j. Sampling - The method available, batch or automated; the volume of sample necessary and in considering graphite furnaces the volume possible, and the capacity.
k. Performance and Specifications - The electronics, monochromator and gas control are described.
l. Operation - Gives the method of calibration, the maintenance necessary and the training required or available for operators.
m. Requirements - Lists the power required, the space necessary, and the weight of the instrument.
n. Features - Lists the features included on the basic instrument.
o. Options - Lists the major options available for the instrument and their cost.
p. Cost - Gives the price of the basic instrument, or if the instrument is modular or custom designed, the price of a representative instrument.
q. Address.

Atomic emission instruments appear under two classifications. The conventional instruments which are part of atomic absorption instruments appear as atomic absorption instruments. Their capability for use as AE spectrophotometers is noted under "Modes of Operation". Atomic emission instruments which incorporate plasma sources and polychromators are included in instrument notes which follow the atomic absorption instruments, and are labelled "Atomic Emission Spectrometers". The information regarding these instruments is largely the same except for the information included in item (k) Performance and Specifications and (m) Requirements. Item (k) describes the Electronics, the Polychromator, the Computer (if the information was available), the Argon Gas Control, and the Source. Item (m) gives the power requirements of the source and the instrument, the coolant necessary, any temperature and humidity requirements. Finally it gives the overall dimensions and weight, if they are available.

No instruments which are used only for AFS are included in the instrument notes; however, many of the manufacturers are willing to adapt their commercial instruments to allow for AF measurements.

6. Acknowledgments

The author is grateful for the help, suggestions and criticisms of Mark Tatro, Mike Routh, Ralph McLaughlin and George Morton.

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CONTENTS

B. Ultraviolet–Visible Spectroscopy

UV-visible spectroscopy depends upon the absorption or emission of electromagnetic radiation by molecules in solution. Each molecule has associated with it, electronic levels, vibrational levels and rotational levels. (See. Fig. 1). When light impinges upon a molecule, the molecule may be excited to higher energy states. Figure 2 shows the electromagnetic spectrum, giving the commonly designated terms for various energy ranges and wavelengths. If the light impinging upon the molecule is relatively low energy, (< 150 μm), primarily rotational levels are excited (in-infrared or microwave region). Light with wavelengths in the infrared (~ 0.8 to ~ 150 μm), corresponds to the energy separation of vibrational levels. The energy of light in the ultraviolet and visible (hereafter UV-vis) corresponds roughly to the energy separation between outer electronic levels.

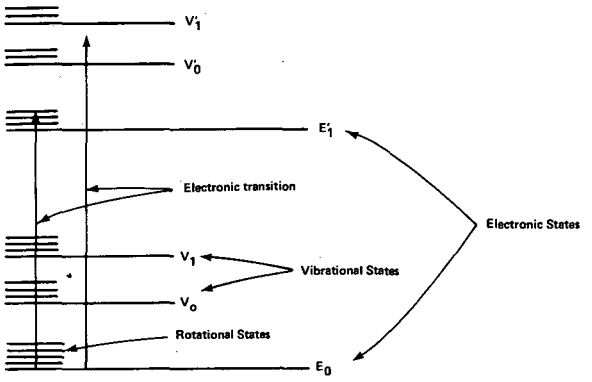


Fig. 1. Energy levels of a diatomic molecule.

UV-vis light falling upon many types of molecules in solution can be absorbed and re-emitted. The position of the absorption or emission maxima (absorption or emission bands) is strongly dependent upon both the metal and the other species in solution. It is possible theoretically, but rarely practically, to use UV-visible molecular spectrometry for qualitative analysis.

The amount of light absorbed or emitted is directly related to the concentration (in

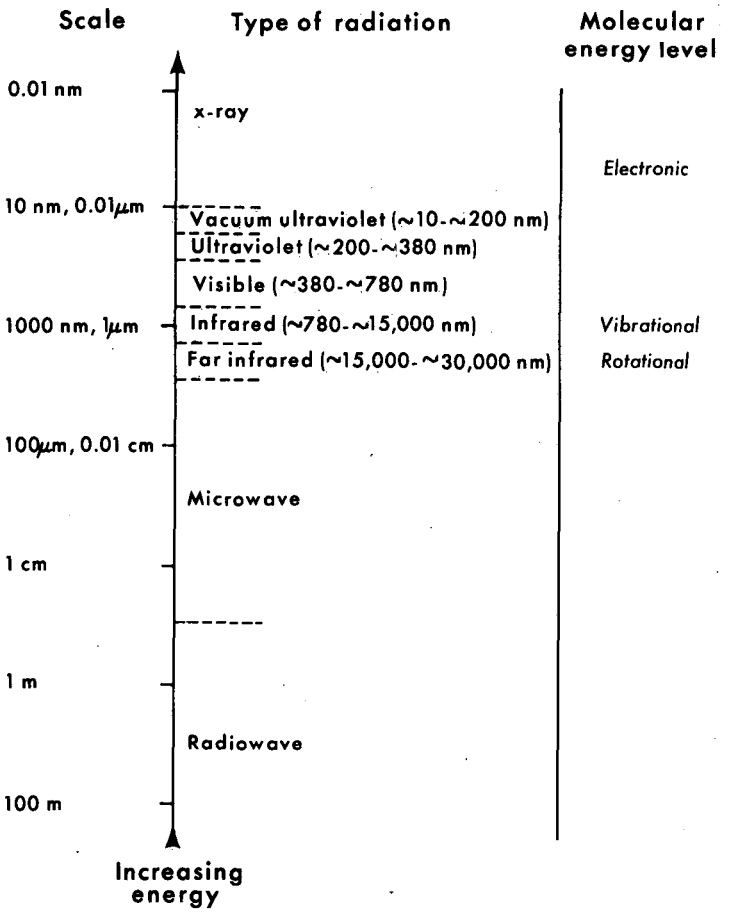


Fig. 2. Electromagnetic spectrum.

grams) of metal complex present in a solution. Measurement of the intensity of these bands provides the basis for determining the concentration of metals in water. To perform a quantitative analysis for a metal, a known complexing agent is added to a solution containing the analyte atom to form a complex which has energy transitions in the UV-visible. The magnitude of the absorption (or emission) maximum is determined, and compared to the magnitude observed when solutions of known concentrations of the compound are measured. To optimize the procedure, an analyst should (1) choose a complex which has an intense band, and is easily formed, (2) verify that the desired species has been formed, (3) choose a species which enhances absorption or emission, (4) determine the best wavelengths to relate intensity and concentration (5) be aware of interferences and (6) recognize other sources of error in the procedure.

This section will first discuss the principles of molecular absorption and emission spectrometry (Section IV,B,1. Principles of Operation). The next Section (IV,B,2) Experimental Techniques, describes the instrumentation used in making optical molecular absorption measurements. Section IV,B,3 summarizes molecular UV-visible techniques and Section IV,B,5 gives the references. A table of the instruments surveyed and the Instrument Notes appear at the end of the Metals in Water Section, after the Atomic Spectrometry Notes. All instruments covered will use the mnemonic UV-VIS, including some which technically operate only in the visible.

1. Principles of Operation

When UV-visible light impinges upon metal compounds, light may be absorbed (Fig. 1) by the molecule. When the light is reemitted, the process is termed luminescence. A variety of instruments, visual comparators, colorimeters, and UV-visible spectrophotometers, can be used to measure absorption in the UV-visible. The theoretical principles which serve as a basis for their design are discussed in Section 1a below; the experimental techniques used in absorption spectrometry are discussed in Section 2a. The principles of operation for instruments measuring luminescence are discussed in Section 1b below; experimental techniques used in measuring fluorescence are discussed in Section 2b.

a. UV-Visible Absorption Spectroscopy. Many metallic compounds when in aqueous solution appear brightly colored because the molecules in solution have selective absorptions in the visible portion of the electromagnetic spectrum. Since the depth and type of the color is dependent upon the compound present and its concentration, colorimetric methods are used for determining the concentration of metals in water. The color of a metal compound in solution is a function of its entire visible spectrum which involves electronic transitions, together with superimposed vibrational-rotational broadening or fine structure. Historically, colorimeters compared the depth of color of an unknown solution to the intensity of color of a series of standards. With the development of the Beckman DU in the early 1940's, spectrophotometric determinations of absorption in the visible portion of the spectrum became very much more precise. The DU enabled the analyst to measure the absorption of a solution at a particular wavelength quickly and easily. Later, the wavelength range covered by commercial instruments was extended from the visible ($\sim$350 - $\sim$800 nm) to include the ultraviolet ($\sim$200 - $\sim$350 nm) as well.

The UV-visible spectrum of a molecule is a function of the electronic energy level separations in the molecule which determine the wavelength of light absorbed (Section (1) below) and the probability of electronic transitions occurring, which determine the relative intensity of absorption bands (Section (2) below). The absolute intensity of a given absorption is a function of the relative intensity of the band, the path length of light through the absorbing solution and the concentration of the absorbing species (Section (3) below).

The reader who is interested in more detailed information regarding UV-vis theory of absorption should refer to the excellent texts by Drago (Ref. 1) and Cotton and Wilkinson (Ref. 2). For further description of the analytical techniques involved, the texts by Willard, Merritt and Dean (Ref. 3) Brown and Sallee (Ref. 4) and Winefordner (Ref. 5) provide a good introduction.

(1) Wavelengths of Absorbed Light. The bands in a UV-visible spectrum of a metal compound arise primarily from electronic transitions, which may be placed in four categories: (1) electronic transitions localized on the metal atom (2) transitions localized in the ligand system (3) transitions between energy states which are non-localized and (4) charge transfer bands, which arise from transitions between levels localized in the metal to those on the ligand system or vice versa.

To explain the position of molecular absorption bands in the UV-visible spectra of metal compounds, it is necessary to consider the electron configuration about the metal atom. Factors which effect the electronic configuration of the metal in a compound are: the electronic configuration of the uncombined

metal atom and the species with which it combines because the components of the complex effect the field the metal experiences.

- Transitions Localized on the Metal Atom

A metal atom in a vapor has a series of electron levels which depend upon the nuclear charge and the number of electrons present within the atomic radius. Electronic transitions between the outer energy levels often involve a change in energy (ΔE) which occurs in the UV-vis. For example, in the transition metals, the lanthanides and the actinides, electronic transitions within the unfilled d and f orbital can occur in the UV-vis region. Given a specific metal atom, one major factor determining the energy separation of its electronics energy levels is the number of electrons about the atom. For example: [Fe^{+++}] complexes which have 5 electrons in the d orbitals plus its inner shell electrons are often reddish in color, whereas [Fe^{++}] complexes are often greenish or yellow.

A second factor is the electronic field about the metal atom. Figure 3 shows the d orbitals of a transition metal in the vapor phase (single electron approximation) which are degenerate (at equal energy). When a metal atom is brought into an electric field, such as that of solvent molecules or complexing agents, its outer shell electronic levels are perturbed. Orbitals which, in a spherically symmetrical field, are of the same energy (degenerate), when placed in a less symmetric field, may have different energy levels (the degeneracy is removed). For example the five 3d orbitals which are normally degenerate when brought into an octahedral field, split into two levels, one triply degenerate, the other doubly, shown in Fig. 3. Other fields can change the relative position of the orbitals, for example a tetragonally distored field can further reduce the degeneracy of the d levels (Fig. 3). Figure 3 shows several typical field symmetries and the orbital splittings which occur due to those fields. The number of levels depends upon the shape of the field present and the magnitude of splitting depends on the field strength, for example, Ti^{+++} in an octahedral field, has a single d electron in the t_{2g} orbitals. If it interacts with a wavelength of light of energy equal to the separation between the t_{2g} and eg orbitals, it will absorb light, often in the UV-vis region.

- Electronic Transitions Localized in the Ligand

Transitions which take place within the electronic energy levels associated only with the complexing agent are said to be "localized" on the ligand. An arrangement of atoms within a ligand which has electronic energy level separations in the UV-visible is termed a

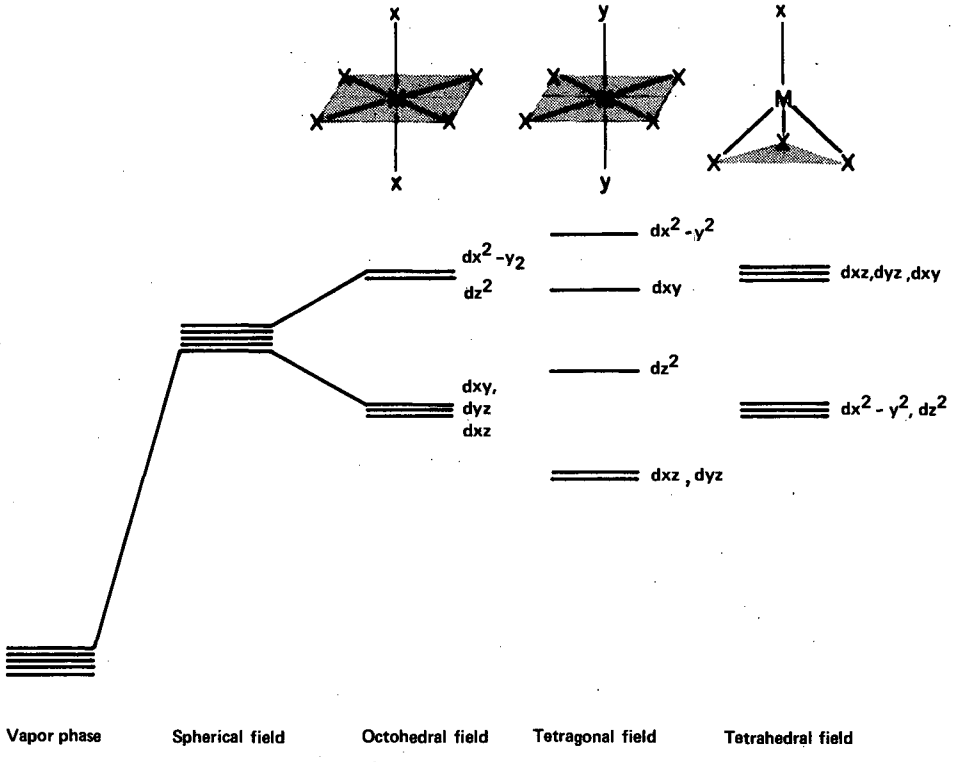


Fig. 3. Splitting of transition metal d-orbitals in various coordination geometries (Ref. 1).

chromophore. Such arrangments are sometimes part of the ligands surrounding the metal atom of interest. Chromophores often have one or more points of unsaturation, parts of a molecule where the bond between two atoms is made of the electronic overlap of two s orbitals and two p orbitals (a π bond), and therefore could accommodate further bonds with other atoms. Electronic transitions within a π bond often occur in the UV (see Table 1). If a molecule has more than one point of unsaturation often referred to as an extended π-system (i.e. anthracene, $(C = C)_2$ etc., see Table 1), electronic transitions associated with them may fall in the visible. [For a further discussion of organic chemistry and bonding, the interested reader is referred to a text, such as that by Morrison and Boyd (Ref. 7)].

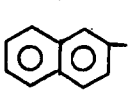
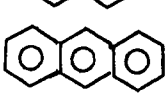
While electronic transitions associated with chromophoric groups are extremely valuable for quantitative and qualitative analysis of organic systems, they are less useful for quantifying metals in water.

- Electronic Transitions Involving Molecule Orbitals and Charge Transfer

When a ligand and metal atom react to form a molecule, some of the orbitals associated with the metal remain primarily associated with the metal. Some associated with the ligand remain primarily ligand orbital. Some orbitals on both the metal and ligand will combine to form molecular orbitals. Electronic transitions between various molecular orbitals may also occur within the UV-vis.

If an electron primarily associated with the metal atom is excited to an orbital associated with the ligand (or vice versa) this transition is called a charge transfer transition. Charge transfer transitions associated with metal-ligand complexes, such as $[CuCl]^+$, $[Fe(SCN)]^{2+}$ and $[PbI]^+$ are usually very intense. Because the bands are so intense, they are well suited to sensitive measurements of trace amounts of metals.

Table 1. Chromphoric groups and associated electronic transitions (adapted from Kolthoff and Elving, Ref. 6)

Chromophore	λ max (nm)	log t
-C=C	190	3.5
$-(C=C)_2$	220	4.2
$-(C=C)_3$	260	4.6
-C≡C	180	< 2
-C=N	190	3.7
-C≡N	170	< 2
-C=0	280	1.3
-COOH	210	1.6
-CONH	210	2.2
 (phenyl)	270	2.4
 (naphthyl)	310	2.4
 (anthracene)	380	2.8

To summarize, the electronic configuration of a metal is strongly perturbed by adding or removing an electron from the complex that is changing its oxidation state. It is also perturbed by the shape and strength of the ligand around it. For example, six $[CN]^-$ about $[Fe]^{+++}$ produce a stronger field and greater splitting than six Cl ions. Changing the temperature and magnetic field can also alter the configuration. Further discussion of electron configuration and electron orbital splitting can be found in Refs. 1,2.

(2) Intensity of Molecular Absorption. The relative intensity of absorption bands depends upon the ability of the compound to absorb light; that is, upon the probability of one of the four types of the above transitions occurring.

A series of "selection rules" are used to predict the probability of an electron transition:

- Electron transitions in which the electron spin changes are forbidden (changes in multiplicity are forbidden).
- If a molecule has a center of symmetry, transitions in which the angular quantum number l, does not change are forbidden.
- "Simultaneous excitation of more than one electron is forbidden". (Ref. 1).

In predicting the likelihood of transitions, "forbidden" becomes less absolute. Breakdown of the selection rules occurs because the rules rely on simplifications. For example, a transition involving a multiplicity change is not allowed in an electronic transition. If fact, because of interaction between the magnetic field of the electron and its orbit (spin-orbit coupling), a singlet state may have some small amount of triplet character, and vice versa. In this case there is overlap of the wave functions and the supposedly forbidden transition occurs. The more forbidden, or the more selection rules a transition appears to break, the weaker the intensity of the absorption band.

The molar absorptivity is a coefficient which provides a quantitative measure of the probability of a transition occurring, per mole of molecules in solution. Theoretically, it depends upon the square of the value of an integral involving the wavefunctions of the initial state, final state and the electric dipole moment between these states. Since all the above factors are difficult to predict quantitatively, the molar absorptivity is determined empirically.

(3) Intensity of Absorption by Solutions. By the eighteenth century, it was found that for dilute solutions, the intensity of light (I) transmitted through a homogeneous solution containing an absorbing species obeys the relationship:

$$I = I_0\, 10^{-abc} \qquad (1)$$

where

I_0 = intensity of incident light
a = absorptivity
b = path length of the absorbing medium
c = the concentration of the absorbing substance.

This expression, the Beer-Lambert Law, may be reformulated

$$\log \frac{I_0}{I} = abc. \qquad (2)$$

As was mentioned in the section on atomic absorption, the quantity, $A = \log (I_0/I)$ is experimentally easy to determine and is defined as the absorbance. This equivalence allows a further reformulation of the equation:

$$A = abc. \qquad (3)$$

The absorptivity of the compound in solution is empirically determined by plotting the concentration of a series of solutions versus the measure absorbance at constant wavelength, path length and temperature. Once the absorptivity is determined, it may be used to calculate the concentration of solutions with unknown concentrations.

b. Molecular Luminescence. When a molecule absorbs energy and then reemits it as light, it is said to luminesce:

$$MX_n + \text{energy} \rightarrow MX_n^* \rightarrow MX_n + h\nu.$$

Two types of molecular luminescence have been defined, fluorescence and phosphorescence. Fluorescence occurs immediately after the molecule is excited, usually within milliseconds. The electronic transition involved is a spin-allowed transition, as is illustrated in Fig. 4. Luminescence which is delayed is called phosphorescence, and is associated with a spin or multiplicity forbidden transition (Fig. 4). An electron which is excited to a higher energy level may undergo "intersystem crossing", changing from one multiplicity state to another. In order to decay to the ground state, E_0, by luminescence, it must undergo a forbidden transition; this is the cause of phosphorescence. An electron excited to an allowed or forbidden state may also decay by a radiationless transition, dissipating its energy through collisional transfer.

The photon energy emitted in fluorescence may be the same, greater or less than the

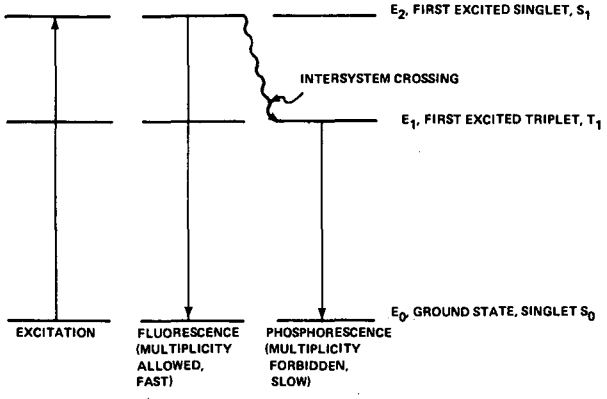


Fig. 4. Mechanisms of luminescence (Refs. 1, 3).

photon energy of excitation. Phosphorescence usually occurs at energies lower than the energy of excitation, but in rare cases can occur at the same or greater energies. Mechanisms of luminescence and the relationship of the luminescent to the excitation energies are shown in Fig. 5. As Fig. 5 shows excitation may be direct, sensitized, or stepwise. In direct excitation, the energy separation of the initial and final steps is equal to the energy of excitation at a single wavelength. Sensitized excitation involves absorption of radiationless energy, such as thermal or collisional, for one of the excitation steps. Stepwise excitation involves the absorption of photons of two exciting frequencies; the frequency separation between the initial and final steps being the sum of the two exciting frequencies.

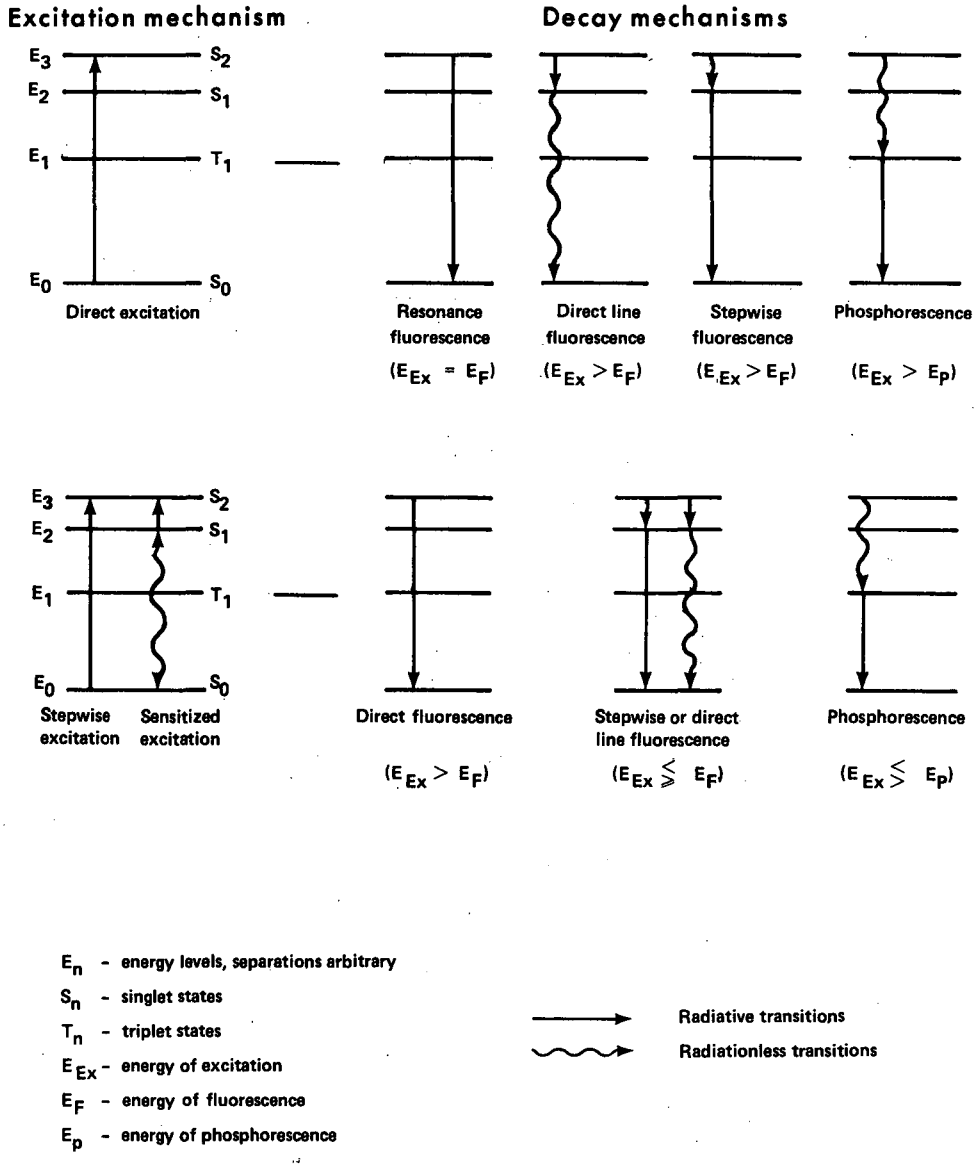


Fig. 5. Several mechanisms which produce luminescence (Refs. 1, 3, 8).

In resonance fluorescence, excitation is to and reradiation is from the same energy level, therefore the energies of photons absorbed and emitted are the same. Direct excitation followed by direct line fluorescence (luminescence to an allowed energy level above the ground state), stepwise fluorescence (luminescence to the ground state following a radiationless transition to an intermediate state) and phosphoresence all occur with photons of energies lower than that of the absorbed photon.

Stepwise excitation followed by fluorescence or phosphorescence can result in frequencies greater than, equal to or less than the excitation frequencies depending upon the energy levels of the initial, final, and intermediate levels.

The intensity of luminescence is a function of the extinction coefficient of the luminescing molecules, ε (which is equal to the absorptivity of the molecule, a, times the molecular weight), the luminescing efficiency, ϕ, the path length, b, the concentration, c, and the intensity of the exciting beam:

$$\text{Luminescence} = k\phi I_0 (1-e^{-\varepsilon bc}). \qquad (4)$$

The factor k was introduced to account for instrument variations and the fact that not all luminescence is detected. The derivation of this equation is straightforward and can be found in Ref. 3.

For dilute solutions Eq. 4 can be approximated:

$$\text{Luminescence} = k\phi I_0 \varepsilon bc. \qquad (5)$$

It is therefore possible to determine $k\phi e$ experimentally by plotting the intensity of emitted light versus the concentrations of known solutions.

2. Experimental Techniques

There are numerous techniques for measuring molecular absorption and fluorescence in the UV-visible portion of the spectrum; many have been used for determination of metals in water, since many metals, particularly the transition metals, which have unfilled d orbitals, form brightly colored complexes in solution.

In Section 2a the techniques used for determining molecular absorption of metals in the UV-visible are described. Instrument notes for UV-vis spectrometers are included at the end of the Metals-in-Water Section, after the Atomic Spectrometer Instrument Notes. Instrument notes for molecular fluorimetry (luminescence) will be included in the later sections (to be updated).

a. Molecular Absorption Techniques. The instrumentation used for UV-visible discrimination can be placed in two categories: (1) visual photometry and (2) UV-visible spectrophotometers and photometers. Visual photometers rely on the eye as a detector and are suitable for only the most rudimentary monitoring of metals. Therefore they are described only briefly in the section below. UV-visible spectrometers rely on an instrumental detector. They may be then categorized as filter photometers, which use filters as the wavelength section device and UV-visible spectrophotometers which use a dispersive element for monochromation. Both these types of instruments are described below in Section (2).

(1) Visual Photometers. This was one of the earliest methods for determining the intensity of absorption. Visual photometers use a human eye as the detector and a brain as the discriminator. Unfortunately, the eye has a very limited spectral range, low accuracy in distinguishing intensities, high fatigue rate, and slow response in comparison to other techniques. Hence, visual detection is limited to a relatively few determinations in which low accuracy is sufficient.

In order to make colorimetric comparisons the relative transmission of white light by the standard and sample is compared, with the observer relying upon his judgment of color intensity. Visual colorimetry usually involves the use of flat bottomed tubes; often daylight reflected from a white surface is used for illumination. The concentration of the unknown may be determined by comparison with a series of known standards and choosing the best match. Alternatively, a single concentrated standard may be used which is diluted by known amounts until a match is obtained with the unknown. These techniques are used today in color kits.

The sensitivity for detection of a colored substance using visual methods can be defined as the smallest weight that can be detected in a column of solution of unit cross section. Sandell (Ref. 9) has compiled a list of sensitivities for the visual perception of a variety of substances. These sensitivities range from 0.01 to 10 μg/mℓ depending upon the substance. In general an observer can distinguish between two solutions which differ in concentration by 7%.

This method is rarely used for monitoring purposes because of the obvious disadvantages associated with relying on the operator as detector and discriminator. Visual techniques have given way to instruments which use inanimate detectors, generally photoemissive devices.

(2) UV-Visible Spectrophotometers and Photometers. Instruments used for

determining the amount of UV-vis light passing through a solution are called spectrometers, spectrophotometers and photometers. Definitions for each are rather specific and may be found in Refs. 3 and 9. Technically, for example, a spectrophotometer measures the "ratio or function of the ratio, of the radiant power of two beams as function of wavelength" (Refs. 3,9).

Despite the availability of the specific definitions, many authors and manufacturers use the terms rather loosely. As a result, most of the instruments commercially available are called spectrophotometers, whether or not their output is the ratio of two beams of light. For simplicity, usage in this volume corresponds to the manufacturers' usage.

Two categories of instrument, commonly used for measuring the absorption of UV-visible light by a solution, may be differentiated by their wavelength selection device. Filter photometers use filters to isolate a wavelength region and UV-visible spectrophotometers use dispersive elements for wavelength isolation. Simple schematics of each are shown in Fig. 6. It is clear that both types of instrument have five major components (a) the radiation source, (b) the optics, (c) the sample area (d) the detector and (e) the data processor.

This section will describe first the components of these instruments in Sections (a)-(e), then the sources of error in Section (f) and finally summarize the instrumentation currently available, its advantages and drawbacks in Section (g).

(a) Radiation Sources for Filter Photometers and UV-Visible Spectrophotometers. The radiation source in a filter photometer or UV-visible spectrophotometer provides a continuum of light from which wavelengths are selected and then passed through the sample. Sources must have a uniform high intensity over the wavelength range. They should be long lived, with high stability over their lifetime. A variety of lamps are available. For work in the visible (350-800 nm), tungsten or tungsten halide lamps are used. Deuterium or quartz-iodide lamps are used for the ultraviolet (190-350 nm). Some of these lamps include both UV and visible in their range. Hydrogen and xenon lamps have also been used.

Providing a source of sufficient intensity in the UV has been a problem. This is aggravated by the fact that many instruments lose their efficiency in this region because of the characteristics of the wavelength isolation device, the absorption of the optical elements and the response of the photodetector.

Instruments using an incandescent light source, such as tungsten or tungsten halide lamp, require a carefully regulated power supply to maintain the stability necessary for

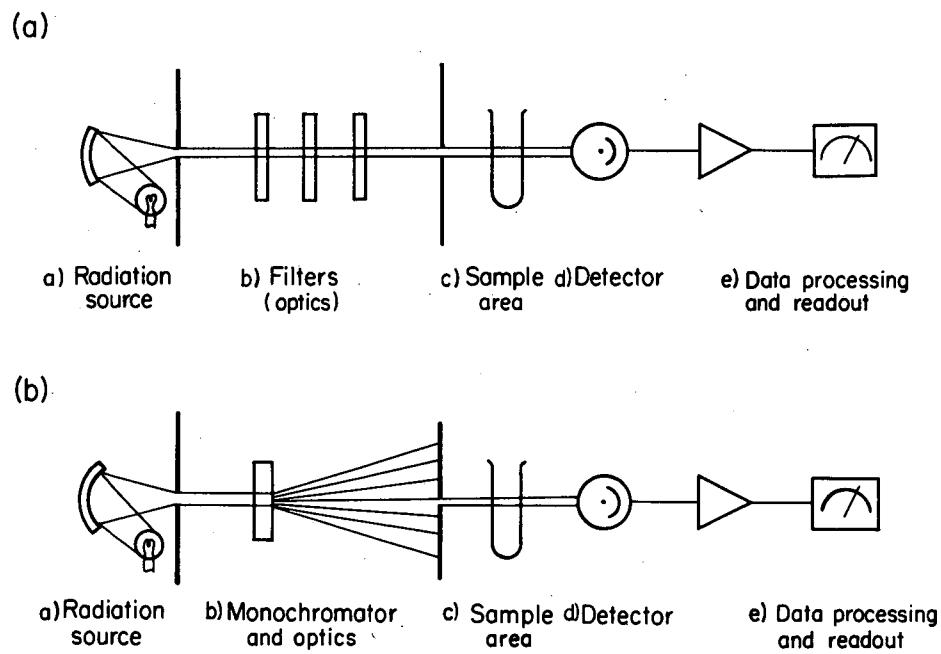


Fig. 6. Schematic diagram of (a) a single beam filterphotometer and (b) a single beam molecular absorption spectrophotometer showing their components [adapted from Ref. 10].

single beam operation. Deuterium arcs require the use of a carefully regenerated dc supply.

Most UV-visible instruments use a two lamp system: one source (e.g. tungsten) for the visible and another (e.g. deuterium) for the ultraviolet. One of the most common problems with UV-visible spectrophotometers a decade ago, was the need to remember to change the light source. Operators frequently forgot and as a result the instrument lost energy and provided worthless results. Many instruments today have an automatic switch over or a reminder system, preventing much wasted time, wasted effort and useless data.

(b) The Optical Systems. The optics of filter photometers and UV-visible spectrophotometers may be divided into the (i) wavelength isolation devices and (ii) the optical path.

(i) Wavelength Isolation Devices. Three types of device are used to select a portion of the ultraviolet or visible electromagnetic spectrum which then passes through the sample: filters, prisms and gratings.

The important characteristics of any wavelength isolation device are its % transmission, its bandpass and the wavelength or wavelengths it transmits. These factors are different for each of the dispersive devices discussed below.

- Filters (Ref. 3)

Filters used in filter photometers allow only certain wavelengths of light to pass through an optical material and then through the sample (Fig. 7). Two types of filters are used, absorption filters (Wratten-type) and interference filters (e.g., Fabry-Perot type).

Absorption filters are often made up of a glass sandwich of a dye in a layer of gelatin, or have an absorbing compound dispersed in an optical material. A single absorption filter is often a cutoff filter, which allows transmission of light above (high-bandpass) or below (low-bandpass) a certain wavelength. Two in combination allow a band of light to pass between the two limits (Fig. 7a).

Wratten type, absorption (Fig. 7a) filters have generally such a wide bandpass, ca. 20 nm, that they are unsuitable for accurate quantita-

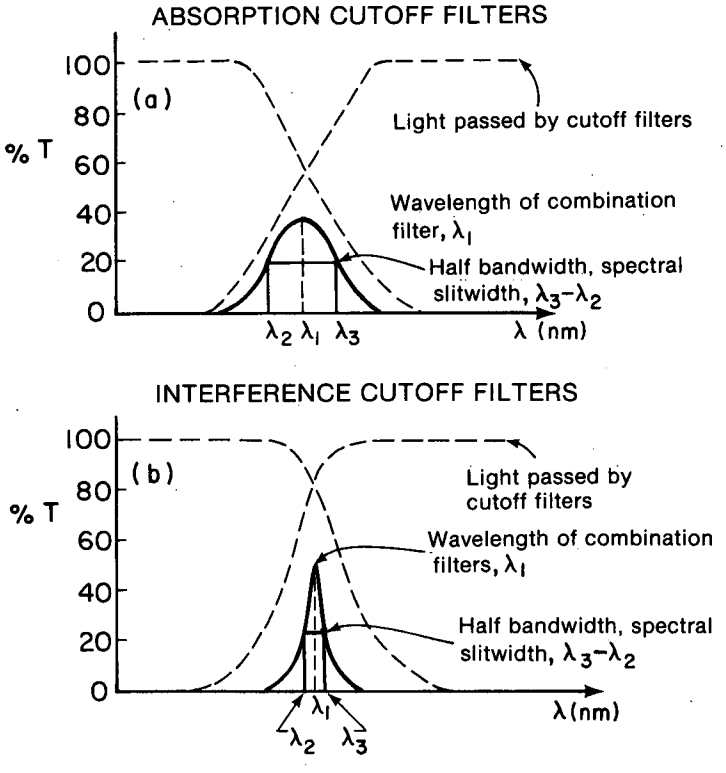


Fig. 7. Absorbance plotted as function of wavelength, illustrating the transmission filters and (b) absorption cutoff filters and (b) interference filters [adapted from Willard, Merritt and Dean, (Ref. 3)].

tive work. They are often used in conjunction with interference filters or dispersive devices to prevent transmission or dispersion of undesirable orders.

Interference filters use dielectric layers, or thin metallic sheets to produce interferences at specified wavelengths which result in selective reflection of unwanted radiation (Ref. 3). A piece of optical material is coated with a semitransparent metal film, and then a spacer film, made of a dielectric. The dielectric is then recoated with semimetallic film and a protective glass is added (Fig. 8). Constructive interference for a desired wavelength, λ, occurs when

$$\lambda = \frac{2\eta b}{m} \qquad (6)$$

where η is the refractive index of the spacer material, b is its thickness, and m is the order number. The necessary thickness of the dielectric is

$$b = \frac{m\lambda}{2} \cdot \frac{1}{\eta} . \qquad (7)$$

From Eq. 7, it is clear that the thickness of the spacer is a function of an integral number of half wavelengths and its refractive index. In order to prevent undesired orders from passing, low and high pass filters are used as is shown in Fig. 7b.

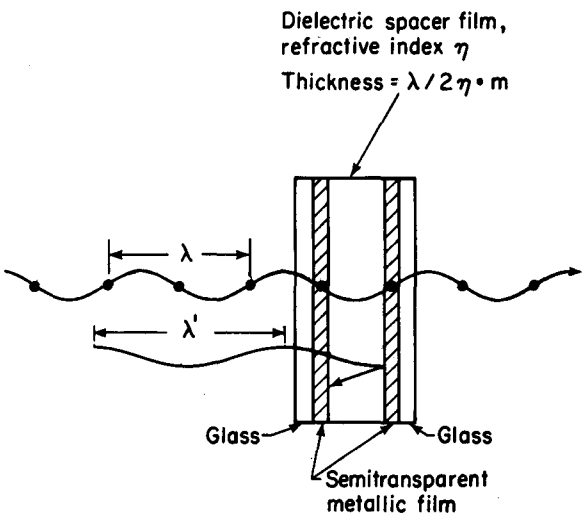


Fig. 8. Construction of a Fabry-Perot interference filter [adapted from Willard, Merritt and Dean, (Ref. 3)].

Interference filters have bandpasses of ca. > 10 nm and alone are not acceptable for high resolution quantitative work.

• Dispersive Elements: Gratings and Prisms

Prisms and gratings are dispersive elements which separate a continuum of light into its component wavelengths. Both prisms and gratings have been discussed extensively in Section IVA, Atomic Spectrometry, Part 1b (3) on monochromators, and in Refs. 3, 5, 8, 11 and 12. To summarize: a prism relies on the principle of change of refractive index of glass (or quartz) with wavelength of light. A grating relies on the fact that different wavelengths of light impinging on a grooved surface will be diffracted in different directions.

As was mentioned in Section IVA, gratings are more commonly used in commercial instruments because they are more simply and cheaply replicated, often have greater dispersion and are less sensitive to humidity and temperature changes.

Several characteristics are important when considering dispersive elements: dispersion, resolution, spectral bandwidth and luminosity.

Dispersion refers to the angular or linear separation of wavelengths. For a grating, it is usually expressed as the reciprocal linear dispersion, $[(d\lambda/d\ell)]$ Å, in Å or nm (10^{-7}cm) per millimeter. To convert angular dispersion $[d\beta/d\lambda)]$ to linear dispersion, $d\ell/d\lambda$, multiply by the focal length of the grating.

Resolution refers to the degree of separation of two closely spaced spectral bands. The degree of resolution is a function of a number of factors including the angular dispersion, effective slit width of the instrument and the focal length of the grating. A specification commonly quoted by the manufacturers, the experimental resolution, depends upon the angular dispersion, the focal length and the actual slit width of the instrument.

Luminosity refers to the amount of light transmitted by the dispersive element. Prisms generally tend to transmit more light than do gratings. For some experiments this can be of great importance; however, for most monitoring purposes, the luminosity associated with gratings is sufficient.

• Monochromators. The monochromator of spectrometers and spectrophotometers passes the light from the source through an entrance slit onto the dispersive element which directs selected wavelengths to an exit slit (Fig. 6b).

As in atomic absorption spectrometry, several arrangements of optics are used, the Ebert, the Littrow and the Czerny-Turner mount.

These are diagramed in Fig. 5, and discussed in Section IVA-1b(3), Optical Systems.

In some high precision instruments, two dispersive elements are used in series, which greatly reduces background interfering light. This type of monochromating system is shown in Fig. 9 and is used in the Varian Cary 17D. Needless to say, a double monochromator can add considerably to the cost of the instrument.

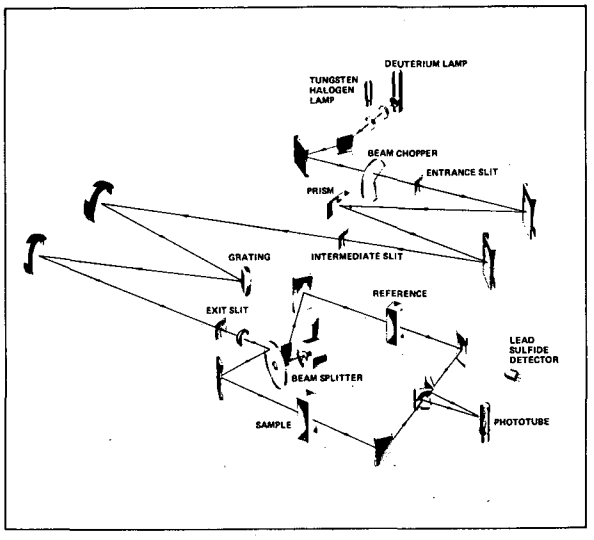


Fig. 9. Optical diagram of the Varian Cary 17D showing the double monochromator (reproduced from the manufacturer's bulletin, Ref. 13 with permission by Varian, n.d.).

Monochromators can be manual or scanning. In a manual monochromator, the operator sets the dispersive element so that light at a particular wavelength passes through the exit slit and through the sample. To change the wavelength, the operator must manually adjust the instrument. A scanning monochromator automatically moves the dispersive element so that a consecutive series of wavelengths pass through the exit slit. The absorbance is recorded at each wavelength, and the operator obtains the UV-visible spectrum of sample over the range of wavelengths of interest.

(ii) Optical Paths. There are two types of light path used in UV-visible struments: double beam and single beam.

• Single Beam Instruments. A single beam instrument passes only one beam of light through the wavelength isolation device and the sample and on to the detector. Figure 6 shows a simple schematic design of a single beam filter photometer and a single beam spectrometer.

The beam of light is often collimated and filtered before it reaches the entrance slit of the wavelength isolator. After it passes the exit slit and sample, the light is normally recollimated and filtered to eliminate higher orders before it impinges upon the detector.

Single beam spectrophotometers are best used for measurements at a single wavelength, since their output is a function of all their components, which can vary with wavelength. Because the optics and electronics involved are usually simpler than those of double beam instruments, they are usually less expensive.

• Double Beam Instruments (Ref. 3). Double beam instruments may achieve a double beam by spatially separating two beams (spatial double beam), by time-sharing (chopped double beam) and even by employing two spatially separated beams and two wavelengths (dual-channel).

In a spatially separated double-beam spectrophotometer the source light generally passes through a single monochromator to a beam splitter which passes one beam through the reference cell and the other through the sample cell onto separate detectors.

In a double beam spectrophotometer which uses a chopper, the beam of light is chopped and individual pulses of light are passed through the sample and reference compartments. The beam is then recombined and impinges on a single detector. The monochromator may come before the beam is chopped or after it is recombined. Figure 10 shows an instrument which uses a time sharing system.

Double beam spectrophotometers compensate for variations due to source fluctuation, or detector response which vary with wavelength. They also electronically subtract absorbance due to interfering species or solvents. The more complicated electronics and optics which are required for double beam operations often add considerable expense. However, double beam instruments are very useful for measuring the absorbance of some samples, particularly those which are turbid or contain interfering ions.

In a dual wavelength monochromator such as the Aminco DW-2™, the beams (Fig. 11) are are diffracted by two monochromators. The beams are then chopped and then pulses, alternatively from one monochromator and then the other, are recombined into a single beam which passes through the sample and then impinges upon the single detector. The detector compares the pulses from the two beams and usually displays them as a ratio. This system is extremely useful for use with turbid samples. Since it monitors two bands simultaneously, the two beams are set to monitor two separate wavelengths, one, λ_1 a sensitive monitor of the analyte, and the other, λ_2, unabsorbing for

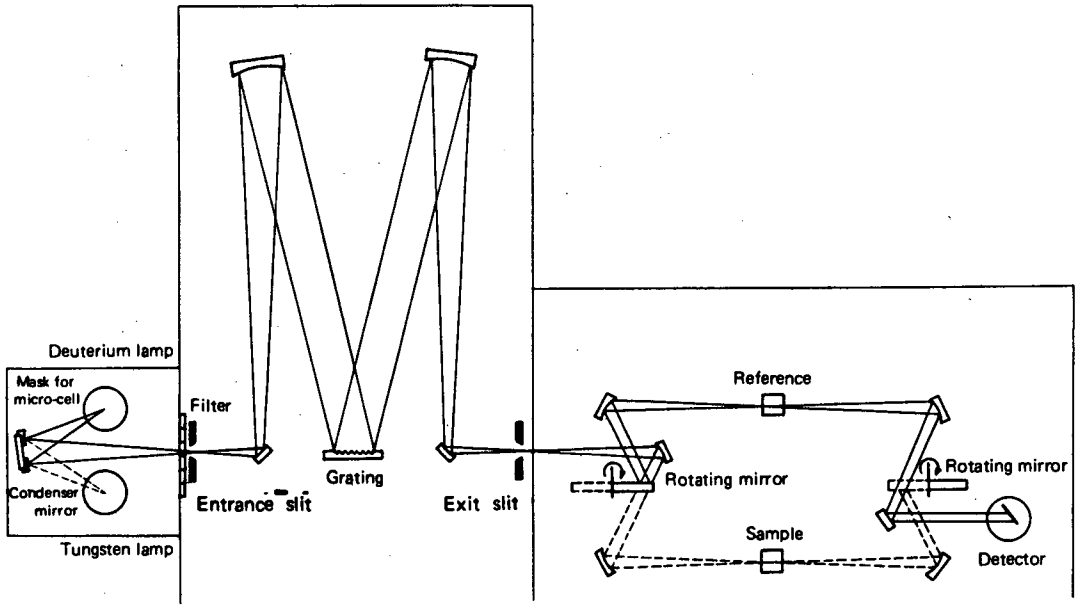


Fig. 10. Schematic diagram of the Shimadzu UV-200S, a double beam spectrophotometer using a chopper and a single detector (reproduced from the manufacturer's bulletin, Ref. 14, with permission by Shimadzu Seisakusho Ltd., n.d.).

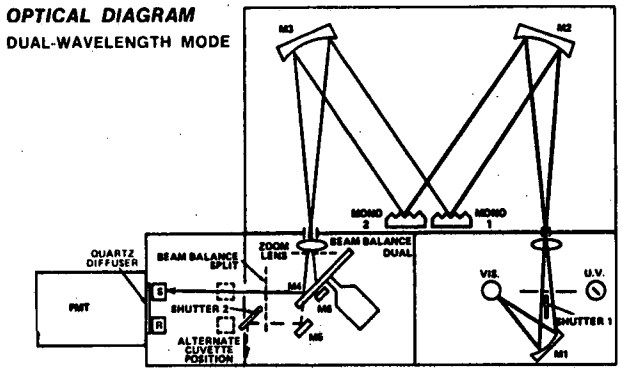


Fig. 11. Schematic diagram of a dual wavelength spectrophotometer, the Aminco DW-2™ (reproduced from the manufacturer's bulletin, Ref. 15, with permission by American Instrument Company, Division of Travenol Laboratories, Inc., n.d.).

the analyte, but having the same absorbance for the interfering species as has λ_1.

(c) The Sample Area. The sample chamber in a UV-visible spectrophotometer minimally holds a sample in a reproducible position for the light beam to pass through. It can also regulate the environment of the sample and control the presentation of the sample.

• Sample Chambers. Many spectrophotometers, (like the Bausch and Lomb Spectronic 20) are designed to hold a single sample in a 1 cm (or smaller) cuvette, test tube or microsampler. Others provide for a range of sizes and numbers of samples. Table 2 lists the size and shape of containers routinely used by other Bausch and Lomb UV-visible spectrophotometers. Many sample chambers allow a sample container of up to 10 cm pathlength. A long pathlength is important for monitoring very low concentrations of metals, since the absorbance depends upon pathlength as well as concentration.

For double beam instruments, sample compartments are designed to hold both the sample cell and reference cell. In addition, many spectrophotometers have multicell chambers, which allow the analyst to examine a series (usually four) of samples in the beam without opening the chamber; sometimes this same option is available for the reference beam as well. Several commercial instruments have a position for turbid samples which places them closer to the radiation source. Other options available, although less applicable to monitoring metals in water, are gel scanners and reflectance attachments.

Sampling can often be automated; controls are available to change the position of cuvettes in the chamber, sippers can be used to inject samples into cuvettes, and flow-through attachments are also available.

• Sample Environmental Control. Sample chambers can be jacketted for temperature control. Usually the system involves a circu-

Table 2. Variety of sample holders available from Bausch and Lomb (Ref. 16)

	Path Length (mm)	Minimum Volume (mℓ)
Test Tubes	10	2.5
	20	10.0
Short Path Cuvettes	1	0.02
	2	0.04
	5	1.0
Cuvette	10	2.0
Long Path Cell	50	14.2
	100	28.4

lating water bath to maintain a constant temperature. For measuring concentrations of metals in water under laboratory conditions, this is rarely essential; however for other types of monitoring, involving kinetic measurements, this attachment is important. Most sample compartments can be purged or cleansed with a non-reactive gas.

Major requirements for any sample chamber are (1) light tightness and (2) flexibility to hold cells of most convenient size. Light leaks and stray light are one of the greatest sources of error in UV/vis spectrophotometry.

• Sample Cells. A variety of cells are available. For visible, single beam work, only high quality glass cells are necessary; for UV-visible work, quartz cells are most often used. If measurements are to be made in double beam then the cells must be carefully matched, or the baseline shift may become a source of error.

Cells come in a variety of shapes (see Table 2), test tubes or flat bottomed cylinders, square cuvettes, usually 1 cm thick; rectangular cuvettes which allow greater pathlength per unit volume, long cylindrical cells, or microcells (pathlengths of ca. 1 nm). Flow-through cells are available for a variety of pathlengths.

(d) Detectors. Various types of photosensitive devices are utilized as detectors; these include vacuum phototubes, gas

Table 3. Photometric detectors (adapted from Kolthoff and Elvings, Ref. 6, with permission by John Wiley and Sons, Inc., copyright 1964).

	Barrier Cell	Vacuum phototube	Gas phototube	Photo-multiplier
Effect	Photovoltaic	Photoemissive	Photoemissive	Photoemissive
Sensing element	Junction of semi-conductor on metal	Alkali metal oxide coating	Alkali metal oxide coating	Alkali metal oxide coating
Frequency range, nm	400-800	200-1000	200-1000	160-700
Type of output	High current or e.m.f.	High current	High current	Very high current
Sensitivity	Moderate, frequency-dependent	High, frequency-dependent	Frequency-dependent	Very high
Response time	Fast	Very fast, 11 sec	Moderately fast	Very fact

phototubes, photomultipliers, photoconductors and photovoltaic cells. The first three are phototubes and depend upon the emission of electrons when photons strike a photosensitive surface. Table 3 compares all three. The other detectors are solid state devices and are not currently widely used. Various photocells are also included in Table 3.

Vacuum photobues include a cathode coated with a light sensitive material and an anode enveloped in a glass tube under a high vacuum. If phototubes are to be used in the ultraviolet, a quartz window is added, or the envelope is constructed of quartz. Electrons are emitted by the cathode if a sufficient number of photons have hit it. They are collected on the anode and returned to the cathode via the external circuit.

Photomultiplier tubes have been described already in Section IVA1b (4) - Atomic Absorption Spectrometry, Detection and Readout Systems. They work on the principle of secondary emission; electrons ejected from the cathode are directed to a series of dynodes each of which emits several electrons for every one which hits it, amplifying the current considerably (Fig. 13 in the section on Atomic Absorption). Because of their sensitivity, photomultipliers are often the detector of preference for low concentration determination. If a particularly large range is to be covered, two detectors are often used for maximum sensitivity.

(e) Data Processing and Readout. Data processing and readout from UV-visible spectrophotometers used for monitoring metals in water varies from simple meter readout of % transmission to digital presentation of the concentration of the solution, with compensation for background effects and interferences.

Most UV-visible outputs generate a DC signal (analog) which minimally is displayed upon a meter linear in % T. Alternatively the output may be processed by null balance where the output signal is compared with a reference signal. The reliability of the electronic signal depends upon the quality of the balance circuit.

Electronically, the signal can be processed to be linear in absorbance or concentration units. It can be processed by an analog to digital converter and then displayed, recorded, printed, or processed by a remote or dedicated computer.

Data processing for double beam instruments is more complex; the actual electronic processing circuitry depends on whether the instrument uses two matched detectors (double beam with two spatially separate beams) or a single detector (double beam using two chopped, recombined beams), or dual wavelengths. If the instrument is double beam using a chopped, recombined beam, a signal, which is the response alternately from the sample and the reference beam, is the output of a single detector. Suitable electronic switching circuits can generate the ratio of the two signals, which can be displayed or recorded as outputs.

The reference signal is also monitored separately to produce a baseline, often at 100% T (0.00A). In many instruments the baseline can be adjusted to any position by using automatic gain, servo-controlled slits or an optical wedge. If automatic gain is used, then the resolution is constant throughout the spectrum; however, the noise level is variable. If servo slits are used, the noise level remains constant but the resolution changes and a complex synchronizing mechanism is necessary. An optical wedge can introduce stray light and scatter problems but the resolution and noise level remain constant. (Ref. 3).

If the instrument is double beam but using two spatially separate beams, the signal is from two separate photomultipliers, which permits less sophisticated signal processing. The net output is still the ratio of the two beams; the reference beam is easily monitored to maintain the baseline. The major disadvantage to this type system is the need for two or more closely matched detectors, which must remain closely matched over a wide range of wavelength and intensity.

Instruments which are dual wavelength must process signals from the single sample at λ_1 and λ_2, and a zero signal. The signals are separated in time; the data output signal is the ratio of the two signals.

A variety of adjustments appear on many instruments:

- Mode of Operation: On many instruments the operator may choose to display the output linearly in absorbance units, % transmission or concentration. The signal is originally linear in % T; to present the absorbance units requires a conversion to a log scale.

To present concentration directly, the absorbance units must be internally multiplied by a factor representing the molecular absorptivity of the analyte species. The molar absorptivity may be fed by an operator or by a dedicated computer which measures the absorbance of several solutions of known concentration, constructs the calibration curve and takes its slope.

Among the other modes available, but less applicable to monitoring metals in water, are a kinetics mode which presents the absorbance as a function of time and a first derivative

mode which shows the change in absorbance with wavelength ($dA/d\lambda$). A derivative mode might be useful for monitoring metals if a researcher suspected an interference band which was only slightly apparent on the side of the band of interest.

• Output Scale Adjustment. This allows the operator to adjust the amplification of the output. The simplest instruments only have a single scale: 0-100% T or possibly 0-1 A. Many instruments now available allow the analyst to expand the scale by up to 50x, or reduce it to 1/3. If a recorder or meter is being used, a 10x scale expansion means that a value of 0.10 A or 10% T is shown at full scale. If the scale is reduced to 1/3, then 3A is shown at full scale. Several instruments allow the analyst to choose a particular absorbance or transmittance range, for example 0.4 to 0.5A, and expand it over the full scale.

Scale expansion can be an important factor for the analyst doing high precision, high accuracy work. For monitoring fresh water, or water with low concentrations of the analyte, scale expansion can save time, and reduce the possibility of error since it may then be possible to omit a tedious concentration or extraction step.

Similarly, expansion to 3A allows the analyst working with turbid, highly concentrated samples to omit dilution steps. This can be important for the analyst working with turbid samples with low concentrations of analyte, since light may be passed through a sample which would ordinarily register no transmittance whatever.

• Zero Adjust. This option allows the analyst to electronically choose the zero point. This flexibility is also useful for the analyst working with highly concentrated or turbid samples, since to operate at 3A for most of the region of interest the analyst can effectively expand to full scale a signal which before expansion covered a few absorbance units. To do this may require the zero adjust. The gain control allows the analyst to control the amplification of the signal. A problem associated with increasing the gain is the concurrent increase in the noise level. A high noise level can be corrected for by damping the signal - see Response below, but if the response time is changed, the operator must expect slower pen response. If a spectrum is being scanned, the analyst must be sure to scan more slowly to compensate for the slower pen response.

This control is advantageous for the analyst working with low energy systems, in that it can amplify a very weak signal and display it over a wider range.

• Adjustable Response Time. This option allows the analyst to control the pen response time. The electronics of the instrument averages the signal over a certain time period, which serves to damp out the noise. This control is useful for those working with low energy systems - and who can afford a slow scan or slow pen response. A low energy, high noise system can arise if there is a need for high resolution, (e.g., if small slits are used - the signal to noise ratio is lowered). High noise, low energy situations can also occur if the sample is strongly absorbing or turbid and the analyst has raised the gain to increase the signal.

• Readout Form. Output can be presented as a temporary or permanent record. The presentation of the output signal may be analog or digital. Analog signals are usually presented on a meter or a chart recorder. Digital signals can be presented as illuminated numbers or recorded by a variety of digital devices.

The meter readout is simple: The instrument itself provides no permanent record, so it is important that the readings be taken carefully and accurately. One obvious disadvantage to this system is that it is impossible to recheck a reported value without taking another measurement.

A recorder provides a permanent record of instrument response and is usually the best method for displaying a spectrum. It allows the analyst to visually check for interference peaks, to determine the peak position at half width - half maximum and to perform a curve resolution if necessary.

Many recorder options are available. The scan speed can vary with wavelength or the measure in which the chart paper is divided (e.g., cm); the chart advance can also be expanded by number of wavelengths or measure of chart paper. The ordinate scale can be changed using scale expansion and zero suppression.

The elaborate synchronization necessary between wavelength, pen and paper drive can add considerable cost to the instruments. If the analyst only expects to look at a single wavelength at one time, another method of display is probably preferable.

For a temporary digital signal, the analog output from the detector can be digitized and presented as a series of digits. These can be manually recorded by the operator. Since the result is presented as digits, there is less likelihood of error due to operator misinterpretation. Alternatively digital output can be stored permanently in several forms - printed page, punched cards, paper or magnetic tape. It can also be fed into a computer for data analysis.

(f) Sources of Error. In molecular absorption spectrophotometry as in atomic absorption spectrometry, there are two categories of error: operational errors and interferences. Operational errors occur because of human error or instrument malfunction during a measurement - in calibration, sampling, and pretreatment, instrument operation or use, or in data analysis. Interferences are sources of error which occur even if the instrument and operator are working properly.

i. Interferences. Three categories of interference can be defined; physical, chemical or spectral interferences.

Physical interferences reduce or enhance the energy reaching the detector by the effect of the physical parameters of the test solution. For example a highly turbid sample reduces the energy reaching the detector and increases the stray light so substantially as to render the measurement difficult or even impossible. The particles in solution creating the turbid appearance both scatter and absorb the incident light. In samples with lesser amounts of turbidity a measurement can sometimes be made by changing the position of the sample (an option available on several commercial instruments) or increasing the gain or slit size. These adjustments can only be made at a sacrifice of sensitivity or resolution, since increasing the gain increases the noise level and increasing the slit size lowers the resolution. Liquid filtration can remove much turbidity, but even a filtered solution can scatter or absorb a substantial amount of light. Also during filtration, the analyte may adsorb to the filter introducing a further error.

Dilution has been used to measure highly turbid samples; however, this also reduces the analyte concentration and consequently may be too low to measure accurately.

Another physical interference inherent in the apparatus is a certain amount of stray light, a problem enhanced by scattering sample solutions. Instrumental stray light is reduced by painting the interior black, introducing a double monochromating system, and filters and baffles before the light impinges upon the sample. Stray light is further reduced by filters which appear after the sample. The analyst should always be sure that the light-tight covers on the sample and optics compartments are closed properly. If a cushioning material is present to prevent stray light, the operator should be sure that it is in good condition. It is possible that atmospheric pollution (SO_x, NO_x or O_3), as well as laboratory solvents and mechanical wear can break down light barrier materials.

The temperature of the solution can influence the reaction products which are formed. If the desired complex is formed in an equilibrium reaction:

$$M + \text{Ligand} \rightleftharpoons [M\ \text{ligand}]$$

then the position of equilibrium can change with varying temperature. The concentration of M is determined by measuring the absorption of an M Ligand transition. If the equilibrium position is not constant, the concentration of [M Ligand] will vary, a situation which leads to erroneous results. Analytical measurements should therefore be made at a fairly constant temperature, although routine monitoring measurements rarely require a jacketted sample chamber.

Researchers working in the far UV should be aware that below 190 nm atmospheric oxygen is highly absorbing thus reducing the energy reaching the detector and creating a low signal/noise ratio. The energy levels and baseline should be checked in this region to be assured of valid results.

Chemical interferences effect the measured signal by chemically changing the apparent amount of analyte present in a solution. To measure the quantity of analyte present in a solution, a complexing agent is added to the solution. The complex formed has a strong absorption band in the UV or visible, which is used to monitor the amount of complex in solution. Any species which chemically inhibits or enhances the complexation reaction, will cause erroneous results if its presence is unsuspected and not compensated for in the standard solutions. An interfering species can either react with the analyte preventing the metal from combining with the desired ligand, or it can react with the ligand preventing complete formation of the desired complex. It may also form a second complex which masks, to some degree, the absorption band of interest (Spectral Interference, below).

It is sometimes possible to prevent the above interferences by adding chemicals which react with interfering metals or ligands. However, the most effective solution often is to extract either the interfering species or the analyte from the solution.

If the absorbing species dissociates or associates in solution, the results may be erroneous, since the retentive concentration of the two forms will vary with total metal concentration. For example, in acidic solution, chromate, $[CrO_4]^{2-}$ and dichromate, $[Cr_2O_7]^{2-}$, are in equilibrium:

$$2[CrO_4]^{2-} + 2H^+ \rightleftharpoons [Cr_2O_7]^{2-} + H_2O.$$

With this type of chemical interference, it is sometimes possible to measure the absorbance at an *isosbestic* point, that is, a wavelength

at which the absorbing species have equal molar absorptivities. If an isosbestic point cannot be determined, then the analyst should consider using a complex which does not dissociate (Ref. 3).

Spectral interferences occur when the species of interest or another species (including the solvent) has an absorption band which overlaps the band of interest. The analyst should be aware of solvent absorption bands, although water does not absorb from 200-800 nm, many common organic solvents, such as benzene and acetone, do. It is sometimes possible to compensate for solvent interference bands, if they are not too strong, using a double beam instrument. However, under normal circumstances, it is better to change solvents.

When complexing agents are added to a solution containing several different metals, several of the metals may react with the ligand, to form colored compounds. The absorption bands often overlap. Frequently, it is possible to determine the amount of absorption attributable to a peak which overlaps another. Several techniques are available. If the concentration of the interfering species is known, then a blank can be prepared which allows the double beam instrument to subtract the value. It is often necessary to extract the interfering ion or the analyte ion from the solution to prevent spectral interference altogether.

ii. Errors due to instrument malfunction or operator error. These errors can be introduced during any of the monitoring steps: sampling, pretreatment, measurement, or data analysis and presentation. Only those directly connected with the determination of metals in water by absorption spectrophotometry will be discussed in this section. These are the errors introduced by malfunctions of the spectrophotometer, or by incorrect procedures used by the operator during the measurement. As with any analytical procedure, the most effective way of avoiding operational errors is to have a skilled, trained operator, who will make fewer mistakes, and will be more apt to recognize that the instrument is malfunctioning. Such an operator may even be able to correct minor malfunctions, make minor adjustments and do routine maintenance.

The correct procedure for operating each particular instrument is beyond the scope of this volume and will not be discussed. A procedure manual accompanies most available instruments and should be followed.

Most ultraviolet-visible instruments are reliable - if used properly, they will quickly and accurately report the absorbance of the solution in their sample chamber. Some common problems to look for are:

- Sample chamber improperly closed, which leads to an increased signal and often increased noise levels. The problem can occur in any UV-visible spectrophotometer, and is prevented by a careful operator.

- Incorrect lamp in use. This causes low energy levels - and high noise levels. Many UV-visible instruments now have automatic switchover or a notice to change over. In manual machines, the prevention is, again, a careful operator.

- Weak source lamp. After a certain number of hours the output from the source lamp may become noisy, weak or unstable. It is good practice to keep a record of the number of hours a lamp has burned and to frequently check its energy and stability after it passes its guaranteed lifetime. The lamp should be carefully aligned when it is replaced. In some instruments, this is not a trivial operation, and the instructions should be followed carefully.

- Unmatched sample cells. If unmatched cells are used, then the baseline of a double beam instrument is uneven and an erroneous readout results. Every time the machine is used the cells should be checked for cleanliness and the baseline checked to make sure the cells and the machine are optically balanced.

- Uncalibrated monochromator. Monochromators do become uncalibrated; usually it is a gradual process. Frequent calibration checks using a known emission lamp such as a mercury vapor lamp, can inform the analyst of the meanings of the wavelength readings obtained. Particularly if the analysis is performed at only one wavelength, the analyst should determine that the absorption is recorded at the correct wavelength.

For any serious trouble which occurs in either the optics or electronics of the instrument, the operator is strongly advised to call the manufacturer for assistance.

(g) UV/Visible Spectrophotometric Instrumentation - A Summary. Existing instrumentation is quite adequate to perform the analyses described in Standard Methods, 14th ed (Ref. 17) or The EPA Handbook (Ref. 18). In choosing a UV-visible instrument, the laboratory has several characteristics to consider:

(i) What is the necessary wavelength range?
(ii) Double beam, single beam or what?
(iii) How flexible should the instrument be and what degree of automation is desirable?
(iv) How elaborate a data-processing - readout system is desirable?

These points are discussed in order below.

(i) What is the necessary wavelength range? An examination of Table 2b in the introduction to Section IV shows that the recommended wavelengths used for determining metals in water cover a very small wavelength range (ca. 400-650 nm). If the instrument is to be used only for performing this set of analyses, then certainly an instrument whose range is only in the visible would be acceptable. Considerable expense can be saved, since not only the optical system but the sample cells can be made of glass rather than the much more expensive quartz.

If the laboratory will be performing analyses on samples using other than the prescribed methods for monitoring metals in water, then the added range into the ultraviolet is an advantage. This allows the analyst to check the purity of reagents, establish the entire UV-visible spectrum of the compounds being analysed, check for interference bands, and establish that desired complexes have been formed.

In the other extreme, instruments which measure absorption below 190-200 nm require use of vacuum or purging equipment, which adds considerable expense. At this time, for routine analytical work, such an expenditure is probably not warranted. Detection of radiation in the near IR (at wavelengths greater than 800 nm), requires an additional source and detector, so adds some additional expense, which may not be practical for laboratories performing routine analyses or with limited funds.

(ii) Double beam, single beam or what? There is a wide variety of optical systems from which one can choose - single beam, double beam (using a chopped beam and single detector), double beam using two beams and two detectors and dual wavelength. With increasing complexity there is a concurrent increase in cost.

Single beam systems are usually simple to operate, but require a longer warm-up time before they stabilize. It is always necessary to record the absorbance of the blank and subtract it from the final reading. The operator must assume that this blank reading will also account for variation in instrumental parameters.

Double beam instruments allow the analyst to electronically subtract the instrumental or solution background from the absorbance reading. The major disadvantage to spatially double beam instruments is the requirement of two detectors matched over a wide range.

Dual wavelength instruments allow the analyst to measure the absorption of the same sample at two separate wavelengths. If one can establish that the signal from the turbidity or any other interference is the same at the wavelength of interest for analyzing a particular metal and at a wavelength where the metal does not absorb, it is possible to use the second wavelength as a reference wavelength.

In general, a double beam system is a worthwhile expense. For highly concentrated or turbid samples, the use of a reference cell is advisable. For dilute solutions the electronic comparison with the reference absorption is useful.

(iii) How flexible should the instrument be and what degree of automization is desirable? Increasing flexibility in an instrument usually implies higher cost and greater complexity in operation. The laboratory purchasing a UV/visible spectrophotometer must examine the variety of purposes it will be used for.

The options associated with the various components have been described in Sections (a)-(e). In general, laboratories working with only a small range of medium concentrations of metals in water need an accurate, precise instrument, but not a particularly flexible one. A laboratory working with a wide range of concentrations, turbid samples, and wishing to perform exploratory qualitative analyses will probably prefer an instrument which has an adjustable gain, slits or both, a scan option and possibly a turbidity position.

Laboratories processing a high volume of samples will usually wish to automate their sampling, measuring, and recording processes. A disadvantage to these options other than the cost is the tendency to regard such an instrument as a "black box." Automation saves considerable operator time, but the instrument still requires an operator who understands how it works and who recognizes erroneous output. The electronics and engineering for automated systems are highly sophisticated and therefore more difficult to maintain.

(iv) How elaborate a data processing readout system is desirable? The variety of data processing and readout options were discussed in Section (e). In general, increased data processing and more elaborate readout save operator time, prevent operator error, but add cost and complexity to the instrument.

Once the type of instrument desired has been established, the laboratory still has a difficult choice to make between very similar instruments. If possible a side by side comparison using a wide range of calibrated samples should be performed, since this task is not currently done by any single agency.

Given the sparse performance data in the specifications, differentiating between several similar instruments is very difficult. The instrument notes at the end of this section and the green page summary tables which precede them may serve as a guide in making this choice. The relative quality of the light source-detection system can be determined by comparing the stability and noise level of the instrument. The stray light and noise level is a guide to the quality of the filtering/baffling system. The resolution, wavelength reproducibility and accuracy indicate the quality of the monochromator. The photometric accuracy, that is, the actual absorbance recorded when a known sample is analyzed, is the measure of the performance of the entire instrument. When it is listed as a specification, the sample tested is usually noted as well. Before relying too strongly on this information, the user should determine that the photometric accuracy was measured on samples which are similar to those of interest.

The minimum detectable limit (mdl) is another measure of the instrument. It is a function of lamp intensity, transmission on the optics, and the sensitivity of the detector. Since the mdl also varies strongly with metal, (see Ref. 9 or 19 for a comparison of sensitivities of a variety of metallic complexes) technique and pathlength, each laboratory should attempt to determine the detection limits of the instruments under consideration for the metals it must monitor in the type of water to be analyzed. Obviously the mdl for Cr(VI) in fresh water will be considerably better than in a turbid waste water sample.

Instrumentation for UV-visible spectrophotometry is of generally high quality. With the approval of amendments to the Clean Water Act (see the Introduction to the volume), P.L. 92-500, and their coming into effect on July 1, 1977, lower and lower detection limits will be necessary. It will be important to develop instruments with higher intensity light sources (for turbid samples), more sensitive detectors and better optics. Concurrently, new methods, including better concentration or extraction techniques and development of compounds with high molar absorptivity at specific wavelengths will be necessary.

To summarize: UV-visible spectrophotometric instruments are widely available, are adequate for routine analytical tasks and have a high performance to cost ratio.

b. UV-visible Luminescence Techniques. Fluorimeters are UV-visible instruments which measure the light emitted by molecular species. They monitor metals in water only to a limited degree, therefore the following description will be brief. It is generally adapted from Refs. 4, 6, and 20.

(1) Experimental Apparatus. A fluorimeter, shown in Fig. 12, is similar in design to a UV-visible spectrophotometer. A beam of light from a radiation source passes through a monochromating device, which directs light of a narrow bandwidth to the sample. If the sample contains a fluorescent compound which is sensitive to light of the wavelength, energy is absorbed and light radiated. A second monochromator is placed perpendicular to the incident beam. Fluorescence from the sample passes through the monochromator and impinges upon a detector.

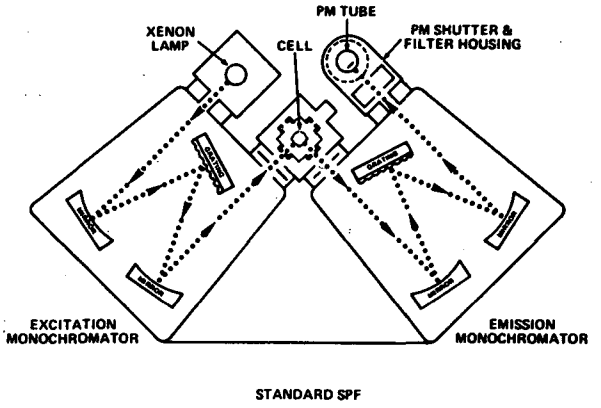


Fig. 12. Schematic diagram of a spectrofluorometer, the Aminco Bowman SPF (reproduced from manufacturer's bulletin, Ref. 21, with permission by American Instrument, Co., Division of Travenol Labs., n.d.

The light source employed is usually a high intensity xenon arc, which provides a continuum from 200-800 nm. The monochromating devices are similar to those described in the section on UV-visible spectrophotometric spectrometers. The data aquisition, processing and readout systems available are also similar to those used in absorption spectrometry.

(2) Sources of Error. Physical, chemical and spectral interferences observed in absorption spectrophotometry can be experienced in fluorimetry. In addition, the problems associated with sample light scatter are more pronounced. A turbid solution may scatter the incident beam of light over a wide angular distribution. The intensity of the scattered radiation could cause an increased signal.

In addition to the operational errors experienced in absorption spectroscopy, the

Table 4. Reported minimum detection limits (mdl's) of trace metals in solution using fluorimetry, (data presented in St. John, Ref. 20)

Element	Reported mdl (µg/ℓ)	Reagent used for optimum reported value
Aluminum	0.2 - 0.8	3-Hydroxy-2-naphthoic Acid morin
Beryllium	0.04- 200	3-Hydroxy-2-naphthoic Acid
Boron	0.5 -10	Dibenzoylmethane
Cadmium	20	p - Tosylaminoquinoline
Calcium	10 - 20	Calcein, Dicarboxydi-methylamino-2,6-dihydroxynaphthalene
Cobalt	0.1 - 60	Salicylfluorene plus H_2O_2
Copper	1 - 300	Tetrachlorotetraiodo-fluoroscein plus o-phenanthroline
Gold	500	Rhodamine B
Iridium	2000	2, 2',2''-terpyridine
Iron	0.8	Luminol plus H_2O_2
Lead	5000	Morin
Magnesium	0.01	N,N'-Bissalicylidene-ethylenediamine
Manganese	2	8-Hydroxyquinoline
Mercury	2	Rhodamine B
Molybdenum	100	Carminic Acid
Nickel	0.06	Al-1-(2-Pyridyazo)-2-naphthol
Osmium	50	4,6-Bis(methylthio-3-amino-pyrimidine)
Ruthenium	1000	5-methyl-1,10-phenanthroline
Selenium	5	2,3-Diaminonaphthalene
Silicon	0.08	Benzoin
Silver	4	Eosin plus 1,10-phenanthroline
Element	**Reported mdl (µg/ℓ)**	**Reagent used for optimum reported value**
Thallium	20	HCl., HBr at 77°K
Tin	100	Flavinol
Vanadium	2000	Resorcinol
Zinc	2	Benzthiazoylmethane, 2,2'-methylenebibenzo-thiazol

effect of errors causing excess stray light scatter is magnified. These include use of dirty glassware, unclean optics and use of a sample chamber which is not light tight.

(3). Summary, Applications and Recommendations. The procedures used for making a fluorometric measurement are very similar to those used in UV-vis absorption spectrometry. A calibration curve must be made, molar absorptivity of the solution determined, and the fluorescence of the sample recorded. Table 4 gives detection limits reported for trace metals using fluorimetry. A comparison of this table with Table 3 in the Atomic Absorption section indicates that for a few metals, notably, boron, beryllium, cobalt, magnesium, nickel, osmium and silicon, fluorimetric techniques are as sensitive or more so, than atomic absorption techniques. A laboratory primarily monitoring for these metals might consider using fluorimetry and applying for alternative method approval.

The major disadvantages of using fluorimetry for monitoring metals in water are the limited number of metals which have detection limits sufficiently low to meet federal standards (without preconcentration) and its limited usage with turbid solutions.

3. Acknowledgments

The author wishes to thank Ralph McLaughlin for his help, suggestions, and criticisms.

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CONTENTS

C. Developing and On-Going Techniques

Developing techniques are those which show great potential but are not used for routine water monitoring, because the procedures have not been sufficiently refined or the instruments necessary are not commercially available. On-going techniques are those which are available and sufficiently sensitive to perform the necessary analyses but, for a variety of reasons, are not the method of choice of most water monitoring labs.

Two techniques, coming under these classifications, which can be used for determination of metals in water but are not normally used for routine water monitoring are x-ray fluorescence spectrometry (XRF) and neutron activation analysis (NAA). They are more extensively used in biological, sedimental and air quality monitoring and are discussed in greater detail in the AIR and BIO volumes of the survey. XRF will be discussed in Part 1 of this section, NAA in Part 2. Principles of operation and experimental techniques will be discussed but instrument notes will not appear.

A wide variety of other techniques are available for the determination of metals in water but used less frequently out of research labs. They include electrochemical techniques such as anodic stripping voltammetry, spark source mass spectrometry, and electron spectroscopy for chemical analysis. Due to space limitations only the electrochemical technique, anodic stripping voltammetry, which is currently gaining usage, will be discussed in Part 3 of this section.

1. X-Ray Fluorescence Spectroscopy

X-ray fluorescence (XRF) spectroscopy is an extremely powerful tool for qualitative and quantitative determination of trace metals in water. When an atom is excited with ejection of an inner shell electron, a photoelectron, usually from a K- or L-shell, it may return to the ground state (or a lower energy state) by a rearrangement of its electrons in which one of its outer shell electrons falls into the hole left by the photoelectron. When the electron changes energy levels, it can emit an x-ray. XRF is based on the principle that the energy of the emitted x-rays depends on the atomic number of the atom (Z) and their intensity depends on the concentration of the atom in the sample.

Although XRF has long been used as a tool for trace analysis of atmospheric particulate and biological samples, it is still not frequently used for monitoring metals in water. This is largely because of the difficulty in sample preparation as compared with that necessary for atomic absorption spectroscopy and the skill and time required to operate and maintain the instruments involved.

Nevertheless, XRF is an expanding, rapidly developing technique. Recently, technological developments have improved detection limits, reduced the time necessary for determinations, and improved the resolution achievable. These developments make the technique a potentially powerful tool for use in determining metals in water.

a. Principles of Operation. The atomic processes involved in XRF are simple and are illustrated in Fig. 1. When a photon or charged particle of sufficient energy interacts with an atom, the atom may be excited ejecting a specific electron out of an inner (usually K or L) shell.

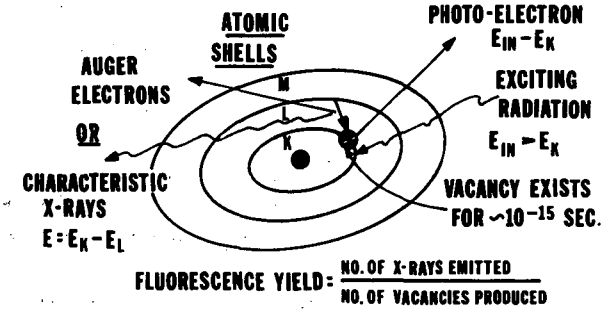


Fig. 1. Atomic processes involved in x-ray fluorescence (from Goulding and Jaklevic, Ref. 1).

The excited atom may return to the ground state (or any lower energy state) by several different mechanisms. An outer shell electron can fall into the vacated inner shell, releasing energy as an x-ray. By measuring the photon energy of this fluorescent x-ray, the atom can be identified. Unfortunately the atom may also rearrange and lose energy via an ejected electron (an Auger electron). For elements with higher atomic numbers (2), the radiative process is favored; the Auger process is favored for elements with low atomic numbers (Ref. 2). Thus as Z increases, the fluorescence yield, which is equal to the number of emitted x-rays per total number of ionizations, increases.

The energy of the emitted radiation is dependent upon the atomic energy level separations and on the atomic number. An energy level diagram showing allowed transitions is shown in Fig. 2. The relationship between the the wavelength, λ, of light emitted and Z was defined by Moseley in 1913 as

$$\frac{c}{\lambda} = a\,(Z-\sigma)^2$$

where c is the speed of light, "a" is a proportionality constant and σ is a constant

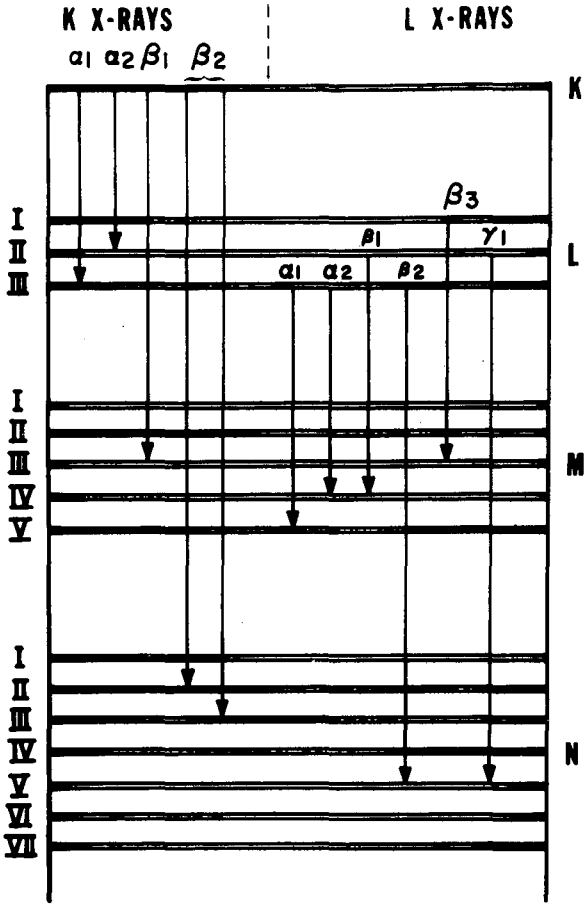


Fig. 2. Atomic energy levels involved in the emission of x-rays (from Goulding and Jaklevic, Ref. 1).

related to the electronic transition series. Energies of interest are usually less than 30 keV, where the K lines of elements of $Z < 55$ and the L lines of the higher elements appear (Ref. 1). Figure 3 shows the energy levels associated with the respective atomic numbers.

The sensitivity and specificity of the technique depend upon a number of factors. Two important fundamental physical factors are the probability that the incident radiation will produce the desired excitation, and the probability that the resulting readjustment of the atom will produce fluorescence x-ray emission.

The relationship between the excitation intensity and the intensity of fluorescence is complex. It depends upon a variety of factors, including the spectrum of the incident radiation, the angle of radiance, photoelectron cross section, the molecular weight and matrix of the analyte, and the absorption pathlength. While the sensitivity of an analysis system can, in principle, be determined on an absolute

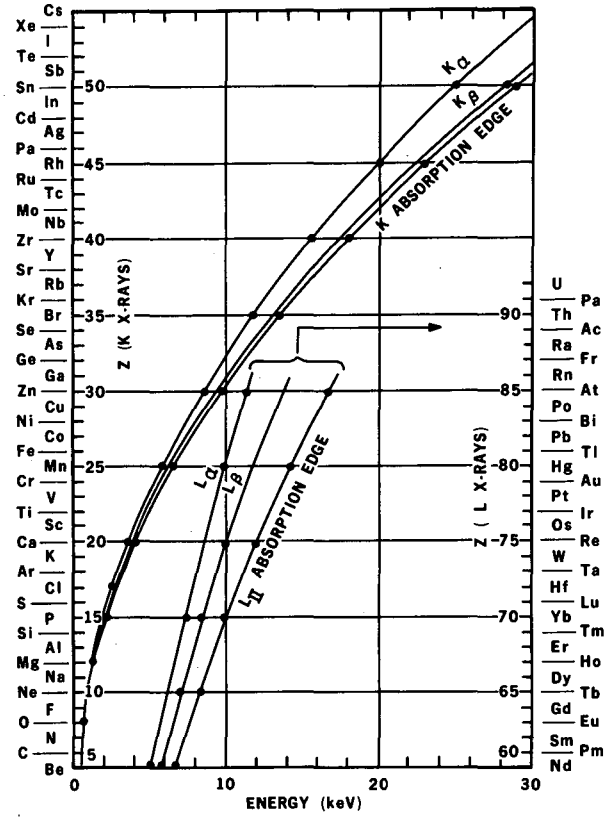


Fig. 3. Atomic energy level vs. Z (atomic number), (from Jaklevic and Goulding, Ref. 3).

basis, in practice, the system parameters are generally calibrated, occasionally using known standards. The analysis of an unknown sample is therefore related to the standards.

The following equation may be used to calibrate:

$$I_i = kA_iC_i$$

where I_i ≡ observed intensity

C_i ≡ the concentration element i

A_i ≡ relative fluorescence probability of elements i, which can be calculated or measured (see Ref. 4).

k ≡ factor containing efficiency, geometry, etc., which must be measured at least one point, by use of standards.

b. Experimental Techniques. X-ray fluorescence analyzers consist primarily of (1) an excitation source, which bombards a sample with sufficient energy to induce fluorescent x-radiation, (2) a sample holder (3) the x-ray spectrometer and (4) detection-readout system. There are a variety of options avail-

able for each of these components. Since the x-ray spectrometer should be optimized to suit experimental needs, it is necessary to look at the various options available for each component, and to compare their advantages and disadvantages. Some of the factors which must be considered when reviewing these options are the accuracy and precision needed in each determination, the cost and time allowable or necessary for each determination, the need for and possibility of multielement determinations, the resolution requirements and the instrumental flexibility. The analyst must consider the ease of calibration and sample preparation and the destruction or preservation of the sample.

The choice of spectral analyzer and its associated detection-readout system influences the choice of every other parameter. The two major types of spectral analysis used are called energy dispersive and wavelength dispersive.

In energy dispersive systems (see an example in Fig. 4), some of the fluorescent x-radiation resulting from irradiation of the sample reaches a detector. When an x-ray photon hits the detector, a signal consisting of a pulse of electronic charge is produced which is proportional to the energy of the x-ray. The energy level indicates the element involved and the number of pulses counted at each energy level over the entire counting time is related to the concentration of the element.

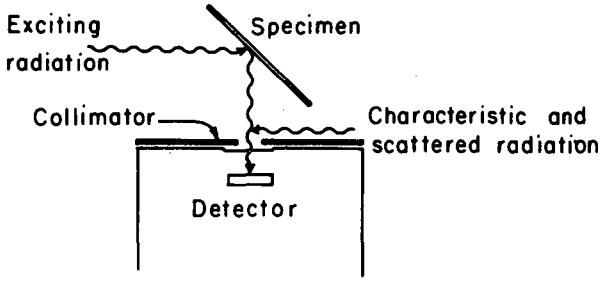


Fig. 4. Schematic of x-ray fluorescence analysis techniques showing typical energy dispersive set-up (from Giauque, et al., Ref. 4).

In wavelength-dispersive systems, (Fig. 5) x-rays emitted by the sample are diffracted by a crystal to an angle according to the Bragg relation: $\sin\theta = n\lambda/2d$. A detector placed at the point to which the wavelength of interest will be diffracted then counts the pulses over the period of excitation. The range of wavelengths involved is scanned. Wavelengths at which the intensities peak indicate the types of atoms involved and the areas under the peaks are related to the concentrations.

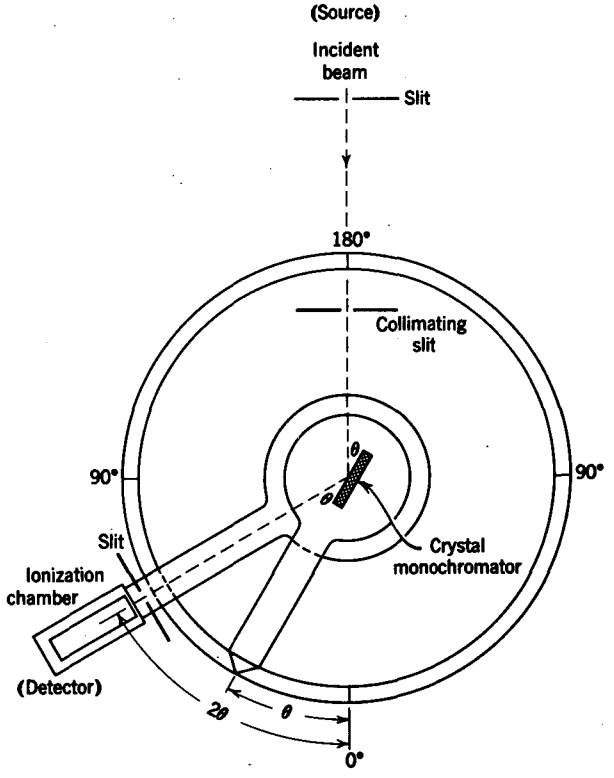


Fig. 5. Schematic diagram of the Bragg spectrometer. To scan a wavelength range, the crystal is rotated at angular velocity $d\theta/dt$, and the detector at angular velocity $d(2\theta)/dt$. (Reproduced from Liebhafsky et al., Ref. 36, with permission by John Wiley, copyright 1960).

The various components associated with XRF instrumentation will be discussed in the following sections: (1) sources of exciting radiation, (2) detectors (3) energy dispersive systems, and (4) wavelength dispersive systems. Section (5) describes various sampling techniques and section (6) analyses and compares the types of XRF methods and instrumentation available.

(1) Excitation Sources. Any source of radiation which is capable of producing vacancies in the inner shells of an atom is a potential excitation source for x-ray fluorescence. The two basic types of excitation currently used for environmental trace element analysis are photons and charged-particles (PIXE) (Ref. 6). Light ions, particularly protons, are principally used for PIXE. Electrons may be used for excitation, but bremsstrahlung produces a high background signal; consequently they are much less frequently used for environmental samples than are positively charged particles. Reference 7 provides a brief but comprehensive review of the techniques available.

(a) Photon-Induced Emission Techniques. This approach is more generally applied for trace metal analysis of aqueous samples, because it is generally more convenient and less costly than PIXE.

The efficiency of production of fluorescent x-rays depends on several well-characterized physical processes. As mentioned in the introduction, it is a function of the energy of the incident x-rays, of the absorption edge and cross section of the element being analyzed, and of the fluorescent yield for the element. A plot of the fluorescent yield vs. atomic number is included in Fig. 6.

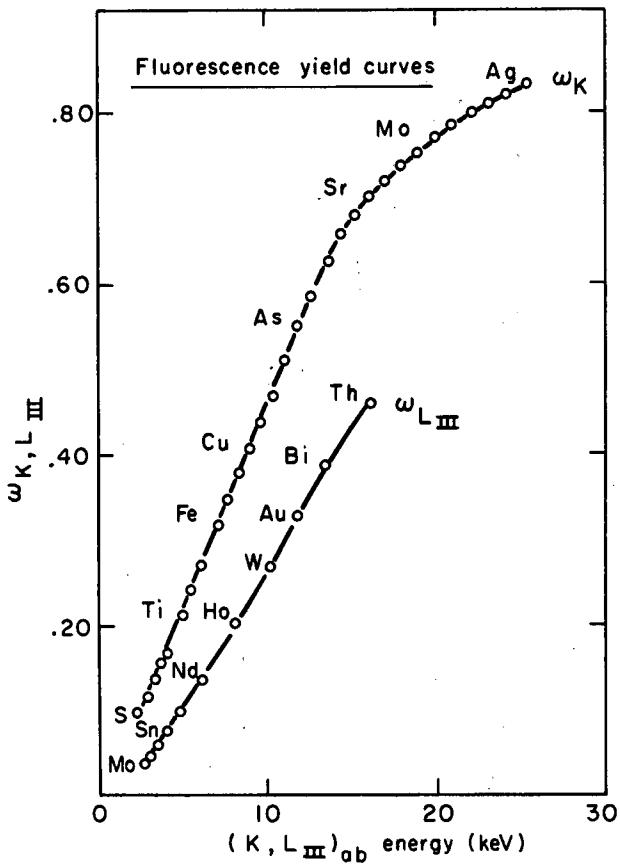


Fig. 6. Theoretical fluorescence yield curves for the K and L_{III} energy levels (from Giauque et al., Ref. 4).

The photoelectric cross section, i.e. the probability of absorption occurring, is highest at incident energy slightly greater that the binding energy of the shell involved. Figure 7 shows the cross section for shell vacancy formations for several metals. Obviously if the incident energy is below the transition energy, excitation is not possible and the photoelectric cross section is zero. It is also clear that the probability of fluorescence decreases at incident energies above the binding energy of the metal of interest. It is important therefore to optimize the energy of the incident radiation in order to maximize the probability for emission from the metals of interest.

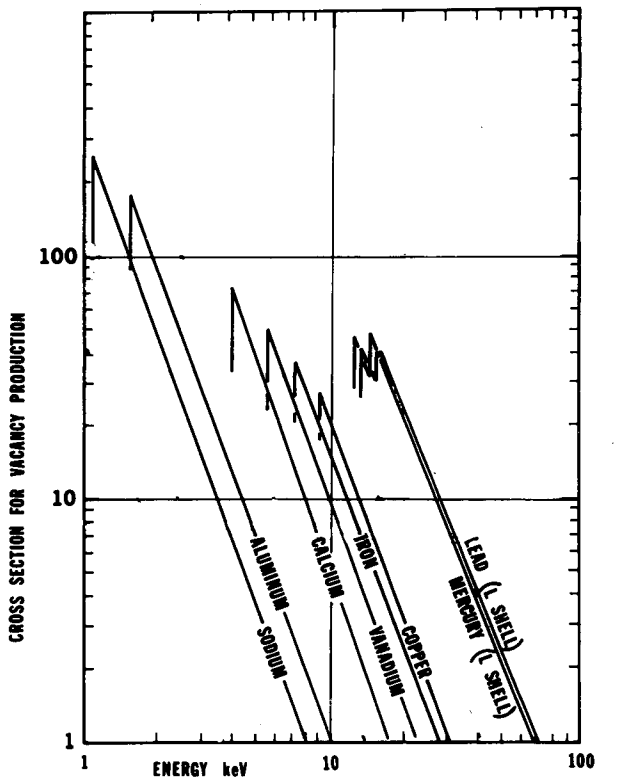


Fig. 7. Cross section for K- (or L-) shell formation in several metals (from Jaklevic and Goulding, Ref. 3).

Photons impinging on a sample are not only absorbed by metals of interest and by the sample matrix and substrate, but also may be elastically (Rayleigh) or inelastically (Compton) scattered. Absorption by the matrix and substrate serve to attenuate the excitation beam. Scattering processes not only attenuate the incident beam, but they can also produce radiation which may impinge upon the detector causing unwanted background. Rayleigh and Compton scattering occur at energies equal to and just below the energy of the incident beam. If a continuum source is used, scatter can occur over a broad range of wavelengths obscuring the fluorescence of interest. If a monoenergetic source is used, scatter occurs in a peak just below the energy of the incident beam (Fig. 8). Thus the problems associated with Rayleigh and Compton scattering are greatly diminished if a monoenergetic source with photon (and scatter) energies higher than the fluorescence peaks of interest is used.

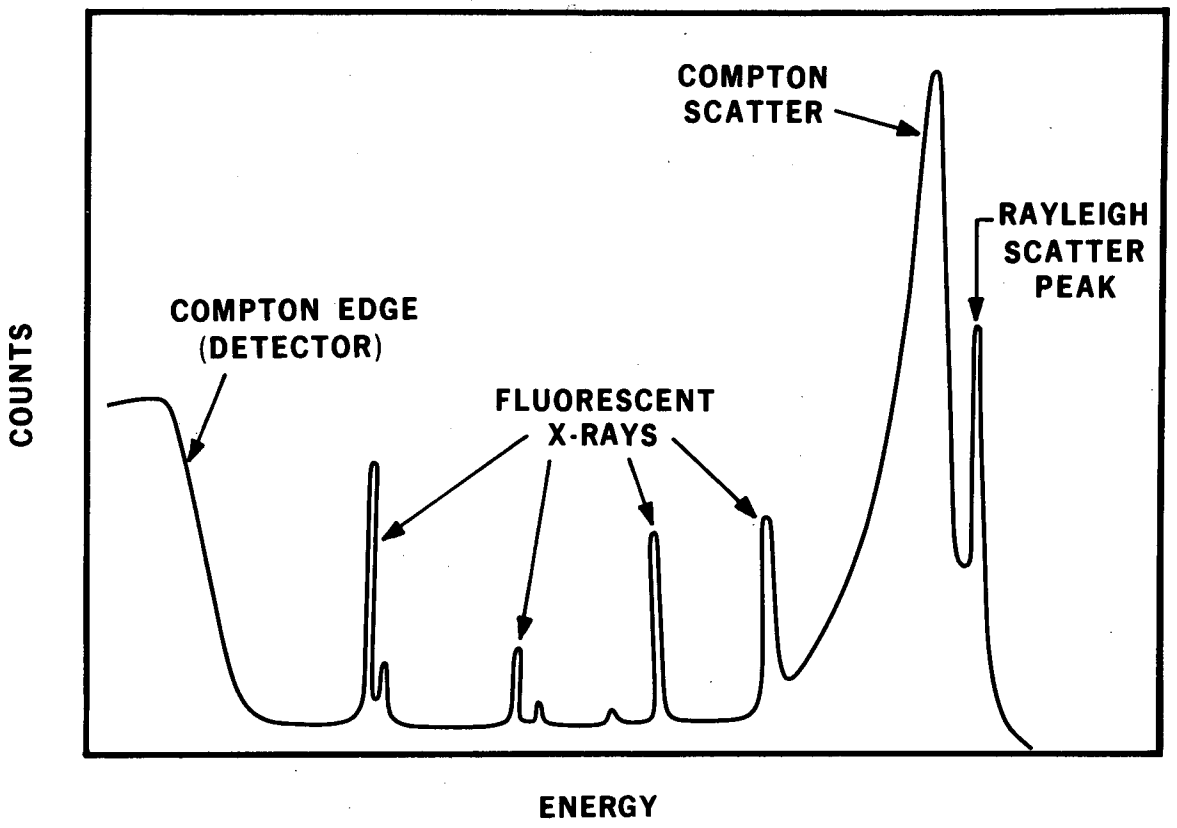


Fig. 8. Response of an energy dispersive spectrometer with monoenergetic photon bombardment of the sample (from Jaklevic and Goulding, Ref. 3).

For some low-Z metals, other considerations outweigh the problems caused by Compton scatter and continuum sources are employed. However, in most cases monoenergetic sources are used and are therefore emphasized in this section. The reader interested in continuum sources is referred to Ref. 5.

Two major methods of obtaining monoenergetic x-ray photon sources are the x-rays from x-ray tubes, either direct or secondarily excited, and photons from radioisotopic decay.

(i) X-Ray Tubes. X-ray tubes are the most commonly used device for obtaining excitation radiation. The conventional x-ray tube consists of a cathode (electron source) and an anode target. Electrons from the cathode are accelerated by a voltage. Upon impact on the anode, the electrons produce a broad range x-ray spectrum. The intensity of this spectrum and its maximum increase with increasing voltage and atomic with the atomic number of the target metal.

Assuming the same target material the maximum shifts to lower λ with increased voltage. Superimposed upon the continuum is the characteristic x ray spectrum of the target material, which appear as a series of band-edges and lines as mentioned above. Figure 9 shows an XRF energy dispersive spectrometer using primary excitation.

Unfortunately, as has been mentioned above when the continuous spectrum of energies from conventional x-ray tubes is used to produce fluorescence in a specimen, a significant number of scattered and bremsstrahlung photons impinge upon the detector producing a large background signal. This difficulty has led to the use of devices which make the x-ray beam more nearly monochromatic. This is commonly done in one of three ways: through the use of a transmission-anode x ray tube, through the use of a secondary-fluorescent target, or the use of filters. For energy dispersive analysis the first two methods are used while for wavelength dispersive analysis, filters are more commonly used.

Transmission-anode x ray tubes (shown in Fig. 10) work on the principle that any metal is a good transmission filter for its own x-rays (Ref. 8). The anode material is chosen to produce characteristic radiation of the desired energy and the accelerating potential chosen to maximize the ratio of

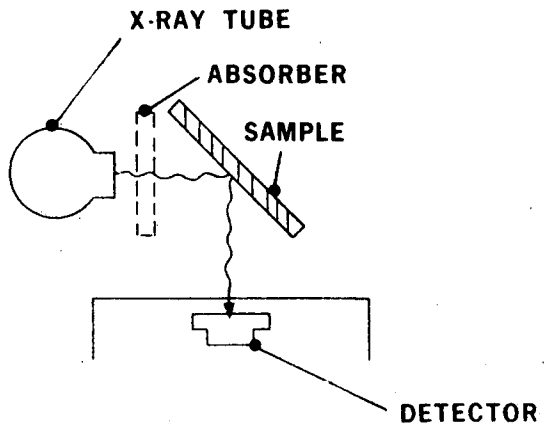


Fig. 9. Energy dispersive XRF spectrometer using primary excitation with optical filters (from Jaklevic and Goulding, Ref. 3).

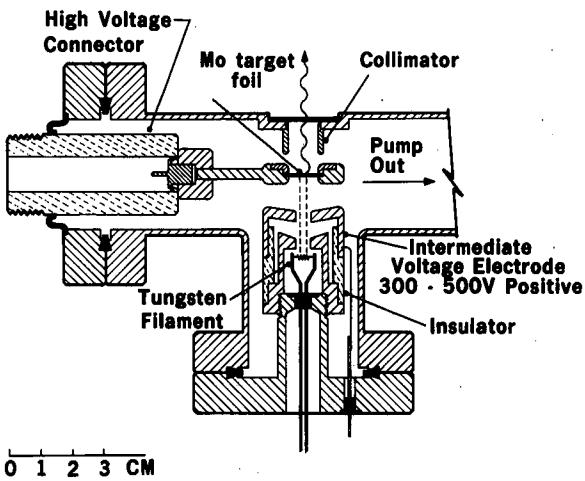


Fig. 10. Schematic of a transmission anode electrode (from Jaklevic et al. Ref. 8).

characteristic to bremsstrahlung x-radiation. The anode thickness is such that it will filter out the lower energy bremsstrahlung. Additional filtering may be used to filter out other unwanted radiation, for example, the Mo K_β line, to produce a more nearly monoenergetic Mo K_α line.

Secondary Fluorescence. This technique uses (Ref. 7) an x-ray beam from a primary x-ray tube to excite radiation from a secondary target. The target may be incorporated in the tube itself, as shown in Fig. 11, or it may be non-integral, and therefore easily changed, as is shown in Fig. 12.

Excitation is most effective using an energy slightly greater than the binding energy of the electrons to be excited in the analysis. This means that a system whereby the exciting secondary fluorescent target can be readily changed to the material which will produce the most appropriate exciting radiation would be extremely useful. Such a system has been used for trace metal analysis in air particulate monitoring systems (Ref. 9). In this system the secondary targets, principal energies of excitation, and the range of atomic numbers that can be excited are as follows:

Target 1	Ti,	4.5 keV, $13 \leq Z \leq 20$
Target 2	Mo	17.4 keV, $20 \leq Z \leq 38$, L for Pb, Hg
Target 3	Tb	44 keV $38 \leq Z \leq 56$.

Filters. Filters are also used to isolate a more nearly monoenergetic excitation beam.

To filter out the bremsstrahlung below a certain wavelength and reduce the intensity of one spectral line (of shorter λ) with respect to another, a thin metal foil with an absorption edge between the two lines may be used as a filter (Fig. 9). In this way, the K_β of copper (1.392Å) for example, can be filtered, leaving the CuK_α at (1.541Å) by (Ref. 10) using a nickel filter which has an absorption edge between the two wavelengths (Ni with 1.488Å K absorption edge).

Another technique used is the "balanced filter" technique (Ref. 11). Two separate measurements are made, first with one filter then another, and the results subtracted. The technique can be highly selective, but is limited due to statistical uncertainties resulting from subtracting two large numbers to obtain a small one. Consequently a long operating time is necessary for good sensitivity, making the technique some what unattractive.

Polarized X-Ray Excitation

This technique, currently used only occasionally in energy dispersive analysis, is based on the principle that polarized-x-rays will not scatter at 90° into their own plane of polarization. A beam which is polarized 90° from the detector will experience a better signal to background ratio. Several researchers (Refs. 12, 13, 14) have reported a significant reduction in background. However, problems do exist in determining the optimum technique for polarization (Ref. 13). Techniques currently available involve multiple scattering, resulting in a prohibitive reduction in beam intensity. (Refs. 3 and 11). This modification is not routinely available with commercial instruments.

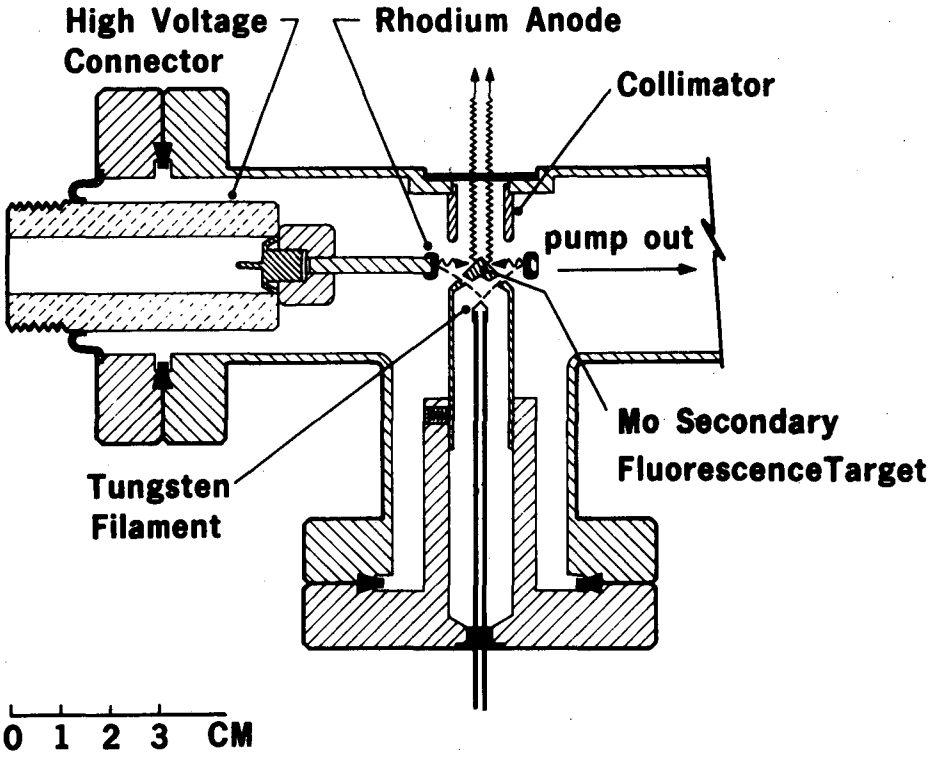


Fig. 11. Secondary fluorescence (a) schematic of a secondary fluorescence x-ray tube with rhodium anode and molybdenum target, (from Jaklevic et al. Ref. 8).
(b) Schematic of a system utilizing a target which is not an integral part of the tube (from Jaklevic et al. Ref. 9).

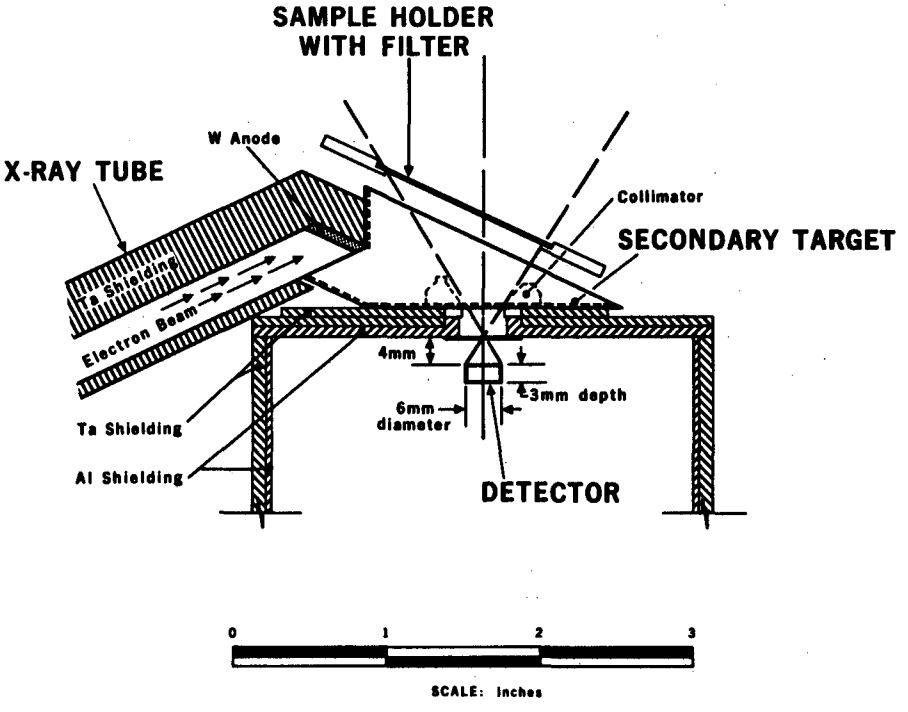


Fig. 12. Polarized x-ray excitation (adapted from Kaufman and Camp, Ref. 12).

Table 1. Relevant properties of primary x-ray and gamma ray sources (from Rhodes, Ref. 11, with permission by the American Society of Testing and Materials, copyright 1971).

Isotope	Half-Life, Years	Mode of Decay	Photon Emission			Normal Activity, mCi
			Energy (keV) and Type	Production,[a] %	Emission,[b] %	
^{55}Fe	2.7	electron capture	5.9, MnK X-rays	28.5	10 to 15	20
^{238}Pu	86.4	alpha	12 to 17, UL X-rays	10	5 to 10	30
^{75}Se	0.33	electron capture	10.5, AsK X-rays 140, gamma rays 270, gamma rays	40 54 56		
^{210}Pb	22	beta	11 to 13, BiL X-rays 47, gamma rays 10 to 1000, bremsstrahlung	24 4 ~ 2	10 to 15	10
^{109}Cd	1.3	electron capture	22.2, AgK X-rays 88.2, gamma rays	107 4	80	1
^{125}I	0.16	electron capture	27, TeK X-rays 35, gamma rays	138 7	100	1 to 10
^{241}Am	458	alpha	59.6, gamma rays 14 to 21, NpL X-rays	36 37	30 0 to 20	1 to 20
^{153}Gd	0.65	electron capture	103, gamma rays 97, gamma rays 70, gamma rays 41, EuK X-rays	20 30 2.6 110	~ 20 ~ 30 ~ 2 ~ 50	1
^{57}Co	0.74	electron capture	136, gamma rays 122, gamma rays 14, gamma rays 6.4, FeK X-rays	8.8 88.9 8.2 51	 ~ 80 0 to 10	1
^{137}Cs	30	beta	662, gamma rays	82	~ 80	

[a] Theoretical yield, percent photons per disintegration.

[b] Approximate practical output, percent photons per disintegration.

[c] Also the use of ^{125m}Te, with similar characteristics to ^{125}I, has been reported.

(ii) Radioisotopic Excitation. Radiosotopes were early sources of monoenergetic radiation for energy dispersive analysis. Use of a radioactive material as a source has the advantage that such a source produces a predictable, constant, calibrated intensity with a known energy spectrum. They tend to be inexpensive to purchase and maintain. Their most obvious disadvantages are that practical sources are considerably less intense than are x-ray tubes; they cannot be "turned-off" when not in use; and a wide variety of sources are required to perform multielemental analyses. Care must be taken that they are not contaminated with unwanted gamma-ray emitters which cannot be shielded from the detector and therefore produce a continuous background (Ref. 1). Of these, the

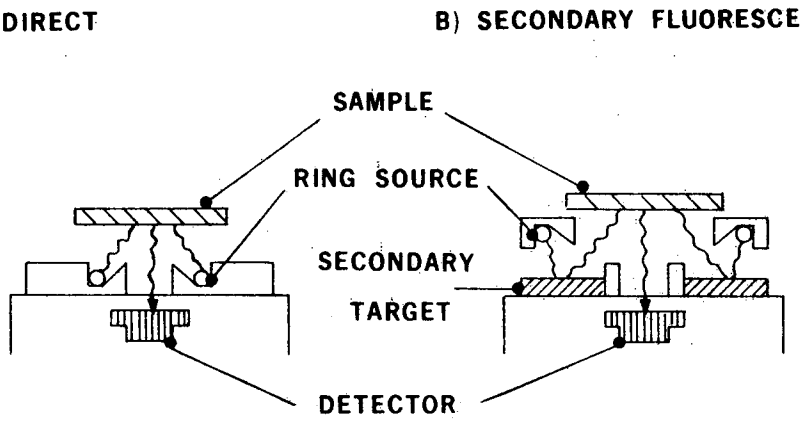


Fig. 13. XRF excitation using radioisotopic excitation. (a) Direct excitation. (b) Secondary excitation, (from Jaklevic and Goulding, Ref. 3).

problem of intensity is most critical. The intensity is so low that radioisotopic sources are almost never used in wavelength dispersive analysis.

The most useful radioactive sources are those which produce monoenergetic photons either as γ-rays from nuclear decay or x-rays from electron capture. One particularly useful source is I^{125} which emits the K line of tellurium.

Table 1 (from Ref. 11) lists some of the radioactive sources which have been found useful. The source activities shown each produce about 10^8 high energy photons/sec. Generally, analysis in the ppm-region requires sources of at least this activity coupled with a system with high-efficiency geometry to perform the analyses in a few minutes.

Use of a secondary target excited by a radioactive source can provide a roughly monochromatic x-ray spectrum. For targets of reasonably high atomic number (Z), the monochromaticity is quite good, and for metals of high (Z), the absorption and fluorescence efficiency is sufficient for useful analysis. However for metals with medium to low atomic numbers, the frequencies are too greatly separated for efficient absorption and subsequent fluorescence becomes too low for useful analyses of the medium-Z elements when targets of the heaviest elements are used. One advantage of using secondary targets is that they can be switched to obtain excitation x-rays of differing wavelengths. A disadvantage is that to obtain sufficient excitation intensity the primary source must have relatively high activity. Sources and targets have been designed and used as assembled units in order to make them more compact.

Practical configurations for primary and secondary excitation are shown in Fig. 13a and b. Other arrangements are discussed in Rhodes (Ref. 11). Generally speaking a ring or annular source (illustrated in Fig. 13) is most flexible and can be used with small semiconductor detectors.

When a specimen of variable composition or shape is analysed, uniformity of excitation and response is very important (assuming that the "average" composition is sought). The annular source configuration has the best uniformity for specimens of size comparable with the annual diameter: nearly flat response across the specimen can be achieved within a few percent.

Encapsulation of sources is an important design consideration: In principle, the source should cover as small an area as possible in the shape of a disk, yet it cannot be made very thick because self-absorption would be a problem. Rhodes (Ref. 11) and Ansell (Ref. 15) discuss these considerations at length.

(b) Charged Particle Excitation. The use of charged particles as the exciting means in x-ray fluorescence energy-dispersive analysis has received considerable attention. The term "fluorescence" is not strictly applicable to particle excitation, and the term charged particle induced "emission" is more commonly used. Among possible particle types are electrons, protons, and alpha particles. However, electrons have the serious difficulty that they produce bremsstrahlung in the specimen, the intensity of which is exceedingly high compared to that of the emitted x-rays. Hence, they do not provide competitive sensitivity, and are seldom used for trace-element analysis of the type considered here.

Protons and alpha particles in the few MeV region are often used for trace metal analysis. It was initially assumed that PIXE

(particle induced x-ray emission) would significantly improve detection limits, since the background bremsstrahlung for heavy particles is significantly lower than for electrons and the cross section for x-ray production is high (Ref. 16).

Experimentally, however, the background has been found to be substantial and is attributed to the bremsstrahlung produced by secondary electrons. Another source of background is Compton scatter of γ-rays from nuclear excited states which can severely limit sensitivities of elements ca. Z = 45.

A paper by Folkman, et al. (Ref. 17) includes thorough calculations of the various contributions to the background in an energy dispersive system. They predict probable detection limits for iron, zinc and lead of ca. 0.1 ppm. This is comparable to the detection limits achievable using photon excitation. Good comparisons of the sensitivities achievable using PIXE and photon-induced x-ray emission are found in Refs. 18-24. Experimental comparisons discussed by Jaklevic and others (19, 25, 26, 27) verify the comparable sensitivities for the two methods for most samples.

The technique is particularly applicable to samples of very small diameter, since the particle beams can usually be very well focussed.

Experimentally, PIXE has several drawbacks. It requires a voltage source to accelerate the charged particles, such as a Van de Graaf generator, the expense of which is prohibitive for most labs performing routine water analyses. Samples must be thin, since alpha particles and protons of a few MeV energy have very short mean ranges, to prevent an extremely high background. Another limitation is that high intensity particle beams, when focussed well, may produce enough local heating to burn a hole in a specimen such as an air filter; but at lower intensities analysis time becomes long. Also many accelerators are difficult to control well (Ref. 25). There are often problems with attaining uniform irradiation of large-area samples with a particle beam of small cross section. Finally, use of PIXE requires highly trained and skilled personel to maintain and use.

(2) Detectors. A number of detectors have been used for detection of x-radiation. These are ionization chambers, gas proportional counters, scintillation detectors, and semiconductor devices. While it is possible to use the latter three for either wavelength dispersive or energy dispersive analysis, scintillation counters and gas proportional counters are most commonly used for wavelength dispersive, and semiconductor detectors are used for energy dispersive. For wavelength dispersive analysis, the resolution is determined by the complex mechanism which aligns the detector and therefore it is possible to use scintillation and gas proportional counters, which have poor resolution, but very high count rates as detectors. For energy dispersive analysis, it is important to use a detector which has good resolution and low noise; for this the semiconductor detector is well-suited. Semiconductor devices are capable of counting at very high rates, but, at a sacrifice of count rate, they can achieve the resolution and noise levels necessary for energy dispersion but longer measurement times must be used. This section will briefly describe how each type of detector works. How the detector is used in each type of XRF system is described in sections (3) and (4), on energy dispersive and wavelength dispersive analysis.

Ionization Chambers and Gas Proportional Counters. An electric potential is applied across two electrodes in a chamber filled with a gas setting up an electric field gradient. The potential must be high enough that if ion-pairs are formed, the ions will tend to drift toward the appropriate electrode rather than recombine. If an x-ray enters the chamber, a number of ion-pairs are formed, proportional to the energy of the x-ray.

In an ionization chamber, the field is strong enough that each electron formed is accelerated to the positive electrode, making a pulse whose energy is not a function of the applied voltage. The number of pulses is proportional to the intensity of the x-radiation.

In a gas proportional counter, as each ion pair is formed, the freed electron is accelerated toward the anode. As the electron accelerates toward the anode, it causes the formation of further ion pairs (gas multiplication). When these electrons hit the anode, an electrical pulse is generated whose size is proportional to the energy of the original x-ray photon (Ref. 26). The number of pulses counted is, of course, proportional to the intensity of the x-ray.

The ability of the gas proportional counter to resolve x-rays of different energies is poor, but it is capable of achieving a very high count rate (50,000 cps vs. 10-20,000 cps for a Si(Li) detector). These detectors are used most typically for metals with low to moderate atomic numbers. (Ref. 23).

Scintillation Counters. A scintillation counter is generally made up of lithium activated sodium iodide crystals [(NaI(Li)] which when hit by an x-ray photon emits radiation in the UV-visible, which in turn produces an electrical pulse from a photomultiplier tube.

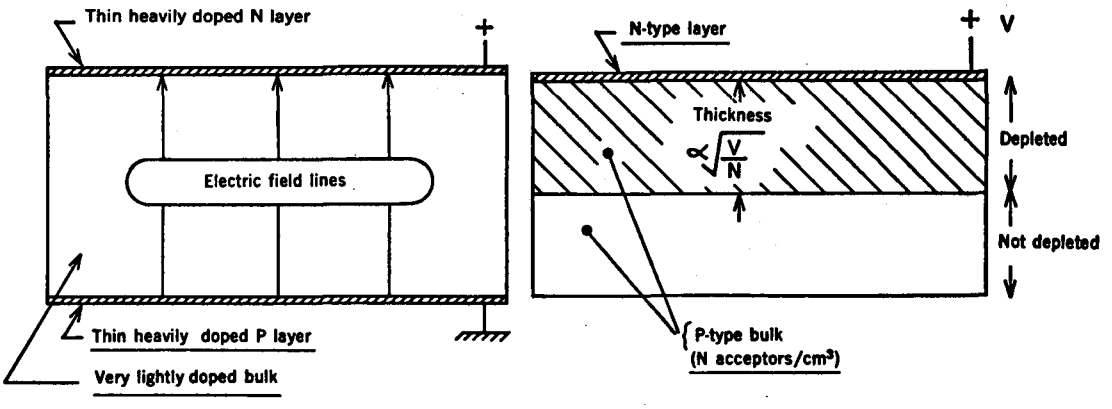


Fig. 14. An idealized semiconductor detector (reproduced from Goulding and Stone, Ref. 28, with permission by the American Association for the Advancement of Science, copyright 1970).

The size of the pulse indicates the photon's energy and their rate of occurrence its x-ray intensity. Scintillation-counters are used to count pulses of higher energy x-rays than are gas proportional counters, having a higher efficiency for metals in the region of Z = 40 to 51. (Ref. 23).

Semiconductor Detectors work on very similar principles to those of an ion chamber. The semiconductor detector can be considered a bulk material with electrical contacts on either side (Fig. 14), the positive electrode is made up of electron accepting material (p-type material) and the negative electode is made up of electron rich material (n-type material). When a potential is applied across the detector, a potential gradient is set up. If an x-ray hits the detector electron-hole pairs are formed which are collected at the electrodes. A pulse (which is proportional to the energy of the x-ray) is generated when the electron reaches the electrodes. The number of pulses indicates the intensity of the radiation. (Ref. 26, 28).

While this description is simple enough, the actual production of a semiconductor detector for use in energy dispersive x-ray analysis is far more complex. There are several important characteristics of the semiconductor materials (all from Ref. 29):

- The electron-hole pairs must be able to be formed and their number should be linearly related to the energy absorbed.
- The carriers of the charge must be able to move through the bulk material to the contacts without being trapped, requiring crystals of exceptional purity and perfection.
- To collect the charges, a field must be maintained across the bulk material, with only a minimal leakage current, so that events are detectable. This means that a semiconductor with a large band gap is necessary.
- The contacts themselves must not inject significant quantities of electrons or holes into the bulk material.

Even after careful choice and development of the detector itself, in order to achieve the necessary resolution, charge collection efficiency, and noise levels for energy dispersive analysis, it was necessary to optimize the electrical field shape of the device (see Refs. 30-32), and the analytical processing circuitry of the system (see Ref. 33). The reader interested in the details and history of these improvements is referred to Refs. 30-33).

Silicon semiconductor devices, lithium drifted to compensate for electrically active impurity centers, are now the most widely used detectors for energy-dispersive analysis. They are stable, have a high count-rate capability, small size and low background. The best reported resolution for an energy-dispersive system using a Si(Li) detector is ca. approximately 150 eV (Ref. 34), at the Cd to Lα and KKα region (~ 3.3 KeV) - see Fig. 15), a significant improvement over the detectors produced 10 years ago. This allows the separation of element pairs as low in the periodic table as carbon/nitrogen. On the other hand, users of wavelength dispersion systems claim a resolution of 3eV also at 3.3 KeV (Fig. 15) or better, which eliminates most line interferences and is able to distinguish between various metallic electronic states. (Ref. 27).

Semiconductor detectors based on germanium were considered possible close competitors to Si(Li) detectors. They have the advantage of potentially better energy resolution, but must be operated and stored at low temperatures, and suffer from high leakage. Also, at energies above about 10 keV, the spectrum from a germanium detector is complicated by the presence of the 'escape peak', due to germanium K x-rays escaping from the detector surfaces and hence degrading the full-energy photopeak.

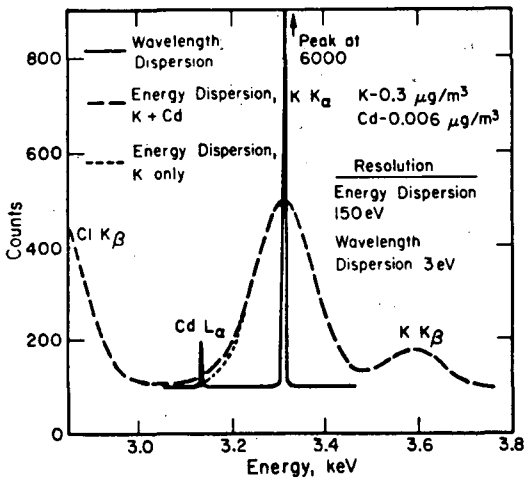


Fig. 15. A comparison of the resolution of wavelength dispersion analysis and energy dispersion analysis at the CdL_α and KK_α and K_β lines (reproduced from Birks and Gilfrich, Ref. 34, with permission by American Chemical Society, copyright 1976).

Detectors not based on semiconductor devices, such as gas-proportional counters and sodium iodide scintillation counters suffer from poorer energy resolution. They, therefore, are unable to differentiate between adjacent metals on the periodic table, which makes them unsuitable for energy dispersive analysis.

The discussion above has indicated that silicon semiconductor detectors, used with nearly monoenergetic excitation radiation from either a radioactive source or an x-ray tube, seem to provide the best combination of parameters for sensitive x-ray fluorescence analysis of trace elements by the energy dispersive technique, especially for medium-Z to high-Z elements.

(3) Energy Dispersive Systems. Prior to mid-twentieth century, a number of energy dispersive detection systems were in use, but none was adequate for rapid, multi-element trace metal x-ray fluorescent spectroscopy. This was particularly true for the determination of the minute concentrations that are involved in environmental contamination analysis, which until about 15 years ago, were usually analyzed with wavelength dispersive systems. Developments of the semiconductor radiation detector in the mid 1960's changed all this, and revolutionized the field of x-ray fluorescence analysis. Such devices have now become widely used as sensitive x-ray detectors.

The spectral analysis and detection-readout systems of an energy dispersive spectrometer rely on the semiconductor device and a complex electronic system to analyze and count the photons impinging upon it.

Electronic Systems

Improvements in the electronics system supporting the detector have significantly improved the resolution of the semiconductor detector, a significant problem of the 1960's; early silicon semiconductors had resolution in the 2 keV range (FWHM), limited primarily by the properties of the preamplifiers. Introduction in 1965 of low noise field effect transistors, (FET's), advances in manufacturing methods and optimization of operating conditions brought the resolution to about 250 to 300 eV limited by the feedback resistor. Developments in the early 1970's enhanced the resolution even further. One approach achieves improved performance by replacing the feedback resistor with light coupling from a light-emitting diode to the photosensitive drain-gate FET junction (Ref. 30). Still further improvement in the performance at high counting rates was achieved by introducing a pulsed-light feedback technique, thereby keeping the preamplifier in the proper range and preventing it from drifting into a non-linear range at high rates. This has been thoroughly described by Goulding et al. (Ref. 3). With a rejection system to elimiante events which occur while an event is already being processed, this system can achieve excellent resolution and can maintain it up to random counting rates in the region of 20,000 cps.

Spectrometers

An energy dispersive spectrometer was shown in Fig. 4. It consists of an excitation source, a sample and a semiconductor device which both analyzes and indicates intensities. A typical pulse height spectrum was shown in Fig. 8.

Many energy dispersive spectrometers are commercially available from companies such as EDAX and Kevex. The commercial instruments are fairly simple to use, but require highly skilled personnel to repair them. In no case should a person not specifically trained in the complex electronics of the system attempt to correct a malfunction.

Because of the extreme simplicity of the geometrical system, energy dispersive spectrometers are readily automated. Such a machine has been working at Lawrence Berkeley Laboratory for more than two years without serious failure (Ref. 9). Most commercially available devices are also automated.

Minimum detection limits (mdl's) are hard to define for XRF systems used for water samples, since it is necessary to concentrate

or obtain dry samples in order to achieve mdl's of less than several µg/ℓ; the mdl is entirely dependent upon the sample size. Further, the mdl can also be strongly controlled by count rate. One group using PIXE reports that to obtain 0.1 to 1µg/ℓ sensitivity, it was necessary to evaporate 20-40 ml of solution (Ref. 35).

Energy dispersive systems are extremely useful for simultaneous multielement determination or qualitative analyses of dry solid samples, particularly for metals in concentrations in the µg/ℓ range. This makes them excellent for determining metals in surrogate materials, but less useful for analysing the water itself. Energy dispersive systems are not useful for speciation, that is, determining the form of the metal present.

(4) Wavelength Dispersive Systems. The wavelength dispersive technique derives its name from the fact that the analysis of the x-ray beam by diffraction much as spectrum analyses can be accomplished with a diffraction grating. In this case a crystal is used as a diffracting element. The phenomenon, long the most important method for x-ray analysis, relies on the fact that crystals (or other similar wavelength analyzers) possess regular three dimensional lattice arrays of atoms. Essentially, the crystal acts as an x-ray grating composed of atoms, from which photons can be coherently scattered so that they are in phase at certain angles. They reinforce each other, producing a diffraction pattern. This "Bragg diffraction" is often mis-named "Bragg reflection". Although this phenomenon and its explanation are quite well known, a brief description is given here.

The conditions for Bragg diffraction are shown in Fig. 16. The three dimensional lattice array of atoms is found to consist of planes of atoms. It can be shown mathematically that x-rays will be diffracted from these planes with an angle of incidence equal to the angle of refraction and satisfying the condition that

$$\sin = \frac{n\lambda}{2d}$$ (Ref. 37).

Though termed "wavelength dispersive", since the wavelength is conceptually the parameter involved, the system is of course also energy dispersive, because energy E and wavelength λ are related by the equation $E = hc/\lambda$ (h is Planck's constant and c is the velocity of light).

There is a wide variety of wavelength dispersive spectrometers; two typical spectrometers are shown in Fig. 17. All include an excitation source, an element used for spectral dispersion, and a detection readout system.

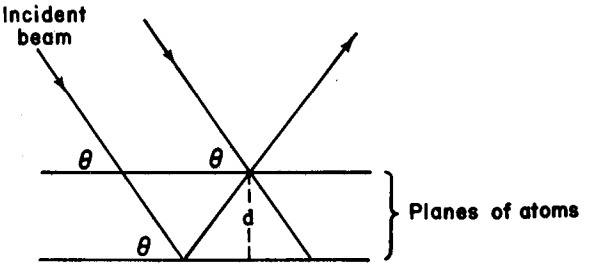
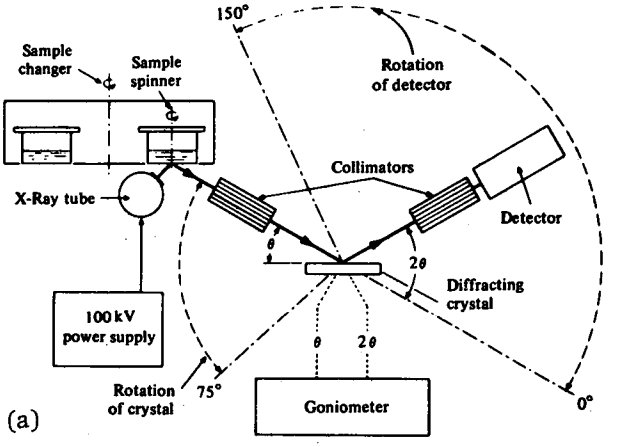


Fig. 16. Conditions of Bragg diffraction (adapted from Liebhafsky, et al. Ref. 36).



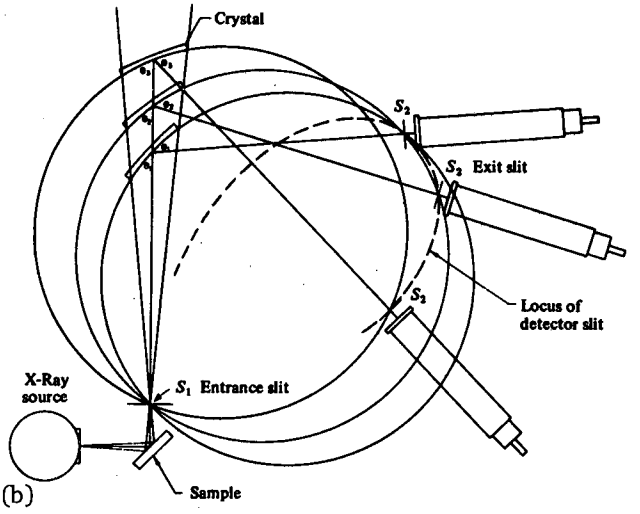


Fig. 17. Geometry of wavelength dispersive x-ray fluorescence spectrometers. (a) Plane crystal (reproduced with permission by Philips Electronics Instruments, n.d.) (b) Curved crystal (reproduced with permission by Applied Research Laboratories, Inc.)

Unlike energy dispersive spectrometers which use the detector to differentiate between the energy of the resultant x-rays and to count the number of pulses, wavelength dispersive spectrometers use a separate component to disperse the radiation and another to determine the intensity of the radiation.

In a wavelength dispersive system, it is necessary to first collimate the x-rays emitted by the sample; the radiation then is diffracted by the dispersive element and impinges upon the detector.

Dispersive elements. Crystals used to diffract the x-rays emitted by the sample may be flat, curved or a variety of other geometries.

Details on choice of crystals and the relative advantage of flat, curved, and other types of crystals are discussed in a number of of standard works, for example, Liebhafsky et al. (Ref. 36) and Birks (Ref. 37).

When the emitted x-rays have passed through the collimator, they impinge upon the analyzing crystal. For each angle of the crystal, only one wavelength will be diffracted at an angle of 2θ (if θ is the angle of incidence). The spacing between wavelengths is, of course, dependent upon the interplanar spacing, d, of the analyzing cyrstal. Looking at the Bragg equation: $\sin\theta = (n\lambda/2d)$, small values of d imply a greater resolution. However, the analyst has to consider that the limiting wavelength for the analysis occurs when $\lambda = 2d$, since 2θ then equals 180°. The limit is actually less, since the goniometer (the device that controls the crystal angle) can usually only attain 2θ of ~ 150°. Figure 18 shows the wavelength ranges of 14 different reflectors displayed, for the angular range (2θ) from 8° to 145°. Table 2 (Ref. 36) explains the compositions of the of the Bragg diffractors shown in Fig. 18 along with some remarks on their performance. One difficulty is that each particular crystal type is only useful over a limited wavelength range because of its interplanar spacing d. The resolution of wavelength dispersive systems is very good. Current systems available report a resolution of ca. 3 eV for some elements (Ref. 27).

Advanced x-ray fluorescnece systems may contain multiple reflectors, each "tuned" geometrically to one (or a few) particular wavelength channel(s). Each spectrometer channel can in this manner be optimized for the particular element being measured, including not only choice of best crystal but

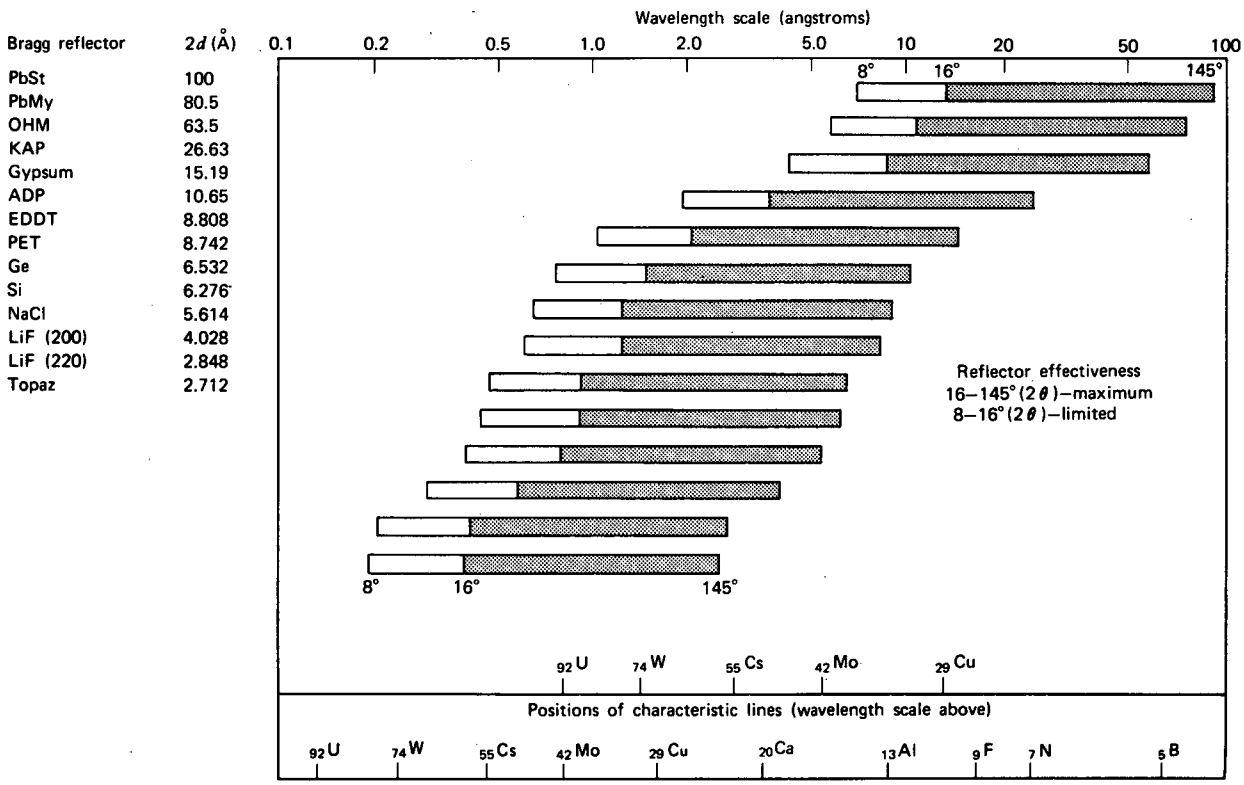


Fig. 18. Flat Bragg reflectors for x-ray emission spectrography; spacings and useful ranges (reproduced from Liebhafsky, et al., Ref. 36, with permission by John Wiley and Sons, copyright, 1972).

Table 2. Further information for flat Bragg reflectors for x-ray emission spectrography (adapted from Liebhafsky et al., Ref. 36, with permission by John Wiley and Sons, copyright 1972).

Bragg Reflector	Name	Remarks
PbSt	Lead stearate	Langmuir-Blodgett grating
PbMy	Lead myristate	All following reflectors are crystals
OHM	Octadecyl hydrogen maleate	Good for determining carbon
KAP	Potassium acid (hydrogen) phosphate	Preferred for determining F or Na
Gypsum	Calcium sulfate dihydrate	May effloresce. Store properly
ADP	Ammonium dihydrogen phosphate	Low intensity
EDDT	Ethylenediamine ditartrate	Low intensity
PET	Pentaerythritol	Higher intensity than the preceding two
Ge	Germanium	Both elements: even orders missing
Si	Silicon	in reflection. Intensity comparable
NaCl	Sodium chloride	Useful but hygroscopic. Store properly
LiF (200)	Lithium fluoride. Note Miller indices	Best general-purpose crystal
LiF (220)	Lithium fluoride. Note Miller indices	Good intensity. High resolution
Topaz	Aluminum fluosilicate (hydrated)	Best resolution

also best geometrical layout, best divergence (acceptance), and best detector set-up. In general, the detectors used in such systems are either flow-through gas proportional counters or scintillation counters, which possess high detection efficiencies and large sensitive areas.

These instruments are currently produced by Siemens, Applied Research Labs., Phillips Electronics and Rigaku Denhi. The Siemens Model MRS-3 has 16 fixed channels and one channel adapted to a scanning monochromator (Ref. 38).

Because Bragg diffraction is not perfectly selective, there is some background at any given angle θ from x-rays whose main diffractive peaks are at other angles. For example, background reflections can arise from geometrical considerations: wavelengths a factor of 2 apart (λ and 2λ, say) will in general both be enhanced at the same angle θ. This background, which can be largely removed by pulse-height selection, is still one of the intrinsic interferences to the technique. Another major interference is the incoherent scattering of the primary radiation by the atoms in the specimen.

Detection Systems

The detector is used to determine the intensities of the various individual fluorescent lines while rejecting backgrounds such as the much more intense (and higher-energy) scattered photons. These backgrounds, while high, are significantly less troublesome than those in energy-dispersive systems. In principle, by varying θ, a single crystal can analyze all wavelengths such that $\lambda > d$. As has been mentioned above, practical limitations can arise from the geometrical relationship which allows the enhancement at the same angle of wavelengths a factor of two apart. In practice they can be separated either by a measurement at some different θ' where the shorter wavelength alone is enhanced, or by pulse light selections.

As has been said earlier, since it is not necessary to use a high resolution detector in wavelength-dispersive systems, it is possible to use gas-proportional or scintillation counters as detectors. The count rate is enhanced (50,000 cps vs. 10-20,000 cps for a Si(Li) detector).

A difficulty with this system, of course, is long analysis time. Unless multi-crystal

systems with many parallel channels are used, each wavelength region must be scanned in sequence, so that a measurement over a wide wavelength range takes considerable time.

The detection limits for wavelength dispersive systems used for water analysis are comparable to those for energy dispersion since the limit is entirely dependent upon sample preparation.

Wavelength dispersive systems are less easily automated than are energy-dispersive systems; however, most manufacturers currently allow for automatic sample introduction. Wavelength dispersion can be used for simultaneous multielement determination only in multicrystal systems. An advantage to wavelength dispersion is its high resolution which shows some indication of being able to differentiate between various oxidation states (Ref. 27). This could be an advantage to those needing to determine the forms of the metal present.

(5) Sampling. Sample preparation presents the greatest difficulty in using XRF for trace metal analysis of water samples. In order to achieve the sensitivity necessary to meet monitoring standards or perform ultratrace analyses, it is necessary to meet monitoring standards or perform ultratrace analyses, it is necessary to obtain a dry, thin, uniform sample. Any pretreatment step is likely to introduce an error into the analysis. Drying a sample completely without introducing contaminants or losing constituents is extremely difficult. Obtaining a uniform, thin sample is even more difficult. Even if both these goals are achieved, the process is likely to be tedious and slow at best. Nevertheless several procedures have been proposed as possible. They are mentioned, briefly, below. The interested reader is referred to the references.

One of the most common techniques involves the use of filter membranes coated with ion exchange resins (Refs. 39, 40, 41). This technique is relatively rapid, but has the disadvantage of not collecting all ions to the same extent or completely. Other techniques involve precipitation of ions in solution followed by collection by filtration (Refs. 42, 43), Richey, et al. suggest a vapor filtration of the solution (Ref. 35) which is independent of the chemistry of the metal. It uses a closed system which prevents contamination and avoids the sputtering involved in most evaporative techniques. Its major drawback is that sample preparation time is often several days.

(6) Comparison, Summary and Conclusions. The performance of actual systems is not easy to summarize. The basic goals of the systems under discussion are sensitivity, accuracy, lack of interference, and multi-element capability. Systems of similar conceptual design and even similar hardware features can be designed and operated to optimize some of these parameters at the sacrifice of others but no system has been designed which optimizes all. This makes any attempt to summarize performance specifications difficult. An excellent summary and comparison has been made in Ref. 23.

The discussions above have indicated that both energy dispersive and wavelength dispersive systems, when used with photon excitation, have sufficient sensitivities to determine a large number of trace elements in a few minutes' counting time when ultratrace concentration methods on thin samples are employed. The proton-induced energy dispersive technique has comparable intrinsic sensitivities while alpha excitation yields somewhat poorer sensitivities.

Other considerations besides sensitivity must be taken into account however. For example, the detailed understanding of the many factors which Giauque, et al. (Ref. 4) have brought to the photon-excited energy-dispersive technique allows very high precision. The particle-excitation systems have not yet been so fully analyzed. This is complemented by an ease of operation and low unit cost which probably make photon excitation the analysis method of choice for most environmental monitoring when XRF is used.

The question of resolution is as yet unanswered. For situations where concentrations remain relatively constant, mathematical deconvolution and comparison to standards of comparable concentration ranges has been shown to provide reasonable accuracy and precision. For situations where relative concentrations or matrices are variable, perhaps the resolution achievable by wavelength dispersion is of somewhat greater value.

The advantages to energy dispersive techniques as compared with wavelength dispersive methods are ease in operation and multi-element capability. Wavelength dispersive instruments require a more complex apparatus and are more difficult to operate.

In conclusion, one must note that for trace element analysis in water samples, the sampling problem is a serious drawback. Particularly in situations where the analyses to be performed involves quantitative determinations of a known set of metals, techniques such as furnace atomic absorption have better minimum detection limits without necessitating such elaborate sample preparation.

The reader is referred to a number of review articles and books for details on the methods of this type of analysis. The standard texts provide brief introductions to the technique (Refs. 10, 44). The review articles

by Goulding and Jaklevic (Ref. 1) and Rhodes (Ref. 45) and the book by Dzubay (Ref. 46) are useful for energy dispersive analysis. For wavelength dispersion analysis the books by Bertin (Ref. 47) and Jenkins and DeVries (Ref. 2) and the book and article by Birks (Refs. 27 and 37) are useful. Particle induced x-ray emission (PIXE) is thoroughly discussed in Ref. 48.

c. Acknowledgments. The author is particularly grateful to Fred Goulding and Joe Jaklevic for the help, suggestions and criticisms.

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CONTENTS

2. Neutron Activation Analysis

Many elements, when bombarded by neutrons, produce isotopes which are radioactive and emit radiations characteristic of those isotopes. These radiations, particularly gamma rays, can be measured and used to identify the isotopes emitting them and hence the elements. The intensity of radiation is proportional to the quantity of element present. This technique for detecting trace elements in a sample is known as neutron activation analysis.

Neutron activation is an extremely sensitive and accurate technique for the qualitative and quantitative determination of some elements in using types of environmental samples. For use in water analysis, there are several important drawbacks which limit its use as a tool for routine monitoring. First it requires the use of a high flux nuclear reactor as a source of neutrons, or possibly a ^{252}Cf source. Even if a reactor is routinely available, analysis costs can be substantially higher than for other techniques. Furthermore for any aqueous sample, elaborate pretreatment of samples is also sometimes necessary, and for most water samples, pretreatment involves preconcentration, which can introduce additional error. This technique measures elemental abundances but can not determine the chemical compound.

Because of these limitations, it is doubtful that neutron activation analysis (NAA) will in the near future achieve as much prominence for routine water analyses for metals. Its accuracy and precision coupled with its sensitivity for some elements will continue to make it an extremely important technique for research.

Many good texts are available on the subject and the interested reader is referred to the brief introductions in Ref. 1, 2. A more detailed description of the technique is included in Ref. 3. Reference 4 is a detailed description of the procedures used for environmental analyses and monitoring, and includes an excellent reference list.

a. Principles of Operation. In the late 1930's V. Henesy and Levi (Ref. 5) proposed that the radioactivity resulting from the action of neutrons on rare earth metals, might be an aid in characterizing complex mixtures of those metals. From this initial proposal, the technique of neutron activation analysis has developed.

If an atom is bombarded by neutrons, a reaction can take place in which a radioactive isotope is formed. The following example illustrates the process:

$$^{55}_{25}Mn + ^{1}_{0}n \xrightarrow{\gamma} ^{56}_{25}Mn$$

(often written: $^{55}Mn(n,\gamma)^{56}Mn$).

The ^{56}Mn is a radioactive isotope and will decay to ^{56}Fe (a daughter element) and characteristic radiation. The decay proceeds by several paths as diagrammed in Fig. 1.

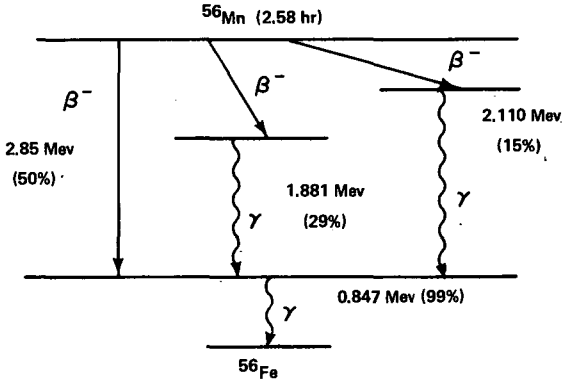

Fig. 1. Decay scheme of ^{56}Mn (reproduced from Willard, Merritt and Dean, Ref. 1, with permission by D. Van Nostrand Company, copyright, 1974).

The energy of the resultant radiation is uniquely characteristic of the parent isotope, while the intensity is characteristic of its quantity. There may be several isotopes of the element being identified. Each isotope which becomes radioactive emits a characteristic radiation. Each gamma ray and each isotope of an element can be used, in principle to determine the amount of that element. In practice there can be considerable interferences between radiations in their measurement and those gamma rays are used which have minimum interference effects. Interferences are determined in calibration studies and their effects are quantitatively removed by careful work.

A sample is bombarded with neutrons and the energy and amount of its radiation is determined. The amount of the analyte present is determined by the following equation:

$$W = \frac{AM}{\sigma^{f}\phi(1-e^{-\lambda t})N_A} \qquad (1)$$

where

W = unknown weight of the element expressed, in grams

A = induced activity of the radioactive isotope in disintegrations/sec at the end of irradiation

ϕ = flux of neutrons used in the irradiation, in neutrons/cm^2/sec

σ = the activation cross section for the nuclear reaction concerned, in cm^2 usually expressed in barns. ($10^{-24} cm^2 \cdot 1$ mb = $10^{-27} cm^2$,

f = fractional abundance of the particular isotope of the element concerned, which leads to the radioactive isotope upon irradiation.

M = atomic weight of the same particular isotope

λ = the decay constant of the induced radionuclide, in sec^{-1}

t = irradiation time, in seconds

N_A = Avogadro's number $6 \cdot 10^{23}$ (Ref. 4).

It is clear that the sensitivity of the technique for a given element will be highly dependent upon the neutron flux and to some extent the irradiation time, as well as the activation cross section for the nuclear reaction concerned.

As with most spectrometric techniques, in careful work the amount of an element present is rarely determined from first principles but by comparison with standards which contain all the elements of interest and which are irradiated at the same time as the unknown. The gamma-rays from the standards are counted under the same conditions as those of the unknown. The weight of the unknown is then determined using the following relation (Ref. 4):

$$\text{weight of element in unknown} = \text{weight of element in standard} \times \left(\frac{\text{activity of element in unknown at the end of irradiation}}{\text{activity of element in standard at the end of irradiation}} \right).$$

b. Experimental Techniques. NAA does not involve the use of a single instrument, and it is more convenient to discuss the technique and the instrumentation involved by considering the steps used in the analytical procedure. NAA involves four important steps: (1) Sample and Standard preparation (2) Irradiation, (3) Detection and (4) Data Analysis. Each is discussed briefly below.

(1) Sample and Standard Preparation. As in any technique used for trace or ultratrace analysis, samples and standards must be prepared with extreme care. Sample containers and equipment used in preparation must be scrupulously cleaned. If any chemistry is performed in order to remove interfering elements, it is essential that the reagents be of the highest quality available, or at the very least it should be known how much contaminant analyte is added. Although aqueous samples can be analysed in their original liquid form, the more common technique involves preconcentration of the sample. The metallic trace content of an aqueous sample can be collected on activated carbon (Refs. 6-9), ion exchange and chelating filters and resins (Ref. 10) or precipitated (Ref. 11). Evaporation and freeze drying techniques are often less than satisfactory (Ref. 10) since they are time consuming and can result in sputtering (losing some sample) and creating an inhomogeous residue. However with proper care and precautions, they can produce satisfactory results (Ref. 12, 13). Preconcentration using absorbing resins or carbon can reduce the possibility of leaching contamination from containers or losing trace quantities adsorbed to container walls which often occurs during transport to a laboratory, unless some chemistry is performed at time of sampling to prevent this.

After obtaining a satisfactory residue, samples are ground to assure a homogeneous sample, mixed with binder and pelletized. It is essential that bulk sample conditions be close to identical, for both sample and standard. This topic is thoroughly discussed in the article by Perlman and Asaro (Ref. 14). A study by Yellin, et al. (Ref. 15) illustrates the precision that is possible if care is taken: two groups working in two locations with the same samples report precisions and agreements of $\pm \leq 1\%$ in many cases.

As has been indicated, the use of standards is important in neutron activation analysis, and there are many schools of thought on how standardization should be done. Robertson and Carpenter (Ref. 4) and DeBruin, Korthoven and Houtman (Ref. 16) recommend preparing standards which are as close as possible in matrix and trace metal concentration to the unknowns. This then permits accounting for interferences by comparing the results. Asaro and others (Ref. 15, 17) have found that with a homogeneous sample, NAA is relatively unaffected by matrix effects and feel that it is more appropriate to have consistent sample and standard bulk form and to account for interferences by using a careful analysis of known factors during data reduction. The software which has been developed to handle interference problems is briefly discussed in Section (4) and in Refs. 15, 16, 18, 19 and 20. Yellin et al. feel that it is necessary to

have all the elements present and therefore all the γ ray energies in the standard which are expected in the unknown (Ref. 15) for accurate measurements. Many other analysts support the idea of the double or triple comparators (Refs. 16, and 20).

(2) Irradiation. The most common source of neutrons used in activation analysis are from nuclear reactors. Depending on the individual reactor facilities, the neutrons can range from nearly thermal neutrons to complex mixtures of fast and thermal neutrons or in some cases primarily fast neutrons. Most of these reactors normally operate in the range of 10 - 1000 kω and produce a neutron flux of from 10^{11} to 10^{13} n/cm^2/sec. (Ref. 4). Because the neutron flux varies substantially throughout the reactor, the set of samples and standards are sometimes rotated in the reactor to compensate for these inhomogeneities in the flux.

The time of irradiation and neutron flux used depend strongly upon the analytes. The procedure used by Asaro et al. is to irradiate initially at 11 kω for 6 mins. and the specimens are counted after ~8 mins. and one hour. A second irradiation is then performed several weeks later (8 hours at 1 MeV - 2.7×10^{13}n sec/cm^2) and measurements do not start until 6 days after that irradiation. The first irradiation allows the detection of Al, Na, Ca, V, Ti and S isotopes and others which have high concentration or intensity of radiation and short half lives. The second irradiation allows the detection of other isotopes with longer half lives (Ref. 15, 17).

(3) Detection. Most of the metals of interest, except Pb and Sn (Ref. 4), form activation products which emit gamma rays in their decay. Therefore, only detectors used for detecting gamma radiation will be considered. Two types of detector are commonly used: The semi-conductor detector, either Ge(Li) or intrinsic Ge or the scintillation counter, NaI(Tl). Ge(Li) or intrinsic Ge detectors have higher resolution and less sensitivity than do scintillation counters. (Ref. 4). Ge(Li) and intrinsic Ge detectors are operated at liquid N_2 temperatures. Intrinsic Ge detectors have the advantage over a Ge(Li) detector that a temperature rise does not injury the detector by causing the Li to drift. Large Ge(Li) detectors which are currently available can have an sensitivity of 25% of 3" ×3" NaI(Tl) detectors at an energy of ~1-1.3 MeV and a distance of 25 cm from the sample. In this case, however, the precision of the measurement is poorer than with a smaller size detector. It is clear therefore, that the type of detector used can depend severely on the metals and interfering elements present, their concentrations, and the need for sensitivity versus precision. The interested reader is referred to Ref. 4 and Ref. 16 and the references contained therein for information on this topic.

(4) Data Analysis. This step is probably the most complex and many approaches have been developed. The raw data obtained is first translated into peaks and their energies and areas determined. Next the peak positions and areas are used to calculate the types and concentrations of metals present. The computer programs used to analyze data must not only handle the complex derivation of some of the peaks such as the genetic relations between isotopes, the different routes to the same isotope and the derivation of different isotopes and radiations from the same isotope (Ref. 20), but it must also consider the experimental and theoretical interferences which can occur, such as background counts, Compton scatter, absorption correction, peak overlap or pileup. An analysis of possible errors and influences and the means to account for them is included in Ref. 15. Even with all the corrections necessary, statistical counting erors still lead to a scatter of results. By careful analysis and elimination of most obvious sources of error, it is possible for many elements to keep the scatter to less than 1% in samples of very similar composition (Ref. 15).

c. Summary. Neutron activation analysis can be shown to be an extremely sensitive technique using standard preconcentration procedures. Minimum detection limits for metals in water solutions can be shown to reach ppb levels, assuming no major interferences as is shown in Table 1. Furthermore the method can be used for qualitative and multielement simultaneous determinations. Its precision and accuracy has been found to be excellent.

On the other hand, the cost of analyzing samples in terms of time, equipment, and personnel training is a major drawback. For most laboratories the cost of a reactor is out of the question. Highly trained and skilled personnel are necessary to run and maintain the systems involved. Last, current procedures for many metals require at least one month to obtain a complete analysis.

d. Acknowledgments. The author is grateful to Frank Asaro, Helen Michel and Julie Jones for their help, criticisms and suggestions.

Table 1. Detection Limits Reported Using NAA for Trace Element Analyses of Fresh Water

Metal	Pretreatment	µg/ℓ	Source
Cr	a	0.05 µg/ℓ ±20%	Ref. 6
Hg	a	0.001 µg/ℓ	Ref. 9
Se	a	0.005 µg/ℓ	Ref. 7
V	a	0.01 µg/ℓ	Ref. 8
As	b	0.1	Ref. 4
Cd	b	50	Ref. 4
Rb	b	Not normally measured using NAA	Ref. 4
Zn	b	1	Ref. 4
Ba	b	5	Ref. 4
B	b	—	Ref. 4
Cu	b	0.1	Ref. 4
Fe	b	10	Ref. 4
Mn	b	0.01	Ref. 4
Ag	g	0.1	Ref. 4

a. Preconcentration on activated carbon

b. Separation by group

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CONTENTS

3. Electrochemical Techniques

Two electrochemical techniques are widely used for the determination of metals in water: anodic stripping voltammetry (ASV) and ion selective electrodes. Anodic stripping voltammetry is a two step process that involves the deposition of an analyte metal ion onto an electrode, and a subsequent step involving electrolytic oxidation of the metal, during which it is determined. The technique is currently gaining usage, and is rapidly developing into a most practical technique for the monitoring lab. ASV will be discussed in more detail in part a of this section.

Ion selective electrodes are used in a potentiometric technique which measures the electrode potential of a solution. From measurements of the potential, it is possible to calculate the activity of the ion in solution, and from this the concentration is inferred. Ion selective electrodes will not be reviewed at this time, however, the interested reader is referred to Refs. 1-7.

a. Anodic Stripping Voltammetry. Anodic stripping voltammetry (ASV) is an extremely sensitive technique for determining certain trace metals in water. Table 1 lists the metals that can be determined (Ref. 8) and their detection limits. ASV is an old technique nique but has received renewed interest in the 1970's. It was currently the subject of several excellent reviews (Refs. 9, 10).

(1) Principles of Operation. The principles of operation have long been known and are fairly simple. ASV involves the plating (reduction) of a metal onto an electrode which serves to concentrate the metal, and the subsequent stripping (reoxidation) of that metal back into solution. This electrochemical preconcentration step is the reason ASV is so much more sensitive than conventional polargraphy. Plating is usually performed at a potential that is sufficient to reduce all of the metals of interest in the solution:

$$M^{n+} + ne^- \xrightarrow{\text{potential}} M.$$

In the steady state the deposition current is described by the equation:

$$i_d = nFAD\frac{C^\circ}{\delta} \qquad (1)$$

where

- i_d is the deposition current,
- n is the number of electrons involved in the reduction,
- F is the Faraday constant,
- A is the electrode surface areas,
- D is the diffusion coefficient,
- C° is the species concentration at the initiations of the deposition, and
- δ is the Nernst diffusion layer thickness.

In any given experiment, the values of n, F, C° and D cannot practically be varied by the user. The surface area of the electrode can be varied by choice of electrode, but the charging current limits the area which can be used practically. The diffusion layer thickness, δ, since it is inversely proportional to the rate of mass transfer, can readily be varied by the use of stirring, rotating electrodes, or flow-through electrolysis techniques.

Table 1. Metals determined using ASV and reported minimum detection limits (mdl).

Metal[a]	mdl (µg/ℓ)	Metal	mdl (µg/ℓ)	Metal	mdl (µg/ℓ)
Arsenic	10[b]	Lead	0.01[c]	Silver	---
Antimony	---	Manganese	---	Thallium	2.0(a.c.)[c]
Barium	---	Mercury	---	Tin	0.01[c]
Cadmium	0.005[c]	Nickel	---	Zinc	0.04[c]
Cobalt	---	Platinum	---		
Copper	0.005[c]	Potassium	---		
Gold	---	Rhodium	10.0[c]		

a. List of metals from Ref. 8
b. Ref. 11
c. Ref. 9

The equations of deposition vary considerably and are quite complex. The reader may refer to Refs. 9 and 12 for equations more detailed than Eq. 1. For a given set of metals in a dilute aqueous solution the parameters that must be carefully controlled are the plating time (t), the rate of stirring, or rotation of electrode (which influences δ), the surface area of the electrodes (A), and to some limited extent (with more highly concentrated solutions), the viscosity of the solution (Ref. 9). The deposition current, i_d (Eqn. 1), decreases with time if, as is generally the case, a finite volume of sample solution is employed. The following equation, the decay of current in controlled potential coulometry, is applicable:

$$i_t = i_d e^{-kt} \qquad (2)$$

where it is the current often to see of electrolysis, i_d is the initial deposition current (at $t = 0$), k is the electrolysis rate constant, and t is the time of the electrolysis. The constant k may be further decomposed:

$$k = \frac{A}{V} \times \frac{1}{\delta} \times D \; . \qquad (3)$$

The term $(\frac{A}{V})$ is a cell geometry factor where A is the area of the electrode and V is the volume of solution. The term δ is the Nernst diffusion layer thickness which depends on the stirring rate. It is obvious that complete deposition occurs only after an infinite or very long time, thus as a practical matter it may not be desirable to deposit more than 10 to perhaps 50% of the species determined.

The potential at which the electrodeposition should be made is defined by the Nernst equation:

$$E = E^\circ + \frac{RT}{nF} \ln \frac{a_{ox}}{a_{red}} \frac{c_{ox}}{c_{red}} \; . \qquad (4)$$

Where E is the potential applied to the electrode, E° is the standard or formal potential of the couple determined, a is the activity coefficient, and c is the analytical concentration. Ox and red denote the oxidized or reduced states of this species of the couple, respectively. Practically, a potential sufficient to give a c_{red} to c_{ox} ratio of at least 1000:1 is employed. Once the metals have been deposited, the polarity of the electrodes is reversed, and the metal(s) reoxidized:

$$M \longrightarrow M^{n+} + ne^- .$$

To carry out the stripping or reoxidation step, the potential is gradually increased and the current measured. The current is made up of two components, a Faradic component resulting from the electrolysis process, and a non-Faradic component due in large part to the charging current. The "charging current" is due to the current flow needed to establish a double layer of cations and anions about the electrode (this occurs in any electrolytic cell). At the peak potential characteristic for each metal the current resulting (i_p) is measured as the metal is oxidized. The stripping current is proportional to the amount of metal plated on the electrode. The stripping current is also dependent on electrode surface area, the rate of change in potential, and on the waveform which is used for stripping thus these must be controlled for reproducibility. The analytical applications of various waveforms are discussed in part (b) of this section. Detailed theoretical considerations concerning the waveforms and stripping currents measured used for ASV are beyond the scope of this text; for these the interested reader is referred to Refs. 12-16.

Although there are theoretical expressions which allow the calculation of the amount of metal present on an electrode, the parameters involved are often extremely difficult to define. Therefore the amount of metal present in a solution is usually determined with a calibration curve (Refs. 12 and 17).

(2) Experimental Techniques. Several important parameters must be considered when using anodic stripping voltammetry. These are: the electrodes that are to be used, the waveform which will be applied, and the type of cell to be employed. This section will first describe the technique generally, then outline the types of electrodes [part (a)], the effects of various waveforms [part (b)], and the variety of cells that can be employed [part (c)]. Part (d) will review some of the interferences that may be encountered, part (e) considers several applications of ASV, and part (f) will summarize the advantages and disadvantages of ASV.

The experimental apparatus for anodic stripping voltammetry is extremely simple: an ASV cell with access for three electrodes: the electrode used for plating and stripping, a reference electrode, and a counter electrode; an inlet for a gas for deoxygenation, and provisions for stirring, if desired. The electronics involved include a three electrode potentiostat, a voltage ramp generator, and a device for measuring currents (Ref. 9). Manufacturers of ASV equipment can supply the system components either separately or as a package.

Preparation of samples for ASV usually is done as recommended in Standard Methods, 14th ed. (Ref. 18). The pH is adjusted for most advantageous deposition of the analyte metal(s), a supporting electrolyte is added to minimize ohmic drop during electrolysis (Ref. 17), and then the solution is degassed to avoid

interferences caused by the electroactivity of the dissolved O_2 (Ref. 19).

An essential precaution when measuring metals at the ppm-ppb range is to carefully avoid any impurities. All reagents should be checked in blanks using ultra pure water, since water is another source of possible contamination.

For trace and ultratrace analysis, it is important to provide some form of stirring or flow through to efficiently deposit the analyte on the electrode. Stirring should be started before electrolysis. The stirring rate should be reproduced carefully each time and should not be too violent.

The potential is then applied to deposit the most electronegative of the species present. The deposition time will depend upon the concentration of the solution, of course, and the stirring, flow, or diffusion rate. A brief rest period follows deposition. The potential on the electrodes is then reversed and the metal is stripped. If the potential is applied in a "voltage ramp", i.e., with increasing potential using one of a variety of waveforms (discussed below in part (b)), the current is recorded as a function of time or potential. (General procedure from Refs. 20, 21). The potential of the cell is always measured with respect to the potential of a reference electrode, whose half cell potential has been well established such as a saturated calomel electrode, or SCE). In the three electrode system, the potential is controlled with respect to the reference electrode, but uses a third electrode to serve as the counter electrode in the cell. If the reference electrode is placed close to the working electrode, the potential (E) can be measured with a negligible contribution of a potential drop due to solution resistance causing an erroneous measurement of E. Such a system is described in detail in Ref. 10.

(a) Electrodes for anodic stripping voltammetry. The electrode used for plating and stripping is an extremely important component in the ASV apparatus. It must be made of a material which is more noble than any of the metals which must be determined, and it should not react with the analyte solution. Because the stripping and plating currents are strongly dependent upon the surface area of the electrode (see Eq. 1); the surface of the electrode should not be degraded or changed after each determination and should be reproducible.

A wide variety of materials have been used for ASV electrodes. Most involve mercury supported in one way or another (Refs. 22-31), a although gold (Ref. 11) and other metals have been used. Mercury has a sufficiently high oxidation potential to allow electrolysis of many metals. Because many of the metals which are determined using ASV are "diluted" by mercury, there is a lower probability of intermetallic compound formation among them. Mercury is not readily attacked by weakly acidic or basic solutions. Like any other metal its effectiveness can be diminished with the sorption or organic or nonmetallic materials on its surface (Ref. 32).

Until recently the most commonly used electrode was the hanging mercury drop electrode (HMDE), and it still enjoys wide usage (Refs. 28-30). A major advantage of the HMDE is its reproducible surface, an important consideration since variations in the surface smoothness and therefore the surface area of solid electrodes may introduce significant errors in the data obtained. The major disadvantages of the HMDE are its limited surface area, instability at high stirring rates, and its tendency to produce peaks which can be ill-defined because of diffusion of the analyte metal into the drop.

In an effort to get better sensitivity from ASV techniques, electrodes with a greater surface area and electrodes which allow a greater rate of deposition of analyte metal on the electrode should be used. It is clear (referring to Eq. 1) that increasing the surface area of the electrode (A) or the rate of stirring would increase the rate of analyte deposition on the electrode and would decrease the time needed to electrolyse a given amount of material.

In an attempt to provide a larger surface area and a small volume of mercury for deposition, a variety of thin film mercury electrodes (TFME) have been developed. A suitable substrate is used to support a thin film of mercury. It must conduct electricity but not be affected by the potentials used in the deposition or stripping process. It must also be impervious, chemically and physically, to the analytical solution.

Several forms of pure graphite, impregnated with wax or chemically treated have been used (Refs. 24, 26, 27 and 31). Dense or glassy graphite electrodes (GCE's) have been found to be stable in analytical solutions and produce stripping currents which are quite high, giving easily defined peaks. Copeland et al. report that they are easily polished and maintained (Ref. 33). They also note that with the thin film, stripping peaks are better defined, since the metal atoms cannot diffuse beyond the thickness of the film.

More porous types of graphite must be impregnated with wax (wax impregnated graphite electrodes--WIGE) or treated in some other way (Ref. 31) to be rendered impenetrable, and to produce strong stripping currents (Ref. 33). While workers comparing the performance of

WIGE's and GCE's generally prefer the GCE, (Refs. 26, 33), Clem and Sciammanna report that a graphite electrode, which had been styrene impregnated, and then irradiated with cobalt-60, was stable in acid. It was also stable to weakly basic solutions for up to six months, and in solutions of pH 1-2, it was stable for several days. This stability permits the technique to be used by much less experienced analyst, to whom solid electrode work can be extremely difficult and frustrating. It also opens the possibility of long-term field work. As more and more bodies of water must be monitored, a sensitive technique which can produce data in real time but which does not need frequent maintenance, will be increasingly in demand.

Several elaborations on the TFME are in use: the spinning glassy carbon electrode (Ref. 24), the tubular electrode (Ref. 27), and a technique known as anodic stripping voltammetry with collection (ASVWC) (Ref. 34). The spinning glassy carbon electrode or Florence electrode alleviates the need for a stirring bar, and detection limits reported by workers using this electrode are in the ppb to sub-ppb levels for copper, cadmium and lead, but many authors report difficulty using it (Ref. 24).

Tubular electrodes were developed to achieve better sensitivity by elimination of the need for a high rate of stirring. Conventional stirring requires a stirring motor that may introduce noise from its brushes, and may introduce fluctuations in results through turbulence or irreproduction. The stripping solution is allowed to flow through the electrodes, and the material plates is then stripped and counted (Ref. 35). ASV with tubular electrodes lends itself easily to automation, giving reproducible results which have been shown to be similar to those obtained with flame AA (after concentration on Chelex 100) for copper, lead and zinc (Ref. 36).

Anodic stripping voltammetry with collection (ASVWC) was developed for use with spinning thin film mercury discs (Refs. 34, 37) to eliminate the background caused by the charging current. Charging current flows in an electrode system to set up a double layer of cations and anions about the electrodes. As metal is oxidized, the charging current must be maintained, which produces a large background component in the measured current for trace analysis. In ASVWC a second electrode at a constant potential is used to immediately replate the oxidized metal, creating a constant background thereby reducing effect of charging on the baseline. The technique has recently been applied to tubular electrodes. As the solution flows through the cell (see Fig. 1), it is oxidized at the initial tubular electrode and immediately

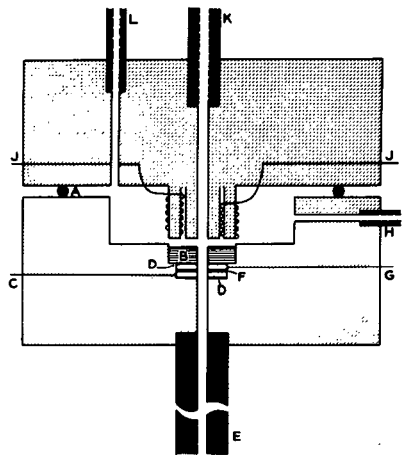

Fig. 1. The twin tubular electrode cell for anodic stripping voltammetry with collection. (Cell shown prior to compression by the bolts) (A) O-ring: (B) Cation exchange membranes: (C) Lead to upstream stripping electrode: (D) Cast epoxy: (E) Sample solution inlet: (F) Teflon spacer: (G) Lead to downstream collection electrode: (H) 0.1 M KCl inlet: (J) Lead to reference electrodes (SSCE's): (K) Sample solution outlet: (1) 0.1 M KCl outlet (reproduced from Schieffer and Blaedel, Ref. 27, with permission by the American Chemical Society, copyright, 1977).

replated at the second electrode, (Ref. 27). The results were found to be linear over a wide concentration range with detection limits in the ppb range.

(b) Waveforms applied in anodic stripping voltammetry. After the analyte metal has been deposited on the working electrode and after a suitable rest period, the analyte metal is reoxidized. An increasing potential (such as a voltage ramp) is applied to the electrodes and the current measured. At the peak potential (E_p) of the analyte metals a current peak (i_p) will be observed.

The waveform of the applied potential ramp can influence the sensitivity of an analysis. Much research, therefore, has been carried out on optimizing the type of ramp which is applied, its timing, and the times at which current measurements are recorded.

Several difference waveforms have been used; most common are the linear (DC) sweep, derivative techniques, ac stripping (ACASV) and differential pulse stripping (DPASV). A multiplicity of other waves have been investigated (see Fig. 2). The earliest waveform applied was a linear scan (Fig. 2a); it is a simple form to treat mathematically and equipment for generating such a changing po-

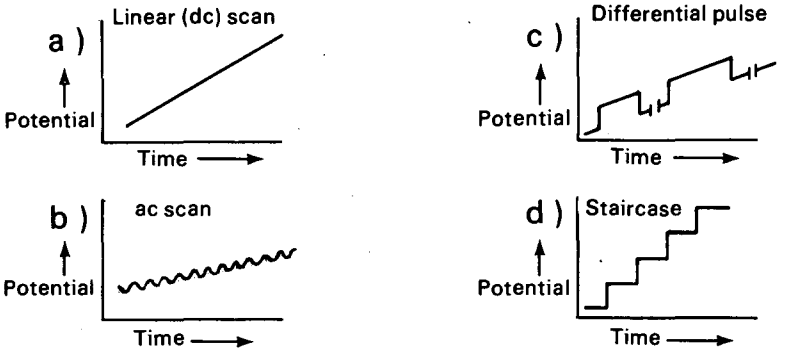

Fig. 2. Waveforms applied during anodic stripping (Refs. 8, 38, 39).

tential is easily available. The limitations are in the resolution achievable, because of the charging currents and a strongly sloping baseline (Ref. 10).

Early derivative techniques used a linear ramp, but displayed the change in current di with respect to potential E as opposed to displaying i vs E. An enhanced sensitivity was reported (~7 for cadmium - Ref. 40) when derivative techniques were first tried. Later techniques involving fluctuating, pulsed or staircase waveforms have enhanced sensitivity even more.

AC stripping involves the superposition of a sine wave over a dc linear ramp (Fig. 2b). Phase sensitive detection has been used to identify the stripping current. This method was found to be substantially more sensitive than linear scan ASV, but less so than DPASV. It requires, of course, a more sophisticated waveform generator and detection unit (Ref. 9), and is therefore more costly than linear sweep ASV.

Differential pulse ASV involves the application of a square wave pulse at regular intervals on the ac ramp (see Fig. 2c). The current is measured just before and near the end of the pulse to allow the charging current to drop off. The difference between the two measurements is displayed as the output. If the dc potential or the pulse is at a value where no metals can be oxidized, the electronics records a flat base line. If, on the other hand, either the dc potential or the pulse is at a half wave potential where one of the analyte metals will oxidize, a substantial difference will be recorded. The size of the differential current peak which results is proportional to the amount of analyte present (Ref. 10).

DPASV, because it is able to subtract the background associated with charging, and because it is a derivative technique, displays a far greater sensitivity and peak resolution

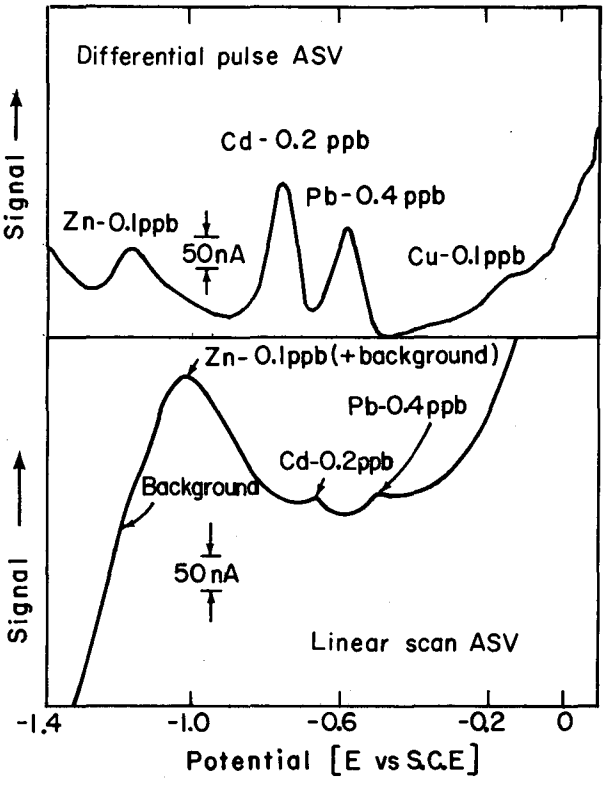

Fig. 3. A comparison of linear scan ASV and differential pulse ASV (synthesized from Copeland and Skogerboe, Ref. 9, with permission by the American Chemical Society, copyright, 1974).

than does linear scan ASV. Figure 3 compares the results of a DPASV determination and a LSASV determination of the same solution (Zn-0.1 ppb, Cd-0.2 ppb, Pb-0.4 ppb, and Cu-0.2 ppb). It is clear from a visual comparison of the results, that peaks using DPASV are more clearly resolved than for LSASV. This means that lower concentrations could be determined or shorter deposition times could be used with DPASV.

Currently researchers are also experimenting with a variety of squarewave waveforms (see Fig. 2d) which they believe would they believe would allow a fast scan rate (Ref. 41). Although they report results comparable to DPASV, DPASV is the more commonly used technique.

(c) Cells. An anodic stripping cell can be a simple vessel with inlets for the three electrodes, a stirring mechanism (if required) and an inlet/outlet for degassing. These can be used as individual units or in a multicell system (Ref. 28). A variety of other types of cells have been developed to enhance the speed of the determination.

Clem (Ref. 42) developed a rotating cell which forced the solution into a thin film on the cell wall, allowing a more rapid purging of the oxygen from the system.

As discussed above, flow-through cells have also been constructed for use with tubular mercury graphite electrodes (Ref. 27, 36, 43). They require no stirring and the constant flow of solution allows rapid deposition of the metal. Such a system readily lends itself to automation as described by Zirino, Lieberman and Clavell (Ref. 36). Measurements for 24 hours at a time at 20 min. intervals were obtained. This apparatus is shown in Fig. 4. The sample is pumped in and normally discharged into the source. At certain intervals a sample is allowed to flow into the sample reservoir and is purged. When the sample is ready, a $Hg(NO_3)_2$ solution is allowed to flow through the cell and a thin film of Hg collected. The sample is then introduced to the cell and the analyte metal plated out. Flow is then stopped. A pulsed potential ramp is then applied until the analyte metals and finally the mercury is stripped from the electrode. The process can then be repeated.

Schieffer and Blaedel (Ref. 27) describe another flow-through cell system which uses twin tubular electrodes for anodic stripping voltammetry with collection as described above [under electrodes-part (a)].

A third type of cell is the thin layer cell (Ref. 22, 44) which allows the analyst

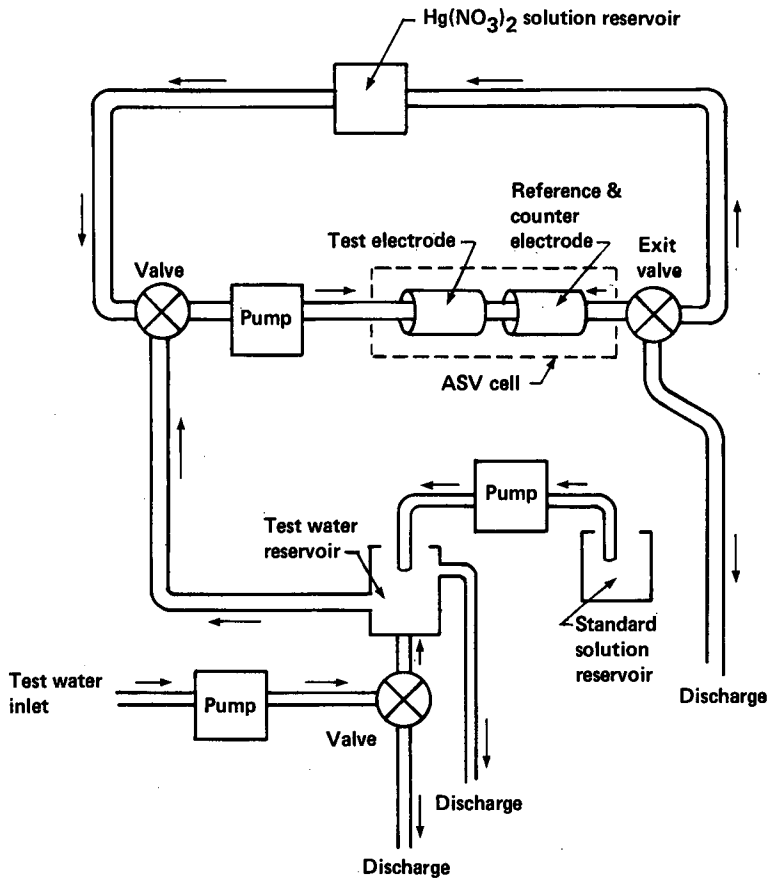

Fig. 4. Schematic diagram of an automated flow-through cell used for anodic stripping voltammetry (adapted from Zirino, Lieberman and Clavell, Ref. 36, with permission by the American Chemical Society, copyright, 1978).

to determine trace and ultratrace quantities of metals (to parts per billion or sub parts per billion levels commonly) with a little as 5 µℓ of solution, although a larger quantity 60 µℓ is more common (Ref. 22). In a thin film cell diffusion to the electrode is rapid, without the need for controlled stirring.

(d) Interferences. As with any analytical technique, a large number of interferences can be encountered when using anodic stripping voltammetry. Some occur in the routine set-up of the apparatus, others involve chemical compound formation in either the amalgam or the analyte solution, and finally there are interferences caused by the electrical components of the system.

It is absolutely essential to be scrupulously clean when using ASV - all reagents such as supporting electrolyte, purging gas, water (ad nauseum) must be purified and maintained in clean equipment. If a determination of low concentration is to be run over a long time span, the analyst must be aware of the possible adsorption of his analyte onto container walls. This can be prevented to some degree by lowering the pH of the solution (Ref. 30), or absorption onto particulate matter in the solution (Ref. 29). The analyst must also guard against degradation of the electrode surface. Acids in solution can attack the electrode surface and in natural waters organic substances can sorb onto it (Ref. 32).

The formation of intermetallic compounds on or in the working electrode and stable complexes in solution can also create serious problems. At relatively high concentrations formation of intermetallic compounds in the mercury can reduce the current signal, seriously broaden the peak, or significantly shift the stripping potential. The most commonly encountered intermetallic compounds which form in mercury are Cu-Zn (Ref. 42), and Zn-Ni (Ref. 45), although mercury itself can also form compounds with cobalt, iron, manganese and nickel (Ref. 17). Barendrecht reports a large numbers of intermetallics which are formed by the noble metals, gold, silver, and platinum. It is clear that if the electrode relies on a noble metal as a substrate or as an active electrode, the analyst should be aware that significant interference can develop with certain metals (i.e. cadmium, zinc, manganese, tin, nickel, and antimony (Ref. 17)). Chau and Lum-Shue-Chan report the interference of Fe(III) with the determination of copper, cadmium, zinc, and lead (Ref. 45).

The use of mercury films or drops as the working electrode reduces some of the problems of intermetallic compound formation since, if the metal ion concentration is small and only a small quantity is reduced, and the resulting metal "dissolves" in the mercury, the probability of compound formation is much less, though not removed altogether.

Another approach to this problem has been the selective plating out of one or more of the species, for example, copper, lead, and cadmium at -0.9V vs SCE, where the zinc is not plated. Once the copper has been stripped the zinc can then be analyzed by plating at -1.4 eV (Ref. 10). Some researchers have used selective plating by controlling the pH of the solution (Ref. 36).

Complex formation in the analyte solution can be an even more serious problem. If an extremely stable complex is formed between a metal ion and a strong ligand, often in early literature referred to as a "sequestering agent," it may not be reduced completely or at all, at the voltages commonly applied. This means that a significant portion of the metal present in solution may not plate out and thus not be determined. (This fact also permits a degree of speciation, discussed below in the summary section under Applications). Special care must be taken in analysing natural water solutions, since many of the organic compounds present in fresh or saline waters serve as excellent ligands.

Metals can often be released from their complexes by the addition of strong acids (Ref. 45) but strongly acidic solutions can affect the stability of the electrodes, degrading the surface. However, in projects where electrodes can be frequently replated and repolished, this technique can be very useful. Reneutralization of the analytical solution has been employed but, unless the sequestering agent has been destroyed, complexes simply reform.

Another solution to the problem of complexing agents is destruction of the agent itself by UV photolyzed hydrogen peroxide, persulfate solutions, or ozonolysis. All three treatments have been found to be efficacious, although the solutions tend to attack the mercury electrodes (Ref. 46).

The most serious interference in the electrical part of the ASV system is the problem of double-layer charging, considered above under "waveforms applied." Most of the different waveforms and measuring techniques have been tried in order to minimize the effect of the charging current, i.e. differential pulse techniques, derivative techniques and ASVWC. Although much progress has been made, the problem has not been completely solved.

(e) Applications. Anodic stripping voltammetry has been applied to a number of monitoring problems for the analysis of trace and ultratrace concentrations of metals in a variety of aqueous environments. Table 2 is a brief list of metals which have been determined

Table 2. Reported applications for ASV

Metal	Type of Sample	Application, Possible application	Reference
Ag	Natural water, rain and snow	Determination	9
As	Natural water. Industrial water	Determination, quality control	11, 47
Cd	Natural waters	Determination, speciation	9, 45, 48
	Seawater	Determination	9, 24
	Estuarine water	Determination	9
	Blood, biological material (oyster)	Possible use for surrogate analysis	9, 22
	Industrial water (Zn plant electrolyte)	Determination, quality control	47
Cu	Natural waters	Determination, speciation	9, 45, 48
	Seawater	Determination	9, 24
	Estuarine water	Determination	9, 36
	Waste water (2° sewage effluent)	Determination, quality control	9, 49
	Blood, biological material (oyster)	Possible use for surrogate analysis	22
Co	Industrial water (Zn plant) (Zn plant electrolyte)	Determination, quality control	47
Hg	Natural water	Determination	9
Ni	Industrial water (Zn plant electrolyte)	Determination, quality control	47
Pb	Natural water	Determination, speciation	9, 45
	Seawater	Determination	9, 24, 26
	Estuarine water	Determination	9
	Blood biological tissue (oyster)	Possible use for surrogate analysis	22
	Industrial water (Zn plant electrolyte)	Determination, quality control	47, 49
Sb	Industrial water (Zn plant electrolyte)	Determination, quality control	47
Sn	Geological materials	Possible use in surrogate analysis	9
Tl	Natural waters, Blood, biological materials	Determination, speciation Possible use in surrogate analysis	9, 48
Zn	Natural waters	Determination, speciation	9, 22
	Seawaters	Determination	9
	Estuarine waters	Determination, speciation	9, 36, 50
	Blood, biological materials (oysters)	Possible use for surrogate analysis	9, 22
	Industrial water (Zn plant electrolyte)	Determination, quality control	47

using ASV; the type of water sample containing the metal, and the application. In most cases, the application was simply the determination of the metal in an aqueous environment for regulatory or documentary purpose. Some of the other applications included determinations for quality control, determination of the binding of the metal in solution, or the species present. It has also been used for the determination of metals in biological and geological specimens suggesting the possibility of using ASV for determing trace metals in surrogate species. The table is by no means comprehensive, but illustrative.

For simple determinations of metals in water, most analysts agree that for ultratrace quantities of Cu, Cd, Pb and Zn, ASV is a valuable technique since the four metals can be determined, virtually simultaneously, in real-time.

ASV provides an excellent solution to the problem of analysis of ultratrace (or trace) quantities in solutions containing high levels of dissolved salts. Pilkington et al. (Ref. 47) report that they use ASV to determine Cd, Cu, Pb, Sb, Co, Ni, Tl and As in a zinc plant electrolyte which contains large quantities of $ZnSO_4$. Cd and Ca they determine directly to 10 ppb; after acidification Sb is determined to 10 ppb, and Pb, Co, Ni, Tl, and As after addition of appropriate chemicals, can be determined at somewhat higher concentrations.

For very similar reason, i.e. high salt concentrations, ASV has been used for determinations of many metals in marine and estuarine waters. Under these conditions there will be strong sodium interferences in atomic absorption spectra, and severe burner clogging problems.

Another timely application is the use of ASV for speciation. Although the techniques involved are still highly experimental, ASV is being used to determine the degree of binding or complexation in natural water systems. In the long term, it may be possible to determine which metal species are environmentally active.

Chau and Lum-Shue-Chan (Ref. 45), O'Shea and Mancy (Ref. 48) and Brezonik et al. (Ref. 32), report determinations of free, labile and strongly bound metal ions by measuring the peak current and potential for untreated water, then measuring the same parameters after treatment of the water to release some or all of the complexed metal ions. Bradford has used ASV to determine which of a series of zinc complexes was present by determining the shift in the stripping peak potential on addition of complexing agent (Ref. 51).

(f) Summary. Anodic stripping voltammetry has been shown to be an extremely sensitive technique for the determination of certain metals in water (Table 1), notably copper, cadmium, zinc, and lead. It can be used to detect trace and ultratrace concentrations of these and other metals, not only in fresh water, but in saline waters, even marine and estuarine waters and in waste waters. The equipment involved is relatively simple, readily available, and not costly.

There are several disadvantages associated with ASV. It is of some concern that only a limited set of metals can be determined using ASV. Further, standard procedures are only now being established; techniques are being continually improved, which means that laboratories using ASV are forced to keep up with new developments. The most critical problem is the need for a highly skilled and trains person to make determinations, maintain the equipment, and interpret the data.

The reader interested in further details on anodic stripping voltammetry is referred to the articles by Copeland and Skogerboe (Ref. 9), and Flato (Ref. 10). For greater background material on electrochemical techniques such as three electrode potentiostats, electrode, and reference electrode construction, the reader could turn to the texts by Willard, Merritt and Dean (Ref. 1), and Sawyer and Roberts (Ref. 2) and for a review article with a great number of current references, see Kissinger's article in Analytical Chemistry (Ref. 52).

b. Acknowledgments. The author is extremely grateful for the criticism, suggestions and help from Jack Harrar and Ray Clem.

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VI. INSTRUMENT NOTES FOR METALS IN WATER

Instrument notes appear in the following order:

Atomic Absorption Instruments, including many which also function as atomic emission spectrometers. — Notes AAS

Atomic Emission Instruments, including plasma excitation. — Notes AES

Ultraviolet-Visible and Visible Instruments — Notes UV-VIS

Each section of notes is preceded by a table on green paper summarizing the notes contained in the section.

Table of Atomic Spectroscopic Instrumentation (Atomic Absorption and Plasma Emission)

Atomic Absorption Instruments

Instrument	Beams	Background Correction	Display	Atomic Emission	Range (nm)	Cost	Remarks
Fisher, Jarrell Ash							
Dial AtomIII	Single	Non Simultaneous	Digital	Yes	190-860	$ 5850	
810	Double	D_2, Simultaneous	Digital	Yes	190-900	15,800	Dual channel, double monochromator
850	Double	D_2, Optional	Digital	Yes	190-900	11,450-16,080	Microprocessor controlled
Hitachi							
170-10	Single		Analog & Digital Available	No	190-900	$ 5700	
170-30	Single		Analog & Digital Available	Yes	190-900	6500	
170-50	Single	D_2, Optional	Analog & Digital Available	Yes	190-900	8100	Pulsed, single beam
170-70	Double	Zeeman (190-900 nm)	Analog & Digital Available	Yes	190-900	19,700	Polarized Zeeman-effect used for background correction
Instrumentation Lab.							
151	Single	D_2, Optional	Digital	Yes	190-900	$ 6990	Zoom lens
157	Single	D_2, Optional	Digital	Yes	180-900	7990	Zoom lens microprocessor controlled
251	Double	D_2, Optional	Digital	Yes	190-900	8530	Dual zoom lens
257	Double	D_2, Optional	Digital	Yes	180-900	9990	Dual zoom lens microprocessor controlled
551, VideoI	Double	D_2, Optional	Digital	Yes	180-900	13,000	Microprocessor controlled with zoom lens, and CRT display
651	Double	D_2, Optional	Digital	Yes	190-900	13,000	Dual channel opt. zoom lens microprocessor controlled
751	Double	D_2, Simultaneous	Digital	Yes	190-900	17,000	Dual channel, zoom lens, microprocessor controlled

(continued)

Table of Atomic Spectroscopic Instrumentation (Atomic Absorption and Plasma Emission) (continued)

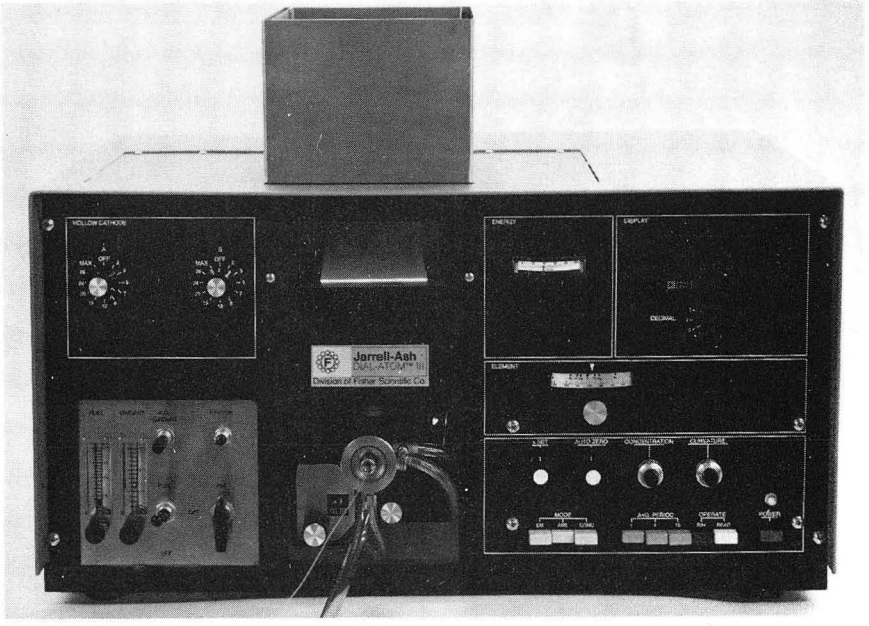
Atomic Absorption Instruments

Instrument	Beams	Background Correction	Display	Atomic Emission	Range (nm)	Cost	Remarks
Perkin Elmer							
272	Single	D_2, Optional	Digital	Yes	190-870	$ 6500	Microprocessor controlled
372	Double	D_2, Optional	Digital	Yes	190-870	8450	Microprocessor controlled
373	Double	D_2, Optional	Digital	Yes	190-870	9600	Microprocessor controlled
560	Double	D_2, Optional	Digital	Yes	180-870	11,700	Microprocessor controlled
703	Double	D_2, Optional	Digital	Yes	180-900	13,450	Microprocessor controlled, high resolution
5000	Double	D_2, Optional	Digital	Yes	190-900	17,000	Microprocessor controlled, time & space shared, option to handle 6 elements automatically
Pye Unicam							
SP191	Single	D_2, Optional	Digital	Yes	190-770	$ 7500	Optional red detector for Rb, Cs
SP192	Single	D_2, Included	Digital	Yes	190-770	8650	Optional red detector for Rb, Cs
SP2900	Double	D_2, Optional	Digital	Yes	190-675 (to 852, opt.)	9475	
Varian							
AA-175	Single	D_2, Optional	Digital	Yes	185-900	$ 6800-9900	
AA-375	Double	D_2, Optional	Digital	Yes	185-900	8600-12,400	Digital signal processor
AA-575	Double	D_2, Optional	Digital	Yes	185-900	12,000	Microprocessor controlled
AA-775ABQ	Double	D_2, Included	Digital	Yes	185-900	17,250	Microprocessor controlled
AA-6	Double	D_2, Optional	Digital	Yes	185-1000	13,200-16,700	

INSTRUMENTATION
FOR ENVIRONMENTAL
MONITORING

Atomic Absorption/Emission Spectrophotometer

Jarrell-Ash Dial-Atom III



Class Laboratory or Field

Description Single beam atomic absorption spectrophotometer

Modes of Operation Absorption and flame emission

Lower Limit of Detection

SENSITIVITY AND DETECTION LIMITS FOR

82-850, 82-810, DA III*

Element	Sensitivity (0.0044 A.) µg/ℓ	Sensitivity (0.300 A.) µg/mℓ	Detection Limit µg/ℓ
Ag	50	3.5	3
Al	500	80.0	50
As	300	30.0	200
Au	150	8.0	10
B	20,000	2000.0	5,000
Ba	300	25.0	20
Be	20	1.5	5
Bi	300	25.0	50
Ca	(40) 20	(3.0) 2.0	(4) 1
Cd	15	1.0	(2) 2
Co	70	5.0	(20) 10
Cr	60	5.0	(10) 5
Cs	50	5.0	5
Cu	40	3.5	(5) 3
Er	600	50.0	50
Eu	400	25.0	20
Fe	50	5.0	10
Ga	1,000	75.0	100
Gd	20,000	1500.0	5,000
Ge	2,000	150.00	200

Element	Sensitivity (0.0044 A.) µg/ℓ	Sensitivity (0.300 A.) µg/mℓ	Detection Limit µg/ℓ
Hf	10,000	750.0	2,000
Hg	3,000	250.0	300
Ho	700	60.0	100
In	330	25.0	30
K	20	1.5	3
La	45,000	5000.0	10,000
Li	15	1.5	1
Mg	3	0.2	0.3
Mn	25	2.5	(3) 3
Mo	300	25.0	30
Na	3	0.3	0.5
Nb	18,000	1500.0	2,000
Nd	10,000	750.0	3,000
Ni	70	6.0	(20) 10
Os	1,100	90.0	200
Pb	250	18.0	(20) 20
Pd	100	8.0	20
Pr	30,000	2000.0	10,000
Pt	1,000	80.0	100
Rb	40	4.0	5
Re	9,000	750.0	700
Rh	100	7.5	10
Ru	650	50.0	200
Sb	400	30.0	100
Se	200	25.0	100
Si	1,000	125.0	200
Sm	6,000	450.0	2,000
Sn	700	60.0	200
Sr	50	4.0	5
Ta	15,000	1200.0	5,000
Te	300	25.0	100
Ti	1,000	90.0	80
Tl	200	16.0	20
U	100,000	7500.0	35,000
V	700	60.0	80
W	6,000	500.0	2,000
Y	3,500	200.0	300
Yb	150	9.0	30
Zn	10	0.7	3
Zr	15,000	1000.0	5,000

*Bracketed values for DA III only.

Multielement Capability: 70 elements, consecutively

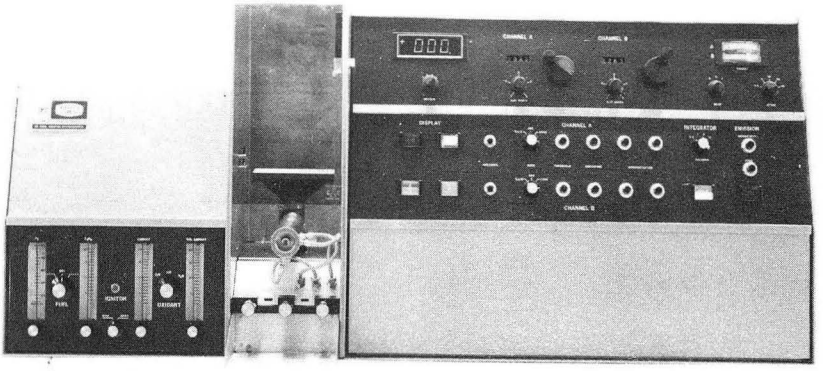
Sampling:
Method: Batch
Volume: 4.5 mℓ aspirated
Capacity: A single sample at a time

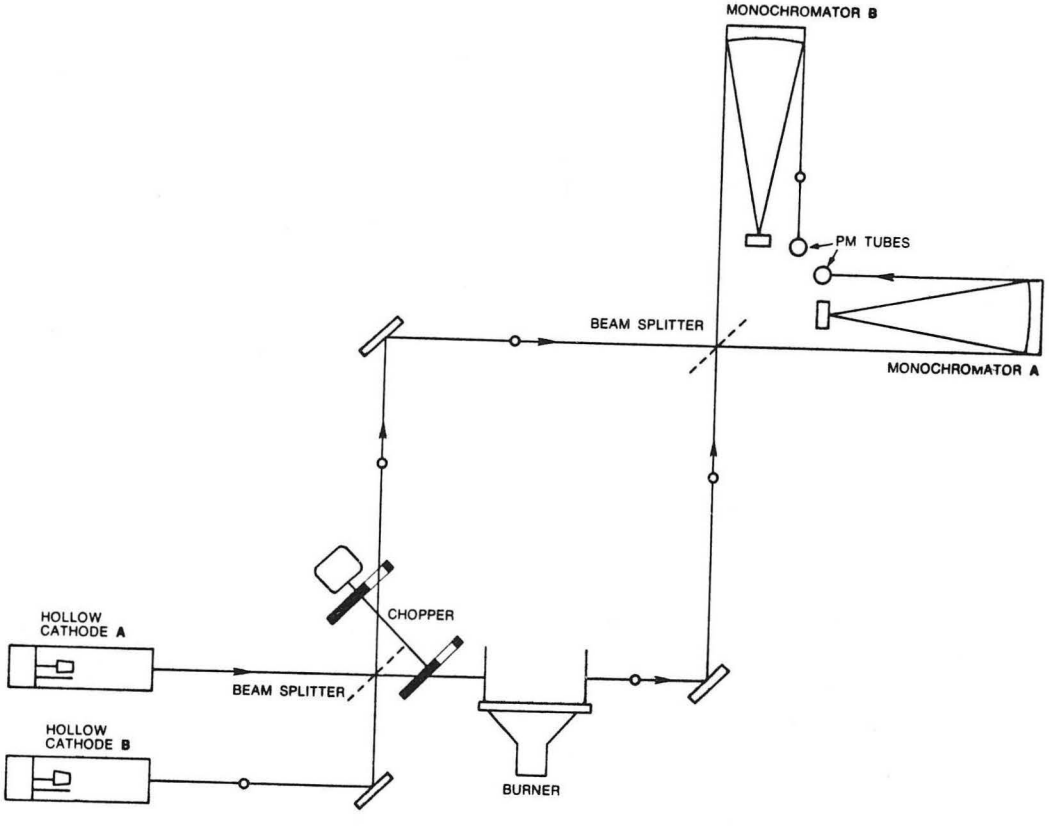
Performance and Specifications	Electronics: Solid state, lock-in amplifier, integrated circuits, crystal clock, preprogrammed analog and digital system Linearity: 8-10 decades - 0.05 RDS on 0.3 at Zn wavelength Scale expansion: 20x Sampling: 1,4,16 sec Detector: Photomultiplier tube Zero drift: Autozero function Readout: Digital Background: Can use D_2 and manually subtract Monochromator: Czerny-Turner mount, 0.25 focal length Grating: 30 × 32mm, 1180 lines/mm, blazed at 300 nm Range: 190-860nm Dispersion: 33 Å/mm Resolution: 0.2 Å/nm with standard 50-75 μ slits Scan speeds: No Wavelength accuracy: ±10Å (±0.1nm) Spectral bandpass: 2.5 Angstroms Gas Control: Premix chamber with electric ignition. Manual change over to auxiliary oxidant Fuel: Single inlet Oxidant: Oxidant and auxiliary inlets Vent: Recommended Burner: Corrosion resistant, stainless steel and titanium top plates Adjustment: Three dimensions, scale on vertical
Operation	Calibration: By standards Maintenance: 23 Service Centers Training: Courses available
Requirements	Power: 115V, 50 Hz or 230V, 60 Hz, 60 watts Size: 41 cm D × 68 cm W × 51 cm H (16" D × 27" W × 20" H) Weight: 80 kg (175 lb)
Features	Single beam Integral flow controls Digital readout Autozero, auto gain control Concentration calibration Curvature correction Electric ignition Field adaptable, withstands frequency, voltage variation Synchronous chopper for flame emission
Options	Graphite tube atomizer FLA-100 $5700, see Fisher Jarrell-Ash C Strip chart recorder 585 Printer 1450 Mercury analysis accessory 550 Selenium, arsenic apparatus 150 Lamps: 70 single element hollow cathode lamps See Fisher Jarrell-Ash A
Cost	Dial-Atom III $5850
Address	Jarrell-Ash Division Fisher Scientific Company 590 Lincoln Street Waltham, MA 02154 (617) 890-4300

INSTRUMENTATION
FOR ENVIRONMENTAL
MONITORING

Atomic Absorption Spectrophotometer

Fisher, Jarrell-Ash, Model 810





Class	Laboratory
Description	Double beam, dual channel atomic absorption spectrophotometer
Modes of Operation	1. Two metals simultaneously in the same sample. 2. Both channels can be used for atomic absorption, or one for AA and the other for flame emission. 3. A minus B mode allows one channel to measure and automatically subtract background absorption from the other. 4. In the A/B ratio mode, one channel can be used to monitor an internal standard, while the other one makes the analytical measurement.

Lower Detectable Limit

SENSITIVITY AND DETECTION LIMITS FOR

82-850, 82-810, DA III*

Element	Sensitivity (0.0044 A.) µg/ℓ	Sensitivity (0.300 A.) µg/ml	Detection Limit µg/ℓ
Ag	50	3.5	3
Al	500	80.0	50
As	300	30.0	200
Au	150	8.0	10
B	20,000	2000.0	5,000
Ba	300	25.0	20
Be	20	1.5	5
Bi	300	25.0	50
Ca	(40) 20	(3.0) 2.0	(4) 1
Cd	15	1.0	(2) 2
Co	70	5.0	(20) 10
Cr	60	5.0	(10) 5
Cs	50	5.0	5
Cu	40	3.5	(5) 3
Er	600	50.0	50
Eu	400	25.0	20
Fe	50	5.0	10
Ga	1,000	75.0	100
Gd	20,000	1500.0	5,000
Ge	2,000	150.00	200
Hf	10,000	750.0	2,000
Hg	3,000	250.0	300
Ho	700	60.0	100
In	330	25.0	30
K	20	1.5	3
La	45,000	5000.0	10,000
Li	15	1.5	1
Mg	3	0.2	0.3
Mn	25	2.5	(3) 3
Mo	300	25.0	30
Na	3	0.3	0.5
Nb	18,000	1500.0	2,000
Nd	10,000	750.0	3,000
Ni	70	6.0	(20)10
Os	1,100	90.0	200
Pb	250	18.0	(20) 20
Pd	100	8.0	20
Pr	30,000	2000.0	10,000
Pt	1,000	80.0	100
Rb	40	4.0	5
Re	9,000	750.0	700
Rh	100	7.5	10
Ru	650	50.0	200
Sb	400	30.0	100
Se	200	25.0	100
Si	1,000	125.0	200
Sm	6,000	450.0	2,000
Sn	700	60.0	200
Sr	50	4.0	5
Ta	15,000	1200.0	5,000

Lower Detectable Limit

Element	Sensitivity (0.0044 A.) µg/ℓ	Sensitivity (0.300 A.) µg/ml	Detection Limit µg/ℓ
Te	300	25.0	100
Ti	1,000	90.0	80
Tl	200	16.0	20
U	100,000	7500.0	35,000
V	700	60.0	80
W	6,000	500.0	2,000
Y	3,500	200.0	300
Yb	150	9.0	30
Zn	10	0.7	3
Zr	15,000	1000.0	5,000

*Bracketed values for DA III only.

Range: ppb to %

Interferences: Minimal for most analysis. Interferences can be overcome by carefully selecting the proper flame conditions, and/or by adding chemical interference suppressants to the sample.

Multiparameter Capability: 70 elements

Sampling:
Method: Batch
Volume: 4-5 ml aspirated
Capacity: Single sample at one time

Performance and Specifications:

Electronics: Synchronous ratio detection with log-to-linear conversion, signal integration, and digital readout. Solid-state plug-in circuit cards.
Linearity: 8-10 decades
Scale expansion: 20x
Detector: Photomultiplier, 2 matched, quartz
Integration: 0.2, 1.0, 3.0, 10 sec
Zero drift: Auto-zero circuit
Readout: Digital, in absorbance, % absorption and concentration
Background: Use of non-absorbing line, continuum source or spectral line of element not in sample

Monochromator: Ebert, 0.4 focal length

Grating: Quartz, 58×58 mm, 1180 lines/mm, blazed at 300 nm
Dispersion: 20.8 Å/mm
Range: 190-900 nm
Spectral bandpass: 15,50,100,200,500 µ slit widths yielding bandpass of 0.3,1,2,4 and 10Å
Wavelength accuracy: ±3Å 0.03 nm
Scan speeds: 2.5,5,10,20,40 Å/min

Gas Control: Four separate fuel and oxidant flow meters, rotary control valves, push button ignition, safety interlock system.
Fuel: C_2H_2,H_2
Oxidant: Air, N_2O
Vent: Recommended
Burner: Pre-mix laminar-flow with 5 and 10 cm slots. Corrosion resistant construction, with titanium tops
Adjustments: Vertical, horizontal, and rotational with indicating scales.

Operation	Calibration: Via standards Maintenance: 23 Service Centers Training Required: Moderate, courses available
Requirements	Power: 115/230 VAC, 50/60 Hz, 300 watts Weight: 215 kg (475 lbs) Dimensions: 56 cm × 130 cm × 69 cm (22 in. D × 51 in. L × 27 in.H)
Features	Double beam Two channel Pre-mix burner chamber Electric flame ignition Auto-zero circuit Signal integration mode Digital read-out of concentration
Options	Automatic gas control programmer $ 890 Strip-chart recorders 585-1100 Burner heads, 5, 10, and interchangeable 5, 10 cm slots 275-290 Graphite tube atomizer (Model FLA-100) 5700 See Fisher-Jarrell Ash C Mercury analyzer 550 Selenium and arsenic apparatus 150 Lamps - 70 single element and 31 multielement lamps see Fisher, Jarrell-Ash A
References	Manufacturer's Specifications
Cost	Model 810 $15,800
Address	Jarrell-Ash Division Fisher Scientific Company 590 Lincoln Street Waltham, MA 02154 Attn: Product Manager, AA (617) 890-4300

INSTRUMENTATION
FOR ENVIRONMENTAL
MONITORING

Atomic Absorption/Emission Spectrophotometer

Fisher Jarrell-Ash, Model 850

Class	Laboratory
Description	Double beam, microprocessor controlled, atomic absorption spectrophotometer
Modes of Operation	Atomic absorption and flame emission

Lower Detectable Limit

SENSITIVITY AND DETECTION LIMITS FOR

82-850, 82-810, DA III*

Element	Sensitivity (0.0044 A.) µg/ℓ	Sensitivity (0.300 A.) (µg/ℓ×10^{-3})	Detection Limit µg/ℓ
Ag	50	3.5	3
Al	500	80.0	50
As	300	30.0	200
Au	150	8.0	(20) 010
B	20,000	2000.0	5,000
Ba	300	25.0	20
Be	20	1.5	5
Bi	300	25.0	50
Ca	(40) 20	(3.0) 2.0	(4) 1
Cd	15	1.0	(0.002) 2
Co	70	5.0	(20) 10
Cr	60	5.0	(10) 5
Cs	50	5.0	5
Cu	40	3.5	(5) 3
Er	600	50.0	50

Element	Sensitivity (0.0044 A.) µg/ℓ	Sensitivity (0.300 A.) (µg/ℓ×10^{-3})	Detection Limit µg/ℓ
Eu	400	25.0	20
Fe	50	5.0	10
Ga	1,000	75.0	100
Gd	20,000	1500.0	5,000
Ge	2,000	150.00	200
Hf	10,000	750.0	2,000
Hg	3,000	250.0	300
Ho	700	60.0	100
In	330	25.0	30
K	20	1.5	3
La	45,000	5000.0	10,000
Li	15	1.5	1
Mg	3	0.2	0.3
Mn	25	2.5	(3) 3
Mo	300	25.0	30
Na	3	0.3	0.5
Nb	18,000	1500.0	2,000
Nd	10,000	750.0	3,000
Ni	70	6.0	(20) 10
Os	1,100	90.0	200
Pb	250	18.0	(20) 20
Pd	100	8.0	20
Pr	30,000	2000.0	10,000
Pt	1,000	80.0	100
Rb	40	4.0	5
Re	9,000	750.0	700
Rh	100	7.5	10
Ru	650	50.0	200
Sb	400	30.0	100
Se	200	25.0	100
Si	1,000	125.0	200
Sm	6,000	450.0	2,000
Sn	700	60.0	200
Sr	50	4.0	5
Ta	15,000	1200.0	5,000
Te	300	25.0	100
Ti	1,000	90.0	80
Tl	200	16.0	20
U	100,000	7500.0	35,000
V	700	60.0	80
W	6,000	500.0	2,000
Y	3,500	200.0	300
Yb	150	9.0	30
Zn	10	0.7	3
Zr	15,000	1000.0	5,000

*Bracketed values for DA III only.

Multiparameter Capability: 70 elements

Sampling

Method: Batch
Volume: 4-5 ml aspirated
Capacity: A single sample at one time

Performance and Specifications

Electronics: Solid state, with plug-in circuit boards
Scale expansion: 0-1000
Detector: Photomultiplier tube
Integration: 0.25-99 sec, continuously variable
Zero drift: Auto-zero circuit
Readout: Digital, in absorbance, concentration, or intensity
Background: Deuterium arc accessory, available (double beam)

Monochromator: Asymmetrical, Czerny-Turner, 0.4 m focal length
Grating: 40×40 mm, 1180 lines/mm, blazed at 240 nm
Range: 190-900 nm
Wavelength Accuracy: ±0.0125 nm ±3Å .03 nm
Dispersion: 20.8 Å/mm
Spectral bandpass: continuously variable slits (0.3-2Å) to change bandpass a maximum of 0.01 nm
Resolution: 0.03 nm

Gas Control: Premix laminar system with electric ignition, oxidant control with safety interlock
Oxidant: N_2O, air, two inlets available
Fuel: C_2H_2,H_2, two inlets available
Vent: Recommended
Burner: Stainless steel head, polypropylene spray, stainless steel nebulizer with tantalum venturi, stainless steel capillary
Adjustments: Three dimensional, all with scales

Operation

Calibration: by standards, computer controlled
Maintenance: 23 service centers
Training: training courses available

Requirements:

Power: 115 V or 230 VAC, 50-60 Hz, 250 watts
Size: 33 cm H × 89 cm W × 48 cm D (17" H × 35" W × 19" D)
Weight: 127 kg (280 lbs)

Features

Double beam
Computer operated
Digital readout
Premix burner chamber
Signal integration
Electric flame ignition
Auto zero circuit

Options:

Automatic programmer	
Graphite tube atomizer	$ 5700, see Fisher, Jarrell-Ash C
Auto gas control panel	1980
Burner heads - 5,10 cm slots	250
Printers	1450
Deuterium background corrector	1200
Hg analysis accessory	550
Se/As accessory	150
Lamps	See Fisher, Jarrell-Ash A
Analog translator	995

Cost

Model 850 $ 11,450 - 16,080

Address

Jarrell-Ash Division
Fisher Scientific Company
590 Lincoln Street
Waltham, MA 02154
Attn: Product Manager, AA
(617) 890-4300

Hollow Cathode Lamps

Jarrell-Ash

Class: Accessory

Description: Hollow Cathode Lamps for use with Jarrell-Ash atomic absorption spectrophotometers, manufactured by Westinghouse

Multiparameter Capability: 70 single element lamps, 31 multielement lamps

Single-Element Lamps

Element	Price	Element	Price
Aluminum	$110-115	Mercury	135
Antimony	140	Molybdenum	115
Arsenic	175	Neodymium	
Barium	140	Nickel	115
††Beryllium	180	Niobium	
Bismuth	150	Osmium	
Boron	145	Palladium	170
Cadmium	130	Platinum	185
Calcium	120	Potassium	160
*Cerium		Praseodymium	
*Cesium	160	Rhenium	
Chromium	115	Rhodium	240
Cobalt	115	Rubidium	
†Copper	125	Ruthenium	190
Dysprosium		Samarium	
Erbium		Scandium	
Europium		Selenium	170
Gadolinium		Silicon	140
Gallium		Silver	120
Germanium		Sodium	160
Gold	170	Strontium	155
Hafnium		Tantalum	
Halmium		*Tellurium	
Hydrogen	175	*Terbium	235
Indium		††Thallium	140
Iridium	245	*Thorium	
Iron	115	*Thulium	235
Lanthanum	190	Tin	140
Lead	135	Titanium	125
Lithium (Natural)	140	Tungsten	125
		*Uranium	250
*Lithium-6	180	Vanadium	180
*Lithium-7	160	Ytterbium	210
*Lutetium		Yttrium	
Magnesium	115	Zinc	120
Manganese	120	Zirconium	145

*Not high spectral output type

†With quartz window which permits use of secondary UV lines of copper.

††Not manufactured by Westinghouse.

Elements	Fisher Catalog No.	Elements	Fisher Catalog No.
Arsenic-Nickel	JA 45-434	Copper-Lead-Zinc-Silver	JA 45-448
Arsenic-Selenium-Tellurium	JA 45-598	Copper-Manganese	JA 45-491
Barium-Calcium-Strontium-Magnesium	JA 45-478	**Copper-Zinc-Iron-Manganese	JA 45-492
Barium-Calcium-Strontium	JA 45-437	Copper-Zinc-Lead-Cadmium	JA 45-597
Calcium-Aluminum-Magnesium	JA 45-450	Copper-Zinc-Lead-Tin	JA 45-438
Calcium-Iron-Aluminum-Magnesium	JA 45-310	Copper-Zinc-Molybdenum	JA 45-496
Calcium-Magnesium-Aluminum-Lithium	JA 45-436	Copper-Zinc-Molybdenum-Cobalt	JA 45-596
Calcium-Magnesium-Zinc	JA 45-311	Gold-Copper-Iron Nickel	JA 45-307
Calcium-Zinc	JA 45-304	Gold-Nickel	JA 45-433
Chromium-Copper	JA 45-306	Iron-Copper-Manganese	JA 45-435
Chromium-Nickel-Iron-Manganese	JA 45-442	Iron-Copper-Nickel-Lead-Zinc	JA 45-302
Cobalt-Chromium-Copper-Iron-Nickel-Manganese	JA 45-599	*Magnesium-Zinc	JA 45-314
Copper-Cobalt	JA 45-305	Molybdenum-Copper-Iron	JA 45-301
Copper-Gallium	JA 45-431	Selenium-Nickel	JA 45-497
**Copper-Iron	JA 45-312	Sodium-Potassium	JA 45-439
		Zinc-Silver-Lead-Cadmium	JA 45-308

High spectral output tubes

Warranty — Manufacturer's Warranty: Official - 5 ampere hours

Manufacturer — Westinghouse

References — Manufacturers Specifications

Cost — Listed above under Multiparameter Capability

Address — Jarrell-Ash Division
Fisher Scientific Co.
590 Lincoln Street
Waltham, MA 02154
(617) 890-4300

Accessory Sample Furnace
Fisher, Jarrell-Ash FLA-100

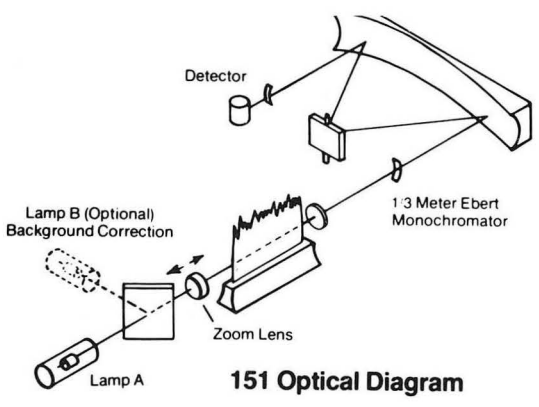
Class	Accessory
Description	Graphite tube atomizer for flameless atomic absorption
Lower Detectable Limit	Aluminum, antimony, arsenic, beryllium, bismuth , cadmium, chromium, cobalt, copper, gallium, gold, indium, iron, lead, manganese, nickel palladium, platinum, selenium, silicon, silver, strontium, tin, tellurium, thallium, vanadium to 10^{-12}g
Range	From 10^{-13}g depending on element
Interferences	Occasional problems with the formation of carbon compounds, selective volatilization and background absorption.
Sampling	Method: batch Volume: 1-50 µℓ
Performance and Specifications	Accuracy: Reproducibility: Linearity: Relative humidity range: Max temperature: max. exceeds 3000°C, recommended not over 2850°C Timers: Dry -0 to 60 sec. Ash 1 - 0 to 180 sec. Ash 2 - 0 to 30 sec. Atomize - 0 to 30 sec.
Requirements	Power: 220 V, 50/60 Hz, 30 amp Weight: 40 kg Dimensions: 44×35×34 cm Cooling water: 1-2 ℓ/min. at 20-30°C Inert gas, argon, 10scfh, 2-20 psig

Features	Choice of air ash or argon pyrolysis Choice of step or ramp steps for dry and ash cycles Choice of ramp or flash atomization
References	Manufacturer's Specifications
Cost	FLA-100
Address	Jarrell-Ash Division Fisher Scientific Company 590 Lincoln Street Waltham, MA 02154 Attn: AA, Product Manager (617) 890-4300

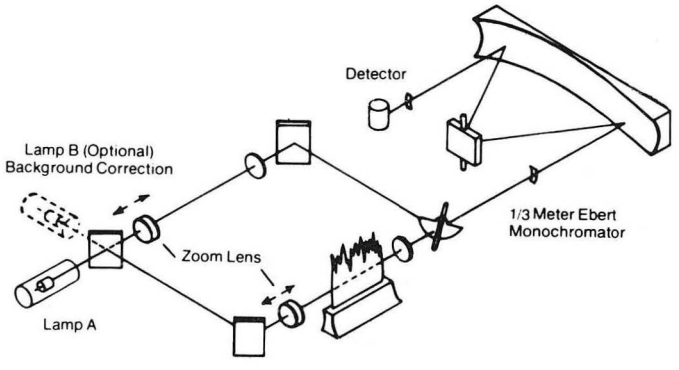
INSTRUMENTATION
FOR ENVIRONMENTAL
MONITORING

Atomic Absorption/Emission Spectrophotometers

Instrumentation Laboratory, IL 151, 251



151 Optical Diagram



251 Optical Diagram

Class: Laboratory

Description:
Model 151: Single beam, zoom lens, atomic absorption spectrophotometer
Model 251: Double, or single beam, dual zoom lens atomic absorption spectrophotometer

Modes of Operation: Absorption or flame emission

Lower Detectable Limit:

Sensitivity is defined as the concentration of an element in an aqueous solution which gives rise to 1% absorption (0.0044 Absorbance).

Detection Limit is defined as that concentration of an element which provides a signal equal to twice the standard deviation of a series of ten blank corrected readings of the element at a concentration close to the blank level.

Element	Sensitivity (µg/ℓ)	Detection Limit (µg/ℓ)
Ag Silver	30	2
Al Aluminum	400	20
As Arsenic	400	100
		1*
Au Gold	100	10
B Boron	9,000	9,000
Ba Barium	100	20
Be Beryllium	10	2
Bi Bismuth	200	40
Ca Calcium	10	1
Cd Cadmium	10	1
Co Cobalt	50	5
Cr Chromium	40	3
Cs Cesium	150	15
Cu Copper	30	2
Er Erbium	400	40
Fe Iron	50	3
Hg Mercury		0.5*
K Potassium	10	1
Li Lithium	20	2
Mg Magnesium	3	0.2
Mn Manganese	20	3
Mo Molybdenum	200	10
Na Sodium	1	0.4
Ni Nickel	50	7
Pb Lead	100	10
Pr Praseodymium	2,000	2,000
Pt Platinum	1,000	50
Rb Rubidium	200	2
Re Rhenium	8,000	800
Rh Rhodium	200	10
Sb Antimony	200	60
		6*
Sc Scandium	100	10
Se Selenium	400	100
		1*
Si Silicon	800	60
Sn Tin	200	80
Sr Strontium	60	1
Ta Tantalum	12,000	800
Te Tellurium	200	10
Ti Titanium	900	50
Tl Thallium	100	30
V Vanadium	600	20

W Tungsten	5,000	500
Y Yttrium	1,800	200
Yb Ytterbium	80	2
Zn Zinc	8	0.6

Note: All sensitivities and detection limits were obtained using an air-acetylene or nitrous oxide-acetylene flame unless otherwise noted. Potassium was added to the aqueous standards to suppress ionization for easily ionized elements.

*Hydride Generator

Range

Absorbance Range: ±3.000
Concentration: Up to 3000

Multiparameter Capability

One element at a time, 66 single element lamps, 21 multielement lamps available

Sampling

Method: Batch or automatic, sample in solution
Volume: 1 µl to 3 ml dependent upon atomization source
Capacity: Up to 12 determinations per minute

Performance

Electronics: Solid state, LED readout, 4 digits and sign

Linearity: Varies with element determined
Stability: 0.005% short term
Scale Expansion: 0.3x to 50x
Detector: R373 photomultiplier
Readout: Four digit illuminated display
Response Time: Integral mode at 1/16, 1/4, 1, 4, or 16 sec
Other: AutoZero, Offline calibration, Four lamp turret with warmup optional
Background Correction:

Monochromator: Ebert mount, 0.33 m

Grating: 1200 grooves/mm blazed at 250 nm
32×32mm
Wavelength Range: 190 to 900 nm
Wavelength Accuracy: Better than 0.05 nm
Wavelength Reproducibility: Better than 0.1 nm
Resolution: 0.04 nm, first order
Reciprocal Dispersion: 2.5 nm/mm
Slits: Curved variable in 7 steps from 0.04 to 2 nm (spectral bandpass)

Gas Control: Solenoid valving, constant level burner drain system, electric ignition, pressure orifice flow control, polypropylene premix chamber safety interlock

Oxidant: Air or N_2O
Fuel: C_2H_2
Venting: 10.2 cm dia., 28 l/min (4" dia., 100 cf/min)
Burner: Standard 10 cm head, N_2O, phase slot heads optional, Teflon lined, titanium jaws
Adjustments: Three dimensional

Operation

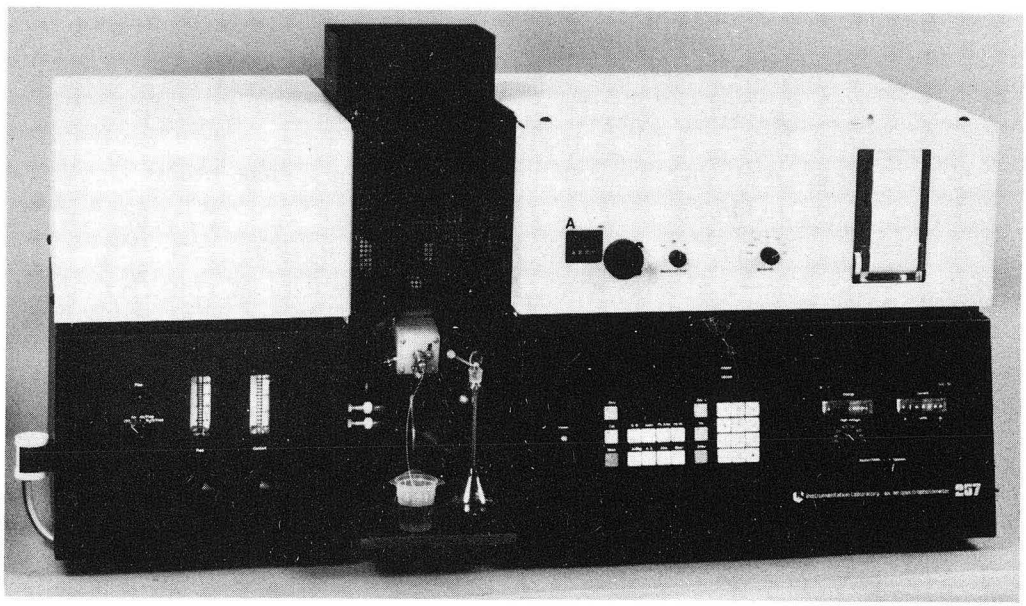
Calibration: Standard samples
Training: Requires about 20 hours depending upon number and complexity of analyses. Three day training course provided, free of charge with purchase at AAS, for 1 operator at 4 U. S. locations
Unattended Period: 1-2 hours with FASTAC Auto Sampler
Maintenance: Service centers throughout U. S.

Requirements	Power: 100, 115, or 230 VAC ±20%, 50 or 60 Hz, 230 W Weight: Model IL 151 -- 127 kg (280 lb) Model IL 251 -- 134 kg (295 lb) Dimensions: 50.8 cm H × 109.1 cm L × 47.7 cm D (20" H × 43" L × 18" D)	
Features	Zoom lens Electric ignition digital meter recorder Four detection modes Automatic update and manual update Peak height and peak area Built-in test circuit Automatic zero curve correction	
Options	Electric wavelength scan	$ 500
	Automatic gas safety system	530
	Background correction and deuterium	1250
	4-lamp turret	900
	Dual grating monochromator	600
	Hollow Cathode Lamps	See Instrumentation Lab A
	Graphite furnace	See Instrumentation Lab C
	Background correction	1250
	IL 254 Fastac Auto Sampler	3950
References	Manufacturer's Bulletin	
Cost	Model IL 151	$ 6990
	Model IL 251	8530
Address	Instrumentation Laboratory, Inc. Jonspin Road Wilmington, MA 01887 (617) 658-5125	

INSTRUMENTATION
FOR ENVIRONMENTAL
MONITORING

Atomic Absorption/Emission Spectrophotometers

Instrumentation Laboratory IL 157/257



Class	Laboratory
Description	Model 157: single beam zoom lens atomic absorption spectrophotometer with microcomputer 257: single or double beam atomic absorption spectrophotometer with zoom lens and microcomputer
Modes of Operation	Atomic Absorption or Flame Emission
Lower Detection Limit	
Range	Absorbance: Up to 2.0A Concentration: Up to 9999
Interference	Depends upon element
Multiparameter Capability	One element at a time, 66 single element lamps, 21 multielement lamps available
Sampling	Method: Batch or automatic, sample in solution Volume: 1 µℓ to 3 mℓ depend upon atomization Capacity: Up to 12 determinations per minute
Performance	Electronics: Solid state, LED readout, 4 digits and sign Linearity: Varies with element determined Stability: 0.005% short term Scale Expansion: Detector: Readout: Digital with RS 232C interface (opt.) in absorbance, emission, concentration peak height, area or running Integration: 0.1 sec to 99.9 sec in 0.1 sec. intervals Zero drift: Auto zero Background: Optional deuterium lamp

Performance (continued)

Monochromator: Ebert-Fastie, 330 mm focal length
Grating: 40 ×40 mm, 1200 lines/mm
Wavelength range: 180-900 nm
Wavelength accuracy:
Resolution:
Dispersion: 2.5 nm/mm
Slits: To achieve 0.04 to 2.0 nm resolution
Wavelength scan: OPT, 5 or 20 nm/mm

Gas Control: Premix laminar, polypropylene premix chamber safety interlock
Oxidant:
Fuel:
Venting:
Burner: High solids head with single 10 cm slot titanium head
Adjustments: Angular during operating, vertical and horizontal

Operation

Calibration: Standard samples, zero and two standards, computer calculates curve, five standards optional
Training: Requires about 20 hours depending upon number and complexity of analyses. Three day training course provided
Maintenance: Available throughout U. S. (6 locations)

Requirements

Power: 115 or 230 V ±10%, 50/60 Hz, 230 W
Weight: 135 kg
Dimensions: 51 cm H, 109 cm L, 48 cm D (20" × 43" × 18")

Features

Microcomputer
Zoom lens
Running mean, peak height and area as well as absorbance, emission and concentration
Auto zero and calibration

Options

Hollow Cathode Lamps	See Instrumentation Lab A
Graphite Furnace	See Instrumentation Lab C
Background correction	$1250
Performance package-five standards memory protection, computer interface	950
Printer (with performance package)	1950
Dual cell mount	
Four lamp turret	900
Motorized wavelength scan	500
Photomultiplier tube R955 (trialkali)	310
Dual grating monochromator	600
IL 254 Fastac Auto Sampler	3950

References

Manufacturer's Bulletin

Cost

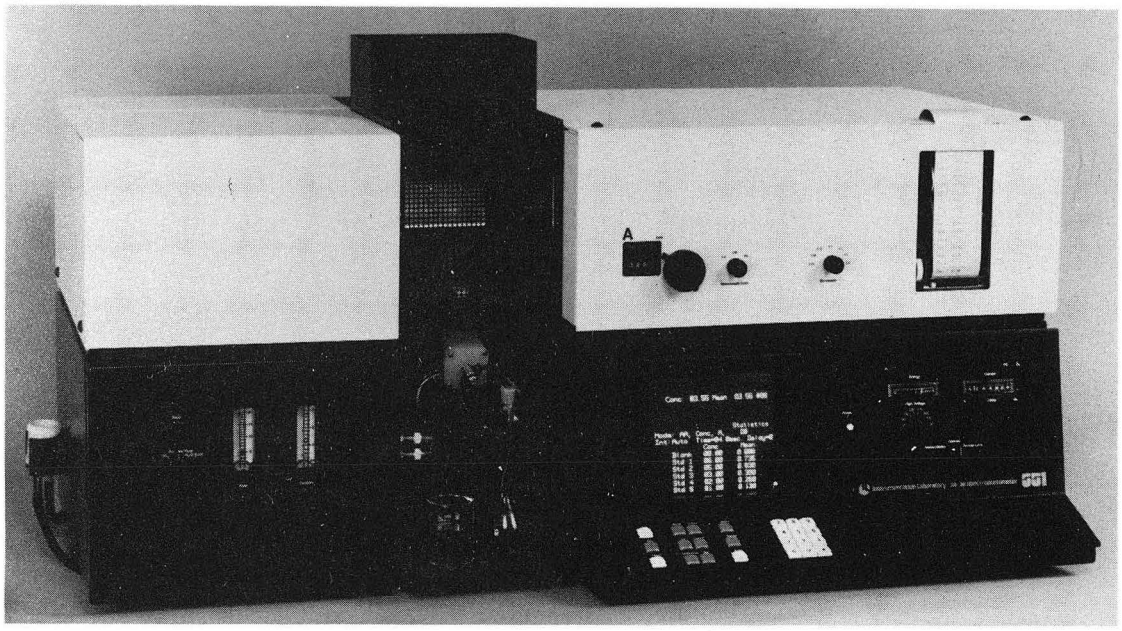
Model IL 157	$7990
Model IL 257	9990

Address

Instrumentation Laboratory Inc.
Jonspin Road
Wilmington, MA 01887
(617) 658-5125

Atomic Absorption/Emission Spectrophotometer

Model IL 551, VIDEO I



Class	Laboratory
Description	Double beam or single beam, zoom lens, atomic absorption spectrophotometer with CRT display and microcomputer
Mode of Operation	Absorbance or flame emission
Lower Detectable Limit	Sensitivity is defined as the concentration of an element in an aqueous solution which gives rise to 1% absorption (0.0044 Absorbance).

Detection Limit is defined as that concentration of an element which provides a signal equal to twice the standard deviation of a series of ten blank corrected readings of the element at a concentration close to the blank level.

Element	Sensitivity (µg/ℓ)	Detection Limit (µg/ℓ)
Ag Silver	30	2
Al Aluminum	400	20
As Arsenic	400	100
		1*
Au Gold	100	10
B Boron	9,000	9,000
Ba Barium	100	20
Be Beryllium	10	2
Bi Bismuth	200	40
Ca Calcium	10	1
Cd Cadmium	10	1
Co Cobalt	50	5
Cr Chromium	40	3
Cs Cesium	150	15
Cu Copper	30	2
Er Erbium	400	40
Fe Iron	50	3
Hg Mercury		0.5*

Lower Detectable Limit (continued)

K Potassium	10	1
Li Lithium	20	2
Mg Magnesium	3	0.2
Mn Manganese	20	3
Mo Molybdenum	200	10
Na Sodium	1	0.4
Ni Nickel	50	7
Pb Lead	100	10
Pr Praseodymium	2,000	2,000
Pt Platinum	1,000	50
Rb Rubidium	200	2
Re Rhenium	8,000	800
Rh Rhodium	200	10
Sb Antimony	200	60 6*
Sc Scandium	100	10
Se Selenium	400	100 1*
Si Silicon	800	60
Sn Tin	200	80
Sr Strontium	60	1
Ta Tantalum	12,000	800
Te Tellurium	200	10
Ti Titanium	900	50
Tl Thallium	100	30
V Vanadium	600	20
W Tungsten	5,000	500
Y Yttrium	1,800	200
Yb Ytterbium	80	2
Zn Zinc	8	0.6

Note: All sensitivities and detection limits were obtained using an air-acetylene or nitrous oxide-acetylene flame unless otherwise noted. Potassium was added to the aqueous standards to suppress ionization for easily ionized elements.

*Hydride Generator

Range

Absorbance Range: ±2.000
Concentration: Up to 9999

Multiparameter Capability

One element at a time, 66 single element lamps, 21 multielement lamps available

Sampling

Method: Batch or automatic; sample in solution
Volume: 1 µl to 3ml dependent upon atomization source
Capacity: Up to 12 determinations per minute

Performance

Electronics: Solid state CRT display readout, 4 digits and sign

Linearity: Varies with element determined
Stability: 0.005% short term
Scale Expansion: 0.1x to 100x
Detector: R373 photomultiplier
Readout: Four digit plus sign CRT display mean, standard deviation
Integration: 0.1 to 99.9 secs at 0.1 sec intervals
Other: AutoZero, auto calibration using value stored in memory, optional 4 lamp turret
Background correction: Optional, deuterium lamp

Monochromator: Ebert-Fastie mount, 0.33 m focal length

Grating: 1200 grooves/mm. blazed at 250 nm, 32×32 mm. Optional dual 40×40 mm gratings for improved efficiency over entire wavelength range

Performance (continued)	Wavelength Range: 180 to 900 nm Wavelength Accuracy: Better than 0.05 nm Wavelength Reproducibility: Better than 0.1 nm Resolution: 0.04 nm first order Reciprocal Dispersion: 2.5 nm/mm Slits: Curved, variable in 7 steps from 0.04 to 2 nm spectral bandpass Wavelength Scan: Opt. 5, 20 nm/sec Gas Control: Solenoid valving, constant level burner drain system, electric ignition, pressure orifice flow control, polypropylene premix chamber, safety interlock Oxidant: Air or N_2O Fuel: C_2H_2 Venting: 10.2 cm dia., 28 l/min (4" dia., 100 cf/min) Burner: Standard 10 cm head, suitable for air, with C_2H_2 or hydrogen, N_2O, three slot heads optional, Teflon lined, titanium jaws Adjustments: Three dimensional
Operation	Calibration: Standard samples, zero plus 1 to 5 standards Procedure: Methods manual provided listing standard conditions for most elements, procedures for common elements stored in memory Training: Requires about 20 hours depending upon number and complexity of analyses - 3 day training course provided for 1 operator at choice of 4 U.S. locations Unattended Period: None Maintenance: Service centers throughout U. S.
Requirements	Power: 100, 115, or 230 VAC ± 20%, 50 or 60 Hz, 230 W Weight: 110 kg (240 lbs) Dimensions: 55 cm H, 109 cm L, 64 cm D (215" H × 43" L × 25" D)
Features	CRT Display, microcomputer Memory protection Double beam, Zoom lens Digital meters, recorder Four detection modes Automatic update and manual update Peak height and peak area, simultaneous display Analytical conditions stored in microcomputer memory Automatic zero Curve correction Automatic calibration
Options	Motorized wavelength scan $ 500 Background correction and Deuterium lamp 1200 4-Lamp turret 900 Dual grating monochromator 600 Hollow Cathode Lamps See Instrumentation Lab A Graphite Furnace See Instrumentation Lab C Computer interface RS232C 200 Printer, printer with interface 1200 - 1400 IL 254 Fastac AutoSampler 3950 Graphics Option - plot of working curves, display of transient absorbance peaks
Peferences	Manufacturer's Bulletin
Cost	Model IL 550, VIDEO I $13,000
Address	Instrumentation Laboratory, Inc., Jonspin Road Wilmington, MA 01887 Tel (617) 658-5125

Performance (continued)	Wavelength Range: 180 to 900 nm Wavelength Accuracy: Better than 0.05 nm Wavelength Reproducibility: Better than 0.1 nm Resolution: 0.04 nm first order Reciprocal Dispersion: 2.5 nm/mm Slits: Curved, variable in 7 steps from 0.04 to 2 nm spectral bandpass Wavelength Scan: Opt. 5, 20 nm/sec Gas Control: Solenoid valving, constant level burner drain system, electric ignition, pressure orifice flow control, polypropylene premix chamber, safety interlock Oxidant: Air or N_2O Fuel: C_2H_2 Venting: 10.2 cm dia., 28 l/min (4" dia., 100 cf/min) Burner: Standard 10 cm head, suitable for air, with C_2H_2 or hydrogen, N_2O, three slot heads optional, Teflon lined, titanium jaws Adjustments: Three dimensional
Operation	Calibration: Standard samples, zero plus 1 to 5 standards Procedure: Methods manual provided listing standard conditions for most elements, procedures for common elements stored in memory Training: Requires about 20 hours depending upon number and complexity of analyses - 3 day training course provided for 1 operator at choice of 4 U.S. locations Unattended Period: None Maintenance: Service centers throughout U. S.
Requirements	Power: 100, 115, or 230 VAC ± 20%, 50 or 60 Hz, 230 W Weight: 110 kg (240 lbs) Dimensions: 55 cm H, 109 cm L, 64 cm D (215" H × 43" L × 25" D)
Features	CRT Display, microcomputer Memory protection Double beam, Zoom lens Digital meters, recorder Four detection modes Automatic update and manual update Peak height and peak area, simultaneous display Analytical conditions stored in microcomputer memory Automatic zero Curve correction Automatic calibration

Options

Motorized wavelength scan	$ 500
Background correction and Deuterium lamp	1200
4-Lamp turret	900
Dual grating monochromator	600
Hollow Cathode Lamps	See Instrumentation Lab A
Graphite Furnace	See Instrumentation Lab C
Computer interface RS232C	200
Printer, printer with interface	1200 - 1400
IL 254 Fastac AutoSampler	3950

Graphics Option - plot of working curves, display of transient absorbance peaks

Peferences	Manufacturer's Bulletin
Cost	Model IL 550, VIDEO I $13,000
Address	Instrumentation Laboratory, Inc., Jonspin Road Wilmington, MA 01887 Tel (617) 658-5125

INSTRUMENTATION
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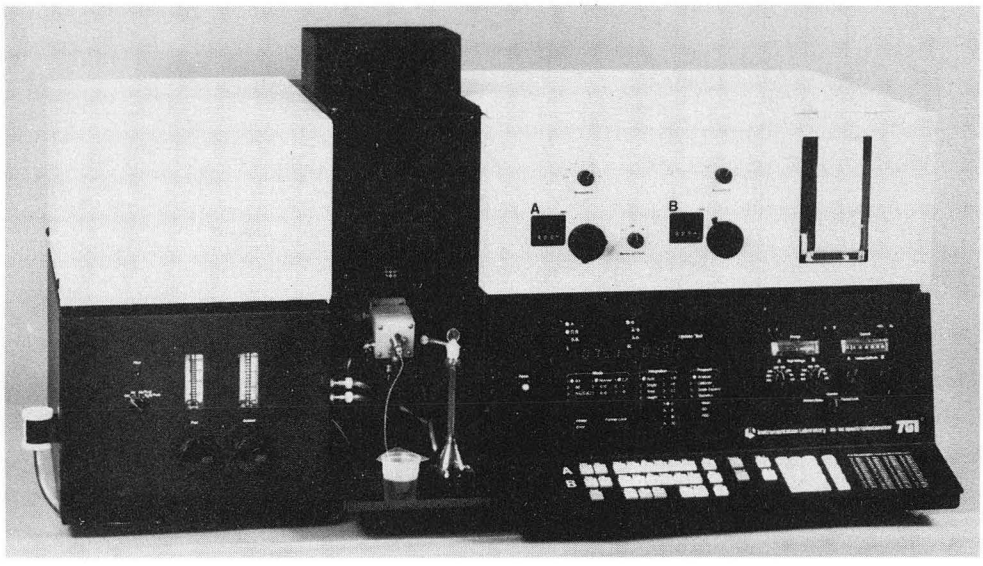
MONITORING

H20-MET
NOTES, AAS
Instrumentation Lab 4
August, 1978

Atomic Absorption/Emission Spectrophotometer

Model IL 651/751



Class

Laboratory

Description

Model IL 751 - dual channel, dual double beam, zoom lens, atomic absorption spectrophotometer with microcomputer

Model IL 651 - single channel, updatable to double channel double beam zoom lens atomic absorption spectrophotometer

Modes of Operation

Absorbance (A,B); Internal Standard A/B, flame emission (A,B; A/B; A-B)

Lower Detection Limit

Sensitivity is defined as the concentration of an element in an aqueous solution which gives rise to 1% absorption (0.0044 Absorbance).

Detection Limit is defined as that concentration of an element which provides a signal equal to twice the standard deviation of a series of ten blank corrected readings of the element at a concentration close to the blank level.

Element	Sensitivity (µg/ℓ)	Detection Limit (µg/ℓ)
Ag Silver	30	2
Al Aluminum	400	20
As Arsenic	400	106 1*
Au Gold	100	10
B Boron	9,000	9,000
Ba Barium	100	20
Be Beryllium	10	20
Bi Bismuth	200	40
Ca Calcium	10	1
Cd Cadmium	10	1
Co Cobalt	50	5
Cr Chromium	40	3
Cs Cesium	150	15
Cu Copper	30	2
Er Erbium	400	40

(continued)

Element	Sensitivity (µg/ℓ)	Detection Limit (µg/ℓ)
Fe Iron	50	3
Hg Mercury		0.5*
K Potassium	10	1
Li Lithium	20	2
Mg Magnesium	3	0.2
Mn Manganese	20	3
Mo Molybdenum	200	10
Na Sodium	1	0.4
Ni Nickel	50	70
Pb Lead	100	10
Pr Praseodymium	20,000	20,000
Pt Platinum	1,000	50
Rb Rubidium	200	2
Re Rhenium	8,000	800
Rh Rhodium	200	10
Sb Antimony	200	60
		6*
Sc Scandium	100	10
Se Selenium	400	100
		1*
Si Silicon	800	60
Sn Tin	1,200	80
Sr Strontium	60	1
Ta Tantalum	12,000	800
Te Tellurium	200	10
Ti Titanium	900	50
Tl Thallium	100	30
V Vanadium	600	20
W Tungsten	5,000	500
Y Yttrium	1,800	200
Yb Ytterbium	80	2
Zn Zinc	8	0.6

Note: All sensitivities and detection limits were obtained using an air-acetylene or nitrous oxide-acetylene flame unless otherwise noted. Potassium was added to the aqueous standards to suppress ionization for easily ionized elements.

*Hydride Generator

Range

Absorbance Range: -0.5 to 2.000
Concentration: Up to 9999

Interferences

Vary with element determined

Multiparameter Capability

Dual monochromators for determination of 2 elements simultaneously or for use of an internal standard

Sampling

Method: Batch or automatic, sample in solution
Volume: 1 µℓ to 3 ml dependent upon atomization source
Capacity: Up to 12 determinations per minute

Performance

Electronics: Microcomputer control of all data reduction functions. 4 digit LED display for each channel. Status panel to show current operating mode
Linearity: Varies with element determined
Stability: 0.005% short term
Scale Expansion: Automatic computation of curve required to fit from 1 to 5 standards
Detector: R372 Photomultiplier in each channel
Readout: 4 digit LED display for each channel. Optional built-in alphanumeric printer
Response time: Integral mode at 1/16, 1/8, 1/2, 1, 4, 8, 16, 32 sec.
Other: AutoZero and autocalibration, simultaneous dual channel operation with background correction

Performance (continued)	Background correction: D_2 arc intensity under microcomputer control Monochromators: Both channels; Ebert mount 0.33 m focal length Grating: 1200 grooves/mm, blazed at 250 nm Optionally, both channels may be equipped with dual 40×40 mm gratings for improved efficiency over entire-wavelength range Wavelength Range: 190 to 900 nm Wavelength Accuracy: Better than 0.05 nm Wavelength Reproducibility: Better than 0.1 nm Resolution: 0.04 nm, first order Reciprocal Dispersion: 2.5 nm/mm Slits: Curved variable in 7 steps from 0.04 to 2 nm spectral bandpass Gas Control: Solenoid valving, constant level burner drain system, electric ignition, pressure orifice flow control Oxidant: Air or N_2O Fuel: C_2H_2 Venting: 10.2 cm dia., 28 l/min (4" dia., 100 cf/min) Burner: Teflon lined, Titanium jaws, single slot burner
Operation	Calibration: Standard samples Procedure: Methods manual provided listing standard conditions for most elements Training: Requires about 20 hours depending upon number and complexity of analyses. 3 day training course provided for 1 operator at choice of 6 U. S. locations Unattended period: 1-2 hours with FASTAC Auto Sampler Maintenance: Service centers throughout U. S.
Requirements	Power: 100,115 or 230 VAC ±10%, 50 or 60 Hz, 375 W Weight: 150 kg (330 lb) Dimensions: 51 cm H ×109 cm L ×58 cm D (20" × 43" × 23")
Features	Two channel, double beam, double-zoom lens Dual recorder outputs with choice of formatted or continuous display Dual LED readouts display in concentration or absorbance for channels A and B, A or B, or A with internal standard Choice of continuous update, manual update, peak height, peak area
Options	Alphanumeric printer, inkless, built-in (with computer interface) $1500 (2300) D_2 arc background correction for both channels 1500 Dual grating monochromators for both channels 1200 4 lamp turret 900 Motorized wavelength scan 500 Hollow Cathode Lamps See Instrumentation Lab A Graphite Furnace See Instrumentation Lab C D_2 arc for 651 900
References	Manufacturer's Bulletin
Cost	Model IL 751 $17,000 Model IL 651 13,000
Address	Instrumentation Laboratory, Inc., Jonspin Road Wilmington, MA 01887 Tel (617) 658-5125

INSTRUMENTATION
FOR ENVIRONMENTAL
MONITORING

Hollow Cathode Lamps

Instrumentation Lab

Class: Accessory

Description: Hollow Cathode Lamps for use with Instrumentation Lab Atomic Absorption Spectrophotometers

Multiparameter Capability

HOLLOW CATHODE LAMPS, Single Element

Cat.No.	Price	Cathode Element	Cat.No.	Price	Cathode Element
62809	$140.00	Aluminum -Al*	62819	$125.00	Nickel - Ni
62931	150.00	Antimony - Sb	62858	160.00	Niobium - Nb*
62836	180.00	Arsenic - As	63144	320.00	Osmium - Os*
62834	150.00	Barium - Ba*	62969	175.00	Palladium - Pd
63300	190.00	Beryllium - Be*	63118	250.00	Phosphorus - P
62932	150.00	Bismuth - Bi	63474	185.00	Platinum - Pt
62916	150.00	Boron - B*	62863	175.00	Potassium - K
62933	150.00	Cadmium - Cd	62981	200.00	Praseodymium - Pr*
62610	125.00	Calcium - Ca	62942	200.00	Rhenium - Re*
62823	180.00	Cesium - Cs	62997	210.00	Rhodium - Rh
62934	125.00	Chromium - Cr	62824	180.00	Rubidium - Rb
62928	125.00	Cobalt - Co	63138	200.00	Ruthenium - Ru
63041	125.00	Copper - Cu	62818	200.00	Samarium - Sm*
62827	200.00	Dysprosium - Dy*	63181	250.00	Scandium - Sc*
62828	200.00	Erbium - Er*	62938	175.00	Selenium - Se
62845	250.00	Europium - Eu*	62939	150.00	Silicon - Si*
62985	200.00	Gadolinium - Gd*	62806	125.00	Silver - Ag
62833	175.00	Gallium - Ga	63059	175.00	Sodium - Na
63472	200.00	Germanium - Ge*	62835	155.00	Strontium - Sr
62935	175.00	Gold - Au	62859	150.00	Tantalum - Ta*
63180	200.00	Hafnium - Hf*	62940	175.00	Tellurium - Te
62829	200.00	Holmium - Ho*	62848	200.00	Terbium - Tb*
62996	155.00	Indium - In	63301	155.00	Thallium - Tl
63145	200.00	Iridium - Ir	63007	250.00	Thulium - Tm
62810	125.00	Iron - Fe	62941	150.00	Tin - Sn
63049	200.00	Lanthanum - La*	62991	145.00	Titanium - Ti*
62927	150.00	Lead - Pb	62844	145.00	Tungsten - W*
63060	150.00	Lithium - Li	62826	260.00	Uranium - U*
62968	125.00	Magnesium - Mg	62973	175.00	Vanadium - V*
62936	125.00	Manganese - Mn	62983	200.00	Ytterbium - Yb*
62847	150.00	Mercury - Hg	62987	200.00	Yttrium - Y*
62937	125.00	Molybdenum - Mo	62811	125.00	Zinc - Zn
62979	200.00	Neodymium - Nd*	62860	150.00	Zirconium - Zr*

HOLLOW CATHODE LAMPS, Multi-Element

63116	210.00	As/Ni	63207	170.00	Ca/Zn
63034	225.00	Ba/Ca/Sr	63174	225.00	Cr/Co/Ni
63133	250.00	Ba/Ca/Sr/Mg	63176	300.00	Cr/Co/Cu/Fe/Mn/Ni
62930	225.00	Ca/Mg/Al	63208	160.00	Cr/Cu
63035	230.00	Ca/Mg/Al/Li	63108	230.00	Cr/Fe/Mn/Ni
63207	$170.00	Ca/Zn			
63174	225.00	Cr/Co/Ni			
63176	300.00	Cr/Co/Cu/Fe/Mn/Ni			
63208	160.00	Cr/Cu			
63108	230.00	Cr/Fe/Mn/Ni	63117	$210.00	Au/Ni
			63106	210.00	Fe/Cu/Mn
63190	160.00	Cu/Co	63171	230.00	Pb/Zn/Ag
			63177	230.00	Mo/Cu/Fe
63131	160.00	Cu/Mn	63173	225.00	Na/K
63134	230.00	Cu/Zn/Fe/Mn			
63135	200.00	Cu/Zn/Mo/Co			
63141	200.00	Cu/Zn/Fe/Ni			
63211	230.00	Au/Cu/Fe/Ni			

Manufacturer — Instrumentation Laboratory, Inc.

Warranty — Two years from date of shipment in IL instruments 6 mos or 5000 m A-hours whichever comes first in instruments from other manufacturers.

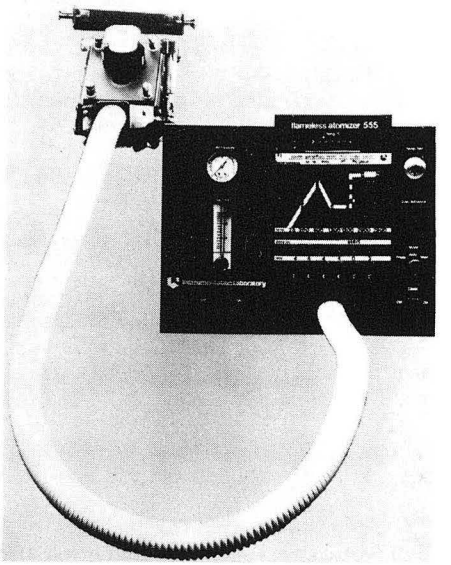
References — Manufacturer's Specifications

Cost — See list under Multiparameter Capability

Address — Instrumentation Laboratory, Inc.
Jonspin Road
Wilmington, MA 01887
Tel (617) 658-5125

INSTRUMENTATION
FOR ENVIRONMENTAL
MONITORING

Furnace Atomizer
for Atomic Absorption Spectrophotometry
IL 555 CTF



Class: Accessory

Description: Controlled Temperature Furnace Atomic Absorption Sampler

Lower Detectable Limit

Approximate sensitivities, IL 555 CTF atomizer

Element	Sensitivity[i] Absolute ($g \times 10^{-12}$)	Sensitivity[i] Relative[ii] ($\mu g/\ell$)	Element	Sensitivity Absolute ($g \times 10^{-12}$)	Sensitivity Relative ($\mu g/\ell$)
Aluminum	0.4	0.04	Manganese	1	0.1
Antimony	8	0.8	Mercury	10	0.1
Arsenic	6	0.6	Molybdenum	6	0.6
Barium	4	0.4	Nickel	2.5	0.25
Beryllium	0.1	0.01	Palladium	20	2
Bismuth	0.5	0.5	Platinum	45	4.5
Cadmium	0.3	0.03	Potassium	10	1
Calcium	40	4	Rhenium	1000	100
Cesium	40	4	Rubidium	30	3
Chromium	0.5	0.05	Selenium	10	1
Cobalt	3	0.3	Silicon	30	3
Copper	0.8	0.08	Silver	0.5	0.05
Europium	9	0.9	Sodium	0.4	0.04
Gallium	5	0.5	Strontium	1	0.1
Germanium	40	4	Tellurium	7	0.07
Gold	1	0.1	Thallium	5	0.5
Indium	11	1	Tin	6	0.6
Iron	0.3	0.03	Titanium	30	3
Lead	5	0.5	Vanadium	15	1.5
Lithium	3	0.3	Zinc	0.2	0.02
Magnesium	0.7	0.07			

Notes: (i) Sensitivity expressed as value giving 1 per cent absorption (0.0044 absorbance units). Weight is in picograms, concentration in micrograms/litre, based on sample capacity of 10µℓ. (ii) In general, lower limit of detection is 1x to 3x lower than quoted sensitivity.

Range	Atomization temperature variable to 3000°C with feedback control over entire range.
Sampling	Method: Batch and semi-automatic and automatic with FASTAC Auto Sampler Volume: 1 µℓ to 80 µℓ Capacity: Depends on sample volume and matrix Temperature Control: Ramp or instantaneous heating in each step, 45 sec. max. time in each step. Closed loop temperature feedback control. Cuvettes: Graphite Round cross section. 4.75 mm × 38 mm long, I.D. Rectangular cross section; 4.75 mm × 4.75 mm × 38 mm long, I.D. Lifetime: 50-1000 shots, depending on temperature levels selected
Performance	Electronics: Solid state, meter readout of temperature Temperature Control; Closed loop temperature feedback via tungsten/tantalum resistance thermometer. Programming: Six step continuously variable. Furnace Cell: Fully sealed cell, can be pressurized during atomization
Operation	Calibration: N/A Procedure: Methods manual provides standard conditions for approx. 200 types of analysis Training: 2 day seminar available Unattended Period: 1-2 hours with FASTAC Auto Samplers Maintenance: Service centers throughout U. S. Temperature: Compensation: Closed loop temperature feedback using special resistance thermometer
Requirements	Power: 220 V ± 10%, 50/60 Hz, 20 amps Weight: 45.5 kg (100 lb) Dimensions: Furnace cell, 8×13×10 cm Programmer, 49×28×32 cm Cooling water: 0.5 to 1 liter/min
Features	UV transmitting quartz cell windows Automatic control of cell access door Printed overlay temperature program cards Meter readout of measured temperature from 25°C to 3500°C with automatic ranging. Cell pressurization and auto clean selectable at operator command Purge gas (argon) flow indicated from 0 to 30 SCHF; cell pressure indication from 0 to 60 psig in pressurization mode.
References	Manufacturer's Bulletin
Cost	Model IL 555 { $4490 when purchased with an IL AA spectrophotometer 4990 when purchased separately
Address	Instrumentation Laboratory, Inc. Jonspin Road Wilmington, MA 01887 (617) 658-5125

Atomic Absorption Spectrophotometer

Hitachi Model 170-10/30

Class	Laboratory
Description	Single beam atomic absorption spectrophotometer
Modes of Operation	Model 170-10 Atomic Absorption Model 170-30 Atomic Absorption/Flame Emission

Lower Detectable Limit

(Unit:ppb)

Ag	1.5	Cu	1	Pb	5
Al*	40	Fe	2	Pd	3.5
As**	1	Ge*	1,000	Pt	20
Au	3	Hg***	0.04	Rh	4
B*	1,100	In	8	Sb	50
Ba	100	K	5	Si*	40
Be*	1	Li	1.5	Sn	140
Bi	40	Mg	0.05	Sr	3
Ca	1	Mn	1	Ti*	40
Cd	0.4	Mo	30	V*	30
Co	2	Na	1	W*	500
Cr	2	Ni	2	Zn	0.6

i) The detection limits listed above are largely dependent on measuring conditions.

ii) Detection limit is defined as concentration at which S/N ratio reaches 2.

iii) For general measurements, sample solution should desirably be at a concentration at least 10 times the detection limit specified above.

iv) (*) denotes detection limit for measurement with the high temperature burner.
(**) denotes detection limit for measurement with the arsenic analyzer accessory.
(***) denotes detection limit for measurement with the mercury analyzer accessory.

Range and Sensitivity	10/30 0-2A, % to ppb 0.0.02A expanded
Multiparameter Capability	69 elements
Sampling	Method: Batch Volume: 2 mℓ
Performance and Specifications	Electronics: Linearity: Model 10 - no curve corrector; 30 curve corrector availability Stability: Scale Expansion: 0.10 ~10 (continuously changeable) Damping: Continuously variable zoom speed control Detector: Photomultiplier Integration: Signal averaging available Model 170-30 Zero drift: Auto-zero (170-30 only), 170-10 control adjustment Readout: Both analog and digital available Background: Optional background drift corrector available Monochromator: Thermally isolated, floating base type; Littrow Grating: 1440 line/mm, blazed at 230 nm Dispersion: 2425 nm/mm Range: 190-900 nm, 3 digit counter Spectral bandpass: 0.4 nm Wavelength accuracy: 3 digital ± 0.5 nm Scan speeds: Gas Control: Rectangular pulse automated ignition, premix chamber, flow controls integral, auto flow control built-in. Oxidant: N_2O, air, argon switch controlled, with safety lock for N_2O Fuel: C_2H_2,H_2 Venting: An exhaust duct should be provided Burner: Single slot, teflon coated, water cooled Adjustments: 3d, scales on vertical and horizontal
Operation	Calibration: By standards Maintenance: Preventive maintenance schedule Training required/available: Some training available in Mountain View, California
Requirements	Power: Model 170-10, 115 VAC, Model 170-30, 115 VAC Dimensions: 85 cm W × 43 cm D × 48 cm H Weight: 65 kg
Features	Single beam operation Auto-ignition Built-in fuel and oxidant controls Safety interlock for N_2O switchover, T valve Scale expansion Zoom response speed control Zero adjust circuit (Model 170-10) Auto zero circuitry (Model 170-30)
Options	Graphite Furnace Atomizer — $ 5700, See Hitachi C Mercury Analyzer — 1622 - 1894 Arsenic Analyzer — 2450 Hollow Cathode Lamps — See Hitachi A Digital and Analog Recorders — 320-2200 Baseline Drift Corrector — 845
References	Manufacturer's Specifications

Cost	Model 170-10AA	$ 5700
	Model 170-30AA	6500
Address	NSI-Hitachi Scientific Instruments Nissei Sangyo Instruments, Inc. 450 E. Middlefield Rd. Mountain View, CA 94043 (415) 969-1100	

Atomic Absorption/Emission Spectrophotometer

Hitachi Model 170-50A

Class	Laboratory
Description	Pulsed, single beam atomic absorption spectrophotometer
Modes of Operation	Atomic absorption/flame emission

Lower Detectable Limit

(Unit:ppb)

Ag	1.5	Cu	1	Pb	5
Al*	40	Fe	2	Pd	3.5
As**	1	Ge*	1,000	Pt	20
Au	3	Hg***	0.04	Rh	4
B*	1,100	In	8	Sb	50
Ba	100	K	5	Si*	40
Be*	1	Li	1.5	Sn	140
Bi	40	Mg	0.05	Sr	3
Ca	1	Mn	1	Ti*	40
Cd	0.4	Mo	30	V*	30
Co	2	Na	1	W*	500
Cr	2	Ni	2	Zn	0.6

i) The detection limits listed above are largely dependent on measuring conditions.
ii) Detection limit is defined as concentration at which S/N ratio reaches 2.
iii) For general measurements, sample solution should desirably be at a concentration at least 10 times the detection limit specified above.
iv) (*) denotes detection limit for measurement with the high temperature burner.
(**) denotes detection limit for measurement with the arsenic analyzer accessory.
(***) denotes detection limit for measurement with the mercury analyzer accessory.

Range and Sensitivity	0-2A, 0.-0.02A expanded, % - ppb
Interferences	None particular
Multiparameter Capability	69 Elements
Sampling	Method: batch, one at a time Volume: 2 mℓ
Performance and Specifications	Electronics: Linearity: Curve corrector Stability: Scale Expansion: 0.1 ×10 (continuous) Damping: Continuously variable zoom speed control Detector: Photomultiplier tube Integration: Signal averaging circuit Zero drift: Built-in auto zero Readout: Analog/digital Background: Two phase balance free system, curvature correction circuit Response time: Zoom system (continuously variable) Monochromator: Thermally isolated, floating base, Littrow mount Grating: 1440 lines/mm blazed at 230 nm Dispersion: 2.25 nm/mm Range: 190-900, 3 digit counter Spectral bandpass: 0.4, 1.1, 2.2 nm Wavelength accuracy: ±0.5 nm Scan speeds: 4 scan speeds (optional) Gas Control: Building pressure, flow controls, premix chamber, water cooled with automated two phase pulse ignition, C_2H_2 gas sensor (optional) Oxidant: N_2O, air with auto switching, safety lock on N_2O Fuel: C_2H_2, H_2 Venting: An exhaust duct is recommended Burner: Single slot provided Adjustments: Three diemsnional, scales on vertical and horizontal
Operation	Calibration: By standards Maintenance: Preventive maintenance schedule Training required/available: Some training and seminars are available at Mountain View, CA
Requirements	Power: 115 VAC Dimensions: 85 cm (W) × 43 cm D × 48 cm H Weight: 65 kg
Features	Single beam operation Pulsed deuterium background correction built-in Auto-zero Auto ignition Gas control pressure gauge, fuel controls built-in N_2O, air selector valve with safety interlock Baseline monitor availability Scale expansion
Options	Mercury analyzer (water dehumidified/cooled - dessicant dehumidified) $ 1622 - 1894 Arsenic Analyzer 2450 Graphite Furnace 5700, See Hitachi C Digital/analog recorders 320-2200 Hollow Cathode Lamps See Hitachi A

References	Manufacturer's Specifications	
Cost	Model 170-50A	$8100
Address	NSI-Hitachi Scientific Instruments Nissei-Sangyo Instruments, Inc. 450 E. Middlefield Rd. Mountain View, CA 94043 (415) 969-1100	

INSTRUMENTATION
FOR ENVIRONMENTAL
MONITORING

Atomic Absorption Spectrophotometer

Hitachi Model 170-70

Class	Laboratory
Description	Double beam, flameless Zeeman atomic absorption spectrophotometer
Modes of Operation	Atomic absorption

Lower Detectable Limit

	Minimum Detection Limit	
	Absolute ($g \times 10^{-12}$)	Relative (ppb)*
Aluminum	20	2
Antimony	300	30
Arsenic	10	1
Barium	80	8
Bismuth	300	30
Cadmium	0.3	0.03
Calcium	4	0.4
Cesium	30	3
Chromium	3	0.3
Cobalt	20	2
Copper	3	0.3
Iron	4	0.4
Lead	4	0.4
Lithium	20	2
Magnesium	0.1	0.01
Manganese	3	3
Mercury	100	10
Nickel	30	3
Potassium	20	2
Selenium	100	10
Silver	0.9	0.09
Sodium	2	0.2
Strontium	20	2
Titanium	200	20
Vanadium	200	20
Zinc	1	0.1

*Based on a 10 μℓ sample

Range and Sensitivity	% to ppb
Interferences	Depends upon element
Multiparameter Capability	35 single element lamps, 9 multielement lamps singly available from Hitachi
Sampling	Method: batch Capacity: singly Volume: Sample area:
Performance and Specifications	Electronics: Linearity: Stability: Scale Expansion: x1 ~ x5 Damping: Continuously variable zoom speed control Detector: Photomultiplier tube Integration: Zero drift: Double beam operation Readout: Concentration linear, 10 mV recorder Background: Zeeman background correction available over entire wavelength range, Senarmon prism polarizer Monochromator: Littrow, thermally isolated floating base Grating: 1440 lines/mm, blazed at 230 nm Dispersion: 2.25 nm/mm Range: 190 ~ 900 nm Spectral bandpass: 0.4, 1.1 and 2.2 nm Wavelength accuracy: ±0.5 Scan speeds: 4 speeds (optional) Magnet: 11 K gauss permanent high density Power Supply: Sheath gas: 2 liters/min Carrier gas: 0 ~ 0.5 liter/min Output: Direct/Peakhold Cooling water: 3 liters/min or more Dimensions: 52 cm (W) ×43 cm (D) ×35 cm (H) Weight: Approx. 55 kg
Operation	Calibration: By standards Maintenance: Preventive maintenance schedule Training required/available: Some seminars available in Mountain View, CA
Requirements	Power: 220V, 20A (Power Supply) Dimensions: 85 cm (W) ×43 cm (D) ×35 cm (H) Weight: Approx. 75 kg
Features	Double Beam Operation, mechanical chopper Polarized Zeeman correction Flameless AA Auto-baseline correction Background correction over entire wavelength range

Options	Recorders	$ 855 - 2200
	Hollow Cathode Lamps - See Hitachi A	See Hitachi A
	Cylindrical and cup type graphite curvettes	~ 27
	Graphite cone	~ 21
	Digital displays	320 - 540
	Mercury analyzer	1622 - 1894
	Arsine analyzer	2450
	Burner heads	115 - 535
References	Manufacturer's Specifications	
Cost	Model 170-70	$ 19,700
Address	NSI-Hitachi Scientific Instruments Nissei-Sangyo Instruments Inc. 450 E. Middlefield Rd. Mountain View, CA 94043 (415) 969-1100	

INSTRUMENTATION
FOR ENVIRONMENTAL
MONITORING

Hollow Cathode Lamps

NSI-Hitachi

Class Accessory

Description Hollow Cathode Lamps

Multiparameter Capability

Single Element Lamps

Cat.No.	Cathode Element	Price
139-3614	Ag Hollow Cathode Lamp	$165
208-2001	Al Hollow Cathode Lamp	160
207-2021	As Hollow Cathode Lamp	230
207-3581	Au Hollow Cathode lamp	250
207-2002	B Hollow Cathode Lamp	210
207-2004	Ba Hollow Cathode Lamp	185
207-2008	Be Hollow Cathode Lamp	250
139-3564	Bi Hollow Cathode lamp	215
208-2008	Cd Hollow Cathode Lamp	180
139-3572	Co Hollow Cathode Lamp	165
208-2010	Cr Hollow Cathode Lamp	160
208-2011	Cu Hollow Cathode Lamp	160
208-2012	Fe Hollow Cathode lamp	160
207-2022	Ge Hollow Cathode Lamp	250
207-2007	Hg Hollow Cathode Lamp	180
207-2018	In Hollow CAthode Lamp	300
208-2016	K Hollow Cathode Lamp	110
207-2019	Li Hollow Cathode lamp	210
139-3592	Mg Hollow Cathode Lamp	165
208-2019	Mn Hollow Cathode Lamp	160
207-2005	Mo Hollow Cathode Lamp	165
208-2021	Na Hollow Cathode lamp	215
139-3597	Ni Hollow Cathode Lamp	160
208-2023	Pb Hollow Cathode Lamp	180
207-2009	Pd Hollow Cathode Lamp	230
139-3601	Pt Hollow Cathode Lamp	260
207-2017	Rh Hollow Cathode Lamp	365
207-2006	Sb Hollow Cathode Lamp	185
207-2019	Si Hollow Cathode Lamp	185
208-2029	Sn Hollow Cathode Lamp	200
139-2012	Ti Hollow Cathode Lamp	170
207-2011	V Hollow Cathode Lamp	245
207-2003	W Hollow CAthode Lamp	170
208-2034	Zn Hollow Cathode Lamp	170

Multiple Element Lamps

Cat.No.	Cathode Element	Price
139-3632	Ca-Mg Hollow Cathode Lamp	$280
208-3000	Cu-Fe-Mn Hollow Cathode Lamp	390
208-3001	Cu-Mn-Si Hollow Cathode Lamp	390
208-3002	Cu-Fe-Ni Hollow Cathode Lamp	390
208-3003	Co-Cr-Cu-Fe-Mn-Ni Hollow Cathode Lamp	535
208-3004	Cr-Cu-Fe-Mn-Ni Hollow Cathode Lamp	490
208-3005	Fe-Mn-Ni Hollow Cathode Lamp	390
208-3006	Cr-Cu-Mn Hollow Cathode Lamp	390
208-3007	Cd-Pb Hollow Cathode lamp	370
208-3008	Cd-Zn Hollow Cathode Lamp	370

Manufacturer NSI-Hitachi

Warranty

References Manufacturer's Bulletin

Cost	Listed above under Multiparameter Capability
Address	NSI-Hitachi Scientific Instruments Nissei Sangyo Instruments, Inc. 450 E. Middlefield Rd. Mountain View, CA 94043 (415) 969-1100

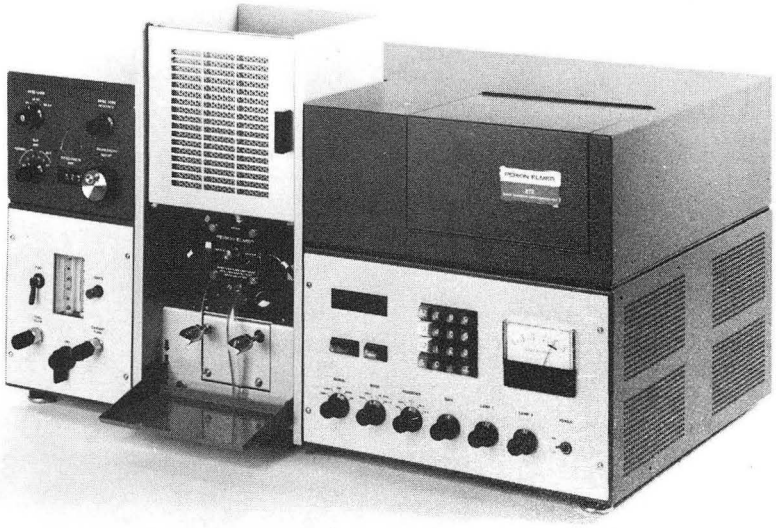
Graphite Furnace
Hitachi GA-2

Class	Laboratory, accessory
Description	Graphite furnace for flameless AAS, with both cup and tube elements
Sensitivity and Range	
Sampling	Method: Batch or automated Max. sample: Tube-20 µℓ, cup-50 µℓ
Performance	Accuracy: Depends upon samples, standards, user Reproducibility: Ca 1-3% C.V. depending on element, conc. Linearity: 200x detection limit depending on element, conc. Max. temperatures: Cup - dry - 200°C ash - 1600°C atomize - 2600°C Tube- dry - 350°C ash - 2200°C atomize - 2800°C Timers: Dry: 60 sec. (max.) Ash: 120 sec. (max.) } continuously adjustable Atomize: 30 sec. (max.) Ramp mode available for all three stages
Requirements	Power: Power supply - 220 VAC, 20A; photometric unit 120V, 10A Size: Power supply - 52 cm × 43 cm × 35 cm; photometric unit 85 cm × 43 cm × 35 cm Weight: Power supply - 55 kg; photometric unit - 75 kg Humidity range: Up to 85% RH at 20°C Temperature: 5-35°C Cooling water: Inert Gas:
Features	
References	Manufacturer's Specifications

Cost	Model GA-2	$5700
Address	NSI-Hitachi Scientific Instruments Nissei Sangyo Instruments 450 E.Middlefield Rd. Mountain View, CA 94043 (415) 969-1100	

Atomic Absorption/Emission Spectrophotometer

Perkin Elmer Model 272



Class Laboratory

Description Single beam microprocessor controlled atomic absorption spectrophotometer

Modes of Operation Atomic absorption, flame emission

Lower Detectable Limit

Model 272
Atomic Absorption Minimum Detection Limits

Element	µg/ℓ	Element	µg/ℓ
Aluminum[1]	20	Lanthanum[1,3]	7,000
Antimony	70	Lead	30
Arsenic[2]	250	Lithium	2.5
Barium[1,3]	30	Lutetium[1,3]	700
Beryllium[1]	2	Magnesium	0.1
Bismuth	100	Manganese	8
Boron[1]	2,500	Mercury	1,000
Cadmium	2	Molybdenum[1]	20
Calcium	2	Neodymium[1,3]	5,000
Cesium	5[3,4]	Nickel	20
Chromium	8	Niobium[1,3]	3,000
Cobalt	15	Osmium[1]	200
Copper	5	Palladium	25
Dysprosium[1,3]	200	Phosphorus[1]	100,000
Erbium[1,3]	70	Platinum	70
Europium[1,3]	100	Potassium	4
Gadolinium[1,3]	2,000	Praseodymium[1,3]	10,000
Gallium	50	Rhenium[1]	700
Germanium[1]	800	Rhodium	10
Gold	30	Rubidium	2[4]
Hafnium[1]	2,000	Ruthenium	80
Holmium[1,3]	100	Samarium[1,3]	3,000
Indium	30	Scandium[1,3]	30
Iridium	1,200	Selenium[2]	80
Iron	10	Silicon[1]	200

Lower Detectable Limit (continued)

Model 272
Atomic Absorption Minimum Detection Limits

Element	µg/ℓ	Element	µg/ℓ
Silver	2	Titanium[1]	150
Sodium	1	Tungsten[1]	2,200
Strontium[2]	4	Uranium[1]	80,000
Tantalum[1]	6,000	Vanadium[1]	160
Tellurium	100	Ytterbium[1,3]	10
Terbium[1,3]	800	Yttrium[1,3]	120
Thallium	70	Zinc	3
Thulium[1,3]	25	Zirconium[1]	2,000
Tin[2]	20		

[1]Nitrous oxide-acetylene flame
[2]Argon-hydrogen-entrained air flame
[3]1000 µg/mℓ K to control ionization
[4]Flame emission with air-acetylene flame

Range

Absorbance to 2.000A, conc. to 9999

Interferences

Multiparameter Capability

64 single element lamps, 17 multielement lamps

Sampling

Method: Batch or automated
Sample area: 22 cm wide; 21 cm deep
Capacity: flame-50/batch
Volume: flame - 1/2 1 mℓ
flameless 10-20 µℓ or less; up to 100 µℓ

Performance

Electronics: Microprocessor

Linearity:
Stability:
Scale expansion: from 0.1 to 50x, continuous
Damping: 0.4, 1, 3 sec.
Detector: Photomultiplier
Integration time: from 0.5 to 20 sec, 0.1 sec intervals
Readout: Digital in absorbance, concentration and emission
Background Correction: Deuterium arc background correction (optional)

Monochromator: Littrow Grating System, focal length 267 mm

Grating: 45 × 45 mm, 1800 lines/mm, blazed at 255 nm
Dispersion: 1.6 nm/mm nominal
Range: 190-870nm
Resolution: 0.2, 0.7, 2 nm

Gas Control: Remote flame ignition, T valve for nitrous oxide

Oxidant: air or N_2O
Fuel: C_2H_2
Venting: Recommended at 300 CTM
Burner: Plastic premix chamber, 10 cm, all Titanium burner head, N_2O burner head, three slot burner head, corrosion resistant nebulizer (opt.)
Adjustments: Three dimensional adjustments

Operation

Calibration: Automatic curve fittings on blank and 2 standards
Maintenance: Service centers in the U.S.
Training: Free training course for one operator at six U.S. locations

Requirements	Power: 105-125 or 200-240 V; 50-60 Hz; 150 watts Weight: 70 kg (150 lb) net or 125 kg (270 lb) gross Dimensions: 43 cm H × 50 cm D × 8 cm W	
Features	Single Beam Optics Microcomputer Controlled Premix Burner Chamber Automatic Flame Ignition Digital Readout Readout in absorption, concentration and intensity Auto zero Auto calibration Signal integration Emission	
Options	Interlocked gas control system with auto sampling	$ 750
	Deuterium arc background correction	1500
	Graphite furnace	See Perkin Elmer-C
	Two lamp turret	550
	Mechnical chopper	220
	Printer, sequencer	1250/1750*
	Typewriter readout	2950
	AS-50 Auto sampling system	2995
	AS-3 Auto sampling system	3750
	Mercury hydride system, MHS/1	3350
	Mercury hydride system MHS/10	995
	AA microsampling	750
	Flameless Hg analysis	600
	AS/Se sampling system	500
	Hollow cathode lamps	See Perkin Elmer-A
	Electrodeless discharge lamps	See Perkin Elmer-B
References	Manufacturer's Literature	
Cost	Model 272	$ 6500
Address	Perkin-Elmer Corporation Instrument Division Norwalk, CT 06856 (203) 762-1000	

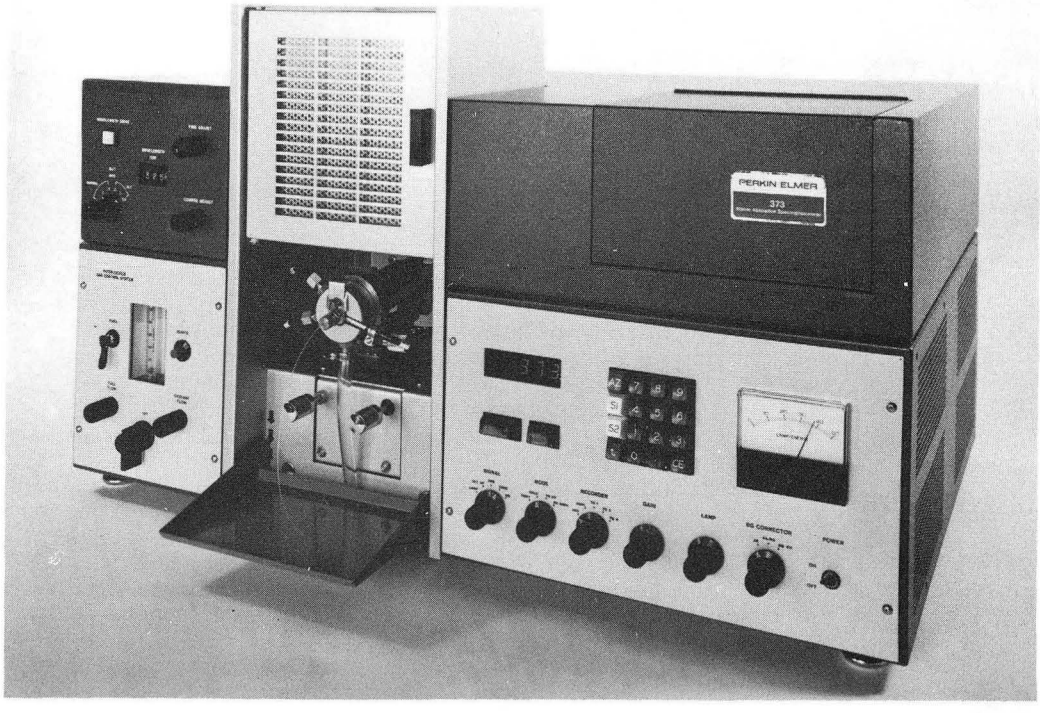
*Depends on time of purchase

INSTRUMENTATION
FOR ENVIRONMENTAL
MONITORING

H20-MET
NOTES, AAS
Perkin-Elmer 2
August 1978

Atomic Absorption/Emission Spectrophotometer

Perkin-Elmer Model 372,373



Class	Laboratory
Description	Double beam, microprocessor controlled, atomic absorption spectrophotometer
Modes of Operation	Atomic absorption, flame emission

Lower Detectable Limits

MODEL 373 MINIMUM DETECTION LIMITS

Element	DL (µg/ℓ)	Element	DL (µg/ℓ)
Ag	2	Mn	3
Al*	30	Mo*	20
As (EDL)	400[a]	Na	0.5
Au	20	Ni	10
B*	900	Pb (EDL)	14
Ba*	20	Rb (FE)	2
Be*	2	Sb (EDL)	40
Bi (EDL)	30	Se (EDL)	100
Ca	1.6	Si*	100
Cd (EDL)	1.6	Sn* (EDL)	190
Co	15	Sr	1
Cr	3	Te (EDL)	38
Cu	2	Ti*	80
Fe	10	Tl (EDL)	130
Hg	150	V*	50
K	<2	W*	2,000
Li	2	Zn	1
Mg	0.1	Zr	1,000

* = nitrous oxide-acetylene flame (air-acetylene used for all other detection limits)
a = detection limit may be improved with use of simultaneous background correction

Range

Absorbance: 0-2A
Concentration: 10^{-4} to 10^{4} µg/ml depending on element and wavelength
Flame Emission: 10^{-4} to 10^{4} µg/ml depending on element and wavelength
Energy (Transmission): Automatically set

Interferences

Most interferences can be overcome by carefully selecting the proper flame conditions, using chemical interference suppressants in the sample, or optional Deuterium Background Corrector.

Multiparameter Capability

64 single element lamps, 17 multielement lamps

Sampling

Method: Batch or automatic
Volume: Flame, 0.5-1 mℓ; flameless, 10-20 µℓ or less, up to 100 µℓ
Capacity: Flame, 50 samples/batch; flameless, 30 samples/batch
Pathlength: 100 mm with air/C_2H_2, 50 mm with N_2O/C_2H_2
Sample area: 22 cm W, 21 cm D

Performance

Electronics: Microprocessor

Linearity: Better than 1%
Stability: Better than 0.1%
Scale Expansion: 0.5 to 50x
Light Source: Hollow cathode lamps, electrodeless discharge lamps
Detector: Multialkali photomultiplier
Integrator: Continuous from 0.5 to 20 sec with 0.1 sec intervals
Readout: Digital linear in absorbance, concentration or intensity
Zerodrift: Auto zero, automatic curve fittings on blank and 2 standards
Background Correction: Deuterium

Monochromator: Littrow grating system, focal length 267 nm

Grating: 64 64mm, 1880 lines/mm, blazed at 250 nm
Wavelength Range: 190 to 870 nm
Wavelength Accuracy: ±0.4 nm
Wavelength Repeatability: ±0.1 nm
Resolution: 0.2 nm, 0.7, 2 nm
Reciprocal Dispersion: 1.6 nm/mm
Slit Width: Two sets of slits, 0.2, 0.7, 2.0 nm bandpass
Stray Light: Negligible

Performance (continued)

Gas Control: Model 373: Integral gas controls, flow meters, T valve to N_2O, with automatic fuel flow adjustment, remote ignition for air based flames, burner head interlock system
Model 372: Integral gas controls, flow meters, T valve to N_2O, remote ignition for air based flames

Fuel: Acetylene
Oxidant: Air or nitrous oxide
Vent: Recommended at 300 CTM
Burner: Model 373 - stainless steel mixing chamber inert coated with plastic, all titanium 10 cm slot head, N_2O and three slot burner heads optional.
Model 372 - plastic mixing chamber, all titanium 10 cm slot head, N_2O and three slot burner heads optional
Adjustments: Model 373 - horizontal and vertical with scale, angular without scale
Model 372 - horizontal, vertical and angular
Options: Model 373-flame sensing and pressure sensing
372-burner head interlock optional
corrosion resistant nebulizer

Operation

Calibration: Automatic curve fittings on blank and two standards
Procedure: Manual provided
Training: Two-day training course included in price
Unattended Period: Not recommended
Maintenance: Service centers in the U.S.
Warm-up Time: 10 seconds at turn on

Requirements

Power: 105-125 or 200-240 volts, 50/60 Hz, 150 watts
Weight: 70 kg net, 125 kg gross
Dimensions: 41 cm high, 50 cm deep, 88 cm wide

Features

Double beam
Microprocessor controlled
Mechanical chopper
Electronic phase regulator
Curvature correction circuit
Auto gain control
Signal integrator
Peak analyzer
Autozero
Electric flame ignition
Safety interlock
Digital readout

Options

HGA-500, HGA-2200 graphite furnace	See Perkin-Elmer C
AS-1 Auto sampler for graphite furnace	$3695/4095*
Recorders	695-1415
Wavelength drive	550
Micro sampling system	750
Flameless AA Hg analysis system	600
Hydride generation system	500
AS-50 Auto sampler, flame	2995
Deuterium arc background correction	1500
PRS printer sequencer	1000/1500* (373) 1250/1750* (372)
Typewriter readout assembly	2950
Lamps - Intensitron ® Hollow cathode lamps	See Perkin-Elmer A
Electrodeless Discharge Lamps	See Perkin-Elmer B
Mercury Hydride System MHS-1	3350
Mercury Hydride System MHS-10	995
Microsampling flame sampler AS-3	3,780

References

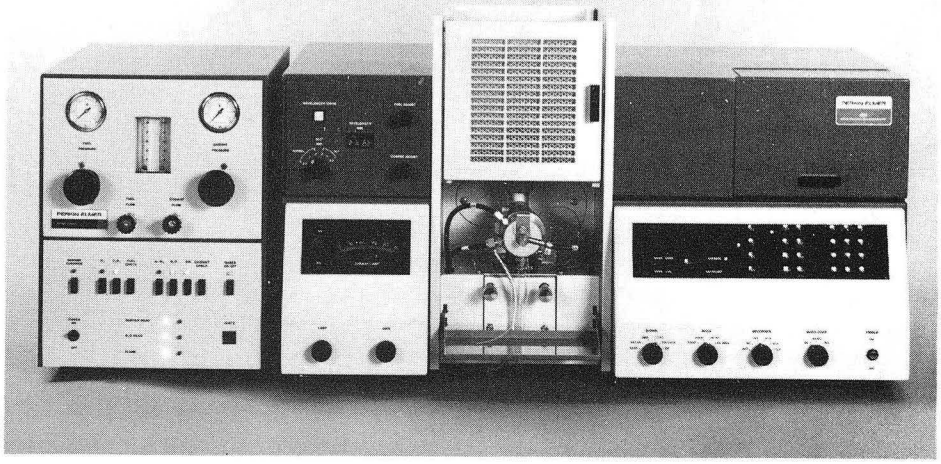
Manufacturer's Bulletin
Perkin-Elmer, Technique and Applications of Atomic Absorption Order No. AA-322G, March 1978

Cost	Model 373	$9600
	Model 372	8450
Address	Perkin-Elmer Instrument Division Norwalk, CT 06856 (203) 762-1000	

*Depends upon time of purchase

Atomic Absorption/Emission Spectrometer

Perkin-Elmer, Model 560



Class

Laboratory

Description

Double beam, microprocessor controlled, time shared atomic absorption spectrophotometer

Modes of Operation

Absorbance, concentration, unchopped or chopped emission

Lower Detectable Limit

Typical Model Minimum Detection Limits

Element	DL (µg/ℓ)	Element	DL (µg/ℓ)
Ag	2	Mn	30
Al*	20	Mo*	20
As (EDL)	400	Na	0.5
Au	20	Ni	10
B*	900	Pb (EDL)	15
Ba*	20	Rb (FE)	0.5
Be*	2	Sb (EDL)	30
Bi (EDL)	30	Se (EDL)	250
Ca	2	Si*	100
Cd (EDL)	15	Sn* (EDL)	70
Co	15	Sr	1
Cr	3	Te (EDL)	70
Cu	2	Tr*	80
Fe	10	Tl (EDL)	30
Hg	200	V*	50
K	5	W*	2000
Li	2	Zn	1
Mg	0.1	Zr*	1000

* = nitrous oxide-acetylene flame (air-acetylene used for all other detection limits)

Range	10^8 orders of magnitude: from 10^{-4} to 10^4 µg/mℓ, depending upon element and wavelength Absorbance: 0-2.000A Concentration: 0-0.009999
Interferences	Minimal for most analysis. Interference can be overcome by carefully selecting the proper flame conditions, using chemical interference suppressants in the sample, or optional Deuterium Background Corrector.
Multiparameter Capability	64 single-element lamps, 17 multi-element lamps
Sampling	Method: Batch or automatic Volume: Flame, 0.5-1.0 mℓ, flameless 10-20 µℓ or less up to 100 µℓ Capacity: Flame 500 samples/batch, flameless 30 samples/batch Pathlength: 100 mm with air/C_2H_2. 50 mm with N_2O/C_2H_2 Sample area: 22 cm W, 21 cm D
Performance	Electronics: Microprocessor Linearity: Stability: Scale Expansion: 0.01 to 100X Damping: 4 switch-selectable positions Detector: Photomultiplier with S-20 cathode Integration Times: 0.2-60, 0.1 sec intervals Readout: Digital Zero drift: Auto zero Background correction: Deuterium arc optional Monochromator: Littrow mount, 267 mm focal length Grating: 64 × 72 mm, 1800 lines/mm, dual blazed at 235 and 600 nm Dispersion: 1.6 nm/mm (nominal) Range: 180-870 nm Spectral bandpass: 0.2, 0.7, 2 nm (2 sets of slits) Accuracy: Scan speeds: Optional (5 nm/min.) Gas Control: Separate control box, containing individual controls and meters for oxidant and fuel pressure and flow. Pushbutton actuated remote flame ignition. N_2O safety interlock. Burner head safety interlock system, automatic switching to N_2O. Oxidant: Air or N_2O Fuel: C_2H_2 Venting: Recommended at 300 CFM Burner: Stainless steel lined with inert plastic, 10 cm single slot, N_2O burner head, three slot burner head, corrosion resistant nebulizer optional Adjustment: Vertical and horizontal with scale, angular without scale
Operation	Calibration: Automatic with standardized solutions, 3 standards may be used reslope available Maintenance: Minimal Training Required: A two day training course is offered free of charge for one operator
Requirements	Power: 105-125 or 200-240V, 50 or 60 Hz, 150 watts Weight: 70 kg net, 125 kg gross Dimensions: 41 cm H × 56 cm D × 88 cm W

Features

Microprocessor controlled electronics
Double beam optics - designed for flame or flameless AA
Premix burner chamber
Pushbutton flame ignition
Flame safety system including burner interlocks, gas pressure sensing, flame sensing, automated N_2O/C_2H_2 ignition and shut-off
Four-digit bipolar readout
Readout in absorbance, concentration, or emission intensity
Automatic curve fitting on blank and up to 3 standards
Auto zero
Peak reader
Averaging feature
Signal integration
Flame emission standard
Independent recorder modes
Auto gain control

Options

Graphite furnace system	See Perkin-Elmer C
A.A. microsampling system	750
Flameless Mercury analysis system	600
High sensitivity As/Se sampling system	500
AS-50 automated sampling system (flame AA)	2995
AS-3 Auto sampling system	3780
Deuterium Background Corrector	1500
Printer sequencer	1000/1500*
Typewriter readout assembly	2950
Recorder	695-1415
Wavelength drive assembly	550
Burner heads, 3 slot, 10 cm; single slot, 5 cm	310
AS-1 Auto sampling unit for graphite furnace	3695/4095*
Lamps Hollow cathode, 64 single element, 17 multi-element	See Perkin-Elmer A
Electrodeless discharge lamps	See Perkin-Elmer B
MHS-1, Mercury/Hydride System	3350
MHS-10 Mercury/Hydride System	995
AA Data System 1 (including a Hewlett Packard 9815A, programmable calculator	4500

References

Manufacturer's Specifications 11,700

Cost

Model 560

Address

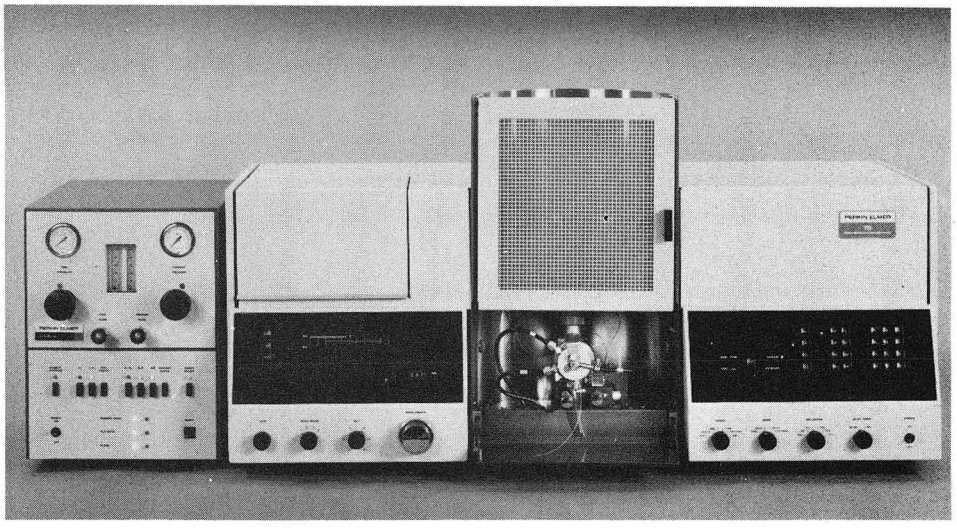
Perkin-Elmer Corporation
Instrument Division
Norwalk, CT 06856
(203) 762-1000

*Depends upon time of purchase.

INSTRUMENTATION
FOR ENVIRONMENTAL
MONITORING

Atomic Absorption/Emission Spectrophotometer

Perkin-Elmer, Model 703



Class Laboratory

Description Double beam, time shared, high resolution Atomic absorption spectrophotometer, with microcomputer

Modes of Operation Atomic absorption or flame emission

Lower Detectable Limit

Typical model 703 minimum detection limits

Element	MDL (µg/ℓ)	Element	DL (µg/ℓ)
Ag	2	Mn	2
Al*	20	Mo*	20
As (EDL)	100	Na	0.2
Au	10	Ni	2
B*	700	Pb (EDL)	11
Ba*	8	Rb (FE)	2
Be*	0.7	Sb (EDL)	40
Bi (EDL)	25	Se (EDL)	75
Ca	0.7	Si*	100
Cd (EDL)	0.7	Sn* (EDL)	99
Co	7	Sr	1
Cr	3	Te (EDL)	26
Cu	1	Ti*	40
Fe	6	Tl (EDL)	9
Hg	36	V*	40
K	<2	W*	1,000
Li	3	Zn	1
Mg	<0.1	Zr*	350

* = nitrous oxide-acetylene flame (air-acetylene used for all other detection limits)

Range

10^8 orders of magnitude: from 10^{-4} to 10^4 µg/ml, depending upon element and wavelength

Absorbance: 0-2.000A

Concentration: 0 - 0.009999

Interferences

Minimal for most analysis. Interference can be overcome by carefully selecting the proper flame conditions, using chemical interference suppressants in the sample, or optional Deuterium Background Corrector.

Multiparameter Capability

64 single-element lamps, 17 multi-element lamps

Sampling

Method: Batch or automated
Sample Area: 20 cm W ×15 cm D
Capacity: flame 500/batch; flameless-30/batch
Volume: flame 0.5-1.0 mℓ, flameless 10-20 µℓ or less up to 100 µℓ
Pathlength: 100 mm with air/C_2H_2, 50 mm with N_2O/C_2H_2.

Performance and Specifications

Electronics: Microprocessor
Linearity:
Stability: precision as good as 0.3%
Scale Expansion: 0.01 to 100X
Damping: 4 switch-selectable positions
Detector: Photomultiplier with S-20 cathode
Integration Times: 0.2 to 60 sec., <0.2 sec intervals
Zerodrift: autozero circuit
Readout: digital, analog (60-10 mV or 0.1 V), EIA RS-232 Interface (Optional)
Background correction: Optional deuterium correction

Monochromator: Czerny-Turner system, 400 mm focal length

Grating: UV, 64×64 mm, 2880 lines/mm, blazed at 210 nm
VIS, 64×64 mm, 1440 lines/mm, blazed at 580 nm
Dispersion (reciprocal Linear): UV, 0.65 nm/mm
VIS, 1.3 nm/mm
Range: 180 to 900 nm
Spectral Bandpass: UV, 0.03, 0.07, 0.2, 0.7, 2,0, 7.0 nm
VIS, 0.06, 0.14, 0.40, 1.4, 4.0, 14 nm
Scan Speeds: Optional, 0.2, 1.5 and 20 nm/min
Wavelength accuracy:

Gas Control: Separate control box, containing individual controls and meters for oxidant and fuel pressure and flow. Pushbutton actuated remote flame ignition. N_2O safety interlock. Flame and pressure sensing safety devices, burner head safety interlock system, automatic switching to N_2O.

Oxidant: Air or N_2O
Fuel: C_2H_2 or H_2
Venting: Recommended at 300 CFM
Burner: Stainless steel coated with inert plastic, 10 cm slot, all titanium head, N_2O burner head, 3 slot burner head, corrosion resistant nebulizer optional.
Adjustments: Vertical and horizontal with scale, angular without scale

Operation

Calibration: Automatic with up to 3 standardized solutions, reslope available, auto curve correction.
Maintenance: Minimal
Training Required: Free two-day training for one operator

Requirements

Power: 105-125 or 200-240 V, 50 or 60 Hz, 200 watts
Weight: 96 kg net, 145 kg gross
Dimensions: 62 cm H× 6 cm D ×120 cm W

Features

Microcomputer controlled electronics
Double beam optics, for flame and flameless sampling
Premix burner chamber
Pushbutton flame ignition
Flame safety system including burner interlocks, automated N_2O/C_2H_2 ignition and shut-off, gas pressure and flame sensing option
Four-digit bipolar readout
Readout in absorbance, concentration, or emission intensity
Automatic curve fitting on blank and 3 standards
Auto zero
Peak reader
Signal integration
Flame emission standard

Options

Graphite furnace	See Perkin-Elmer, C
AS-1 Automated flameless sampling system	$ 3695/4095*
A.A. microsampling system	750
Flameless Mercury analysis system	600
High sensitivity As/Se sampling system	500
As-50 automated sampling system	2995
AS-3 flamesampling system	3780
Deuterium Background Corrector	1500
Printer sequencer	1000/1500*
Typewriter readout assembly	2950
Recorder	695/1415
Wavelength drive assembly	
Gas controls: Pressure, flame sensing programmable	
Burner Heads	310
Intensitron ® Hollow Cathode Lamps	See Perkin-Elmer A
Electrodeless Discharge Lamps	See Perkin-Elmer B
MHS-1 Mercury Hydride System	3350
MHS-10 Mercury Hydride System	995

References

Manufacturer's Specifications
Perkin Elmer, Technique and Applications of Atomic Absorption, Order No. AA-322G, March, 1978

Cost

Model 703 $13,450

Address

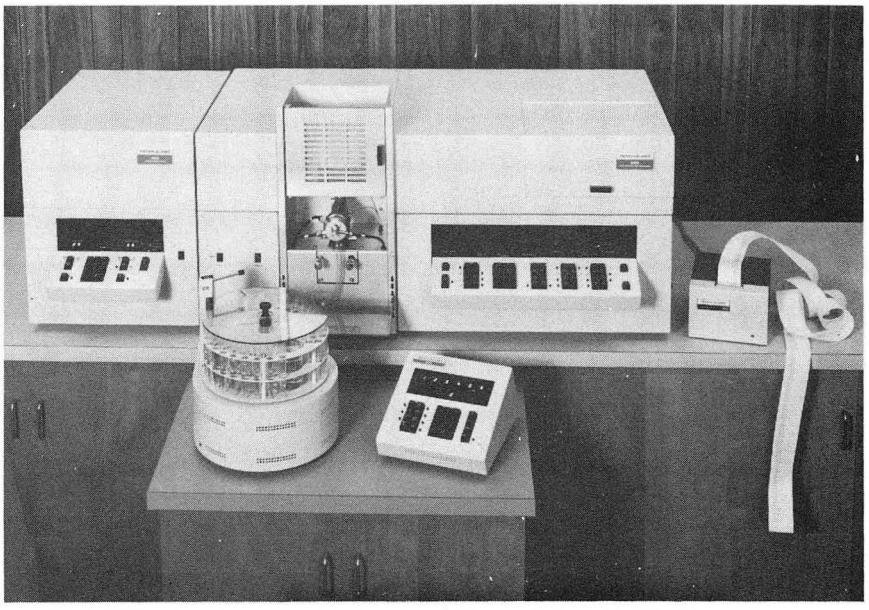
Perkin-Elmer Corporation
Instrument Division
Norwalk, CT 06856
(203) 762-1000

*Depends upon time of purchase

INSTRUMENTATION
FOR ENVIRONMENTAL
MONITORING

Atomic Absorption/Emission Spectrophotometer

Perkin Elmer Model 5000



Class	Laboratory
Description	Double beam, time and space shared microprocessor controlled atomic absorption spectrophotometer with digital readout, optional capacity for handling 6 elements automatically
Modes of Operation	Atomic absorption, flame emission
Lower Detectable Limits	As good or better than 703, especially with background correction
Range	Absorbance: 0-2.000A Concentration: 0-9999 with two points past decimal
Interferences	
Multiparameter Capacity	64 single element lamps, 17 multielement lamps. Up to 6 elements automatically but not simultaneously
Sampling	Method: Batch or automated Sample Area: 25 cm W - 18 cm deep Capacity: Flame-50/batch: flameless 30/batch Volume: Flame-5-10mℓ; flameless 10-20μℓ or less, up to 100μℓ Pathlength: 10 cm with air/C_2H_2; 5 cm with N_2O/C_2H_2
Performance and Specifications	Electronics: Microprocessor Linearity: Stability: Scale Expansion: Continuously variable 0.01x to 100x Damping: 0.3 to 10 secs Detector: Multialkali cathode with UV transmitting window (185-930 nm) Integration Times: 0.2 to 99 sec, less than 0.2 sec intervals average, or individual readings and average Zerodrift: Automatic Readout: Digital Background Correction: Deuterium arc and quartz halide sources for correction over the whole wavelength range (optional)

Performance and Specifications (continued)

Monochromator: Czerny-Turner, 408 mm focal length
Grating: Automatically controlled - UV - 2880 lines/mm, 84×84 mm blazed at 210 nm, VIS - 1440 lines/mm, 84×84 mm blazed at 580 nm
Dispersion (reciprocal linear): UV - 0.65 nm/mm
VIS - 1.3 nm/mm
Spectral Range: 190-900 nm
Grating changeover: 450 nm
Spectral Bandpass: UV - 0.03, 0.07, 0.2, 0.7 and 2.0 nm
VIS - 0.08, 0.14, 0.4, 1.4 and 4.0 nm
Scan Speeds: 0.25, 0.50, 1.0, 2.5, 5.0, 10, 25, 50 nm/min
Wavelength Accuracy:
Slit: 2 sets of 5 slits to give spectral bandpass as listed above

Gas Control: Individual control, pressure and flow, and metering for fuel and oxidants, safety interlock for N_2O. Push button switch over. Can be automatically sequenced (optional).
Oxidant: 2 oxidants
Fuel: 3 fuels
Venting: Recommended
Burner: Premix laminer flow, adjustable stainless steel, 10 cm, titanium, single slot burner
Adjustments: Vertical and horizontal scales, angular without scale

Computer: Dedicated microcomputer

Operation

Calibration: Automatic curve fitting with up to 3 standards, reslope available
Maintenance: Usual PE
Training Required: Training course comes with purchase and is highly recommended.

Requirements

Power: 105-125 or 200-240V, 50/60 Hz, 250 W (300 W with background correction)
Weight: 173 kg (380 lb)
Dimensions: 61 cm H ×75 cm D× 119 cm W

Features

Microcomputer controlled
Double beam optics
Premix burner chamber
Pushbutton flame ignition, safety interlock
Six digital bipolar readout
Readout in absorbance, emission and concentration
Autocalibration, reslope, curve correction
Auto zero
Peak reader
Signal integration

Options

PRS-10 Printer Sequencer	$ 1000/1500*
TR-2 Teletypewriter Readout	2950
Optional Communications Interface	600
Magnetic Card Reader	750
Background Correction	1850
Motorized 6-Lamp Turret	1100
AS-50 Autosampler (flame)	3200
Graphite Furnaces	See Perkin Elmer C
MHS-1 Mercury/Hydride System	3350
MHS-10 Mercury/Hydride System	995
Hollow Cathode Lamps	See Perkin Elmer A
Electrodeless Discharge Lamps	See Perkin Elmer B
AS-1 Auto Sampler (graphite furnaces)	3695/4095*
Electrodeless Discharge Lamps	
AA Microsampling System	750
Flameless Mercury System	600
Hydride Generation System As/Se	500

*Depends upon time of purchase

References	Manufacturer's Specifications and Price List	
Cost	Model 5000	$17,000
Address	Perkin Elmer Corporation Instrument Division Norwalk, CT (203) 762-1000	

INSTRUMENTATION
FOR ENVIRONMENTAL
MONITORING

Hollow Cathode Lamps

Perkin Elmer, Intensitron Hollow Cathode Lamps

Class — Accessory, Laboratory

Description — Single, Multi-Element Hollow Cathode Lamps

Multi-Element Capability

Elements marked (*) require a nitrous oxide-acetylene flame

303-6009	Al	Aluminum*	$150.00	303-6047	Ni	Nickel*	$145.00
303-6010	Sb	Antimony	170.00	303-6023	Nb	Niobium*	200.00
303-6011	As	Arsenic	220.00	303-6048	Os	Osmium*	500.00
303-6012	Ba	Barium*	150.00	303-6049	Pd	Palladium*	175.00
303-6013	Be	Beryllium*	220.00	303-6050	P	Phosphorus*	270.00
303-6014	Bi	Bismuth	170.00	303-6051	Pt	Platinum	175.00
303-6015	B	Boron*	150.00	303-6052	K	Potassium*	175.00
303-6016	Cd	Cadmium	170.00	303-6053	Pr	Praseodymium*	200.00
303-6017	Ca	Calcium	125.00	303-6056	Re	Rhenium*	200.00
303-6021	Cr	Chromium	125.00	303-6057	Rh	Rhodium	225.00
303-6022	Co	Cobalt	145.00	303-6059	Ru	Ruthenium	200.00
303-6024	Cu	Copper*	145.00	303-6060	Sm	Samarium*	200.00
303-6025	Dy	Dysprosium*	200.00	303-6061	Sc	Scandium*	250.00
303-6026	Er	Erbium*	200.00	303-6062	Se	Selenium	195.00
303-6027	Eu	Europium*	250.00	303-6063	Si	Silicon*	150.00
303-6028	Gd	Gadolinium*	200.00	303-6064	Ag	Silver	125.00
303-6029	Ga	Gallium	175.00	303-6065	Na	Sodium	175.00
303-6030	Ge	Germanium*	200.00	303-6066	Sr	Strontium	150.00
303-6031	Au	Gold	195.00	303-6068	Ta	Tantalum*	175.00
303-6032	Hf	Hafnium*	200.00	303-6069	Te	Tellurium	195.00
303-6033	Ho	Holmium*	200.00	303-6070	Tb	Terbium*	200.00
303-6034	In	Indium	150.00	303-6071	Tl	Thallium	150.00
303-6036	Ir	Iridium	300.00	303-6073	Tm	Thulium*	250.00
303-6037	Fe	Iron	125.00	303-6074	Sn	Tin	170.00
303-6038	La	Lanthanum*	200.00	303-6075	Ti	Titanium*	150.00
303-6039	Pb	Lead	170.00	303-6076	W	Tungsten*	150.00
303-6040	Li	Lithium	150.00	303-6077	U	Uranium*	250.00
303-6042	Mg	Magnesium	145.00	303-6078	V	Vanadium*	150.00
303-6043	Mn	Manganese	125.00	303-6079	Yb	Ytterbium*	200.00
303-6044	Hg	Mercury	150.00	303-6080	Y	Yttrium*	200.00
303-6045	Mo	Molybdenum	125.00	303-6081	Zn	Zinc	145.00
303-6046	Nd	Neodymium*	200.00	303-6082	Zr	Zirconium*	150.00

Multi-Element Intensitron Hollow Cathode Lamps

303-6092	Calcium-Magnesium (Ca-Mg)	$215.00	303-6102	Cobalt-Copper-Iron-Molybdenum (Co-Cu-Fe-Mn-Mo)	$315.00
303-6093	Calcium-Zinc (Ca-Zn)	215.00	303-6103	Chromium-Cobalt-Copper-Iron-Manganese-Nickel (Cr-Co-Cu-Fe-Mn-Ni)	345.00
303-6094	Chromium-Cobalt-Copper-Manganese-Nickel (Cr-Co-Cu-Mn-Ni)	315.00	303-6105	Copper-Iron-Manganese-Zinc (Cu-Fe-Mn-Zn)	295.00
303-6095	Sodium-Potassium (Na-K)	245.00	303-6106	Tellurium-Tin (Te-Sn)	265.00
303-6096	Chromium-Copper-Nickel-Silver (Cr-Cu-Ni-Ag)	295.00	303-6107	Aluminum-Copper-Iron-Titanium (Al-Cu-Fe-Ti)	275.00
303-6097	Calcium-Magnesium-Zinc (Ca-Mg-Zn)	265.00	303-6108	Silver-Chromium-Copper-Iron-Nickel (Ag-Cr-Cu-Fe-Ni)	315.00
303-6098	Ruthenium-Platinum (Ru-Pt)	295.00	303-6110	Aluminum-Calcium-Copper-Iron-Magnesium-Silicon-Zinc (Al-Ca-Cu-Fe-Mg-Si-Zn)	370.00
303-6099	Aluminum-Calcium-Magnesium (Al-Ca-Mg)	265.00	303-6112	Silver-Aluminum-Chromium-Copper-Iron-Magnesium (Ag-Al-Cr-Cu-Fe-Mg)	345.00
303-6101	Copper-Iron-Nickel (Cu-Fe-Ni)	265.00			

Warranty	Spectrum: 2 years from shipment date Intensity and Absorbance: Exceed or meet "specifications to which all new lamps are tested for a period of six(6) months from date of shipment".
Manufacturer	Perkin Elmer
References	Manufacturer's Specifications
Cost	Listed above under Multiparameter Capability *
Address	Perkin Elmer Corporation Instrument Division Norwalk, CT 06856 (203) 762-1000

*A 10% discount is applicable toward the simultaneous purchase of 7 or more lamps and a 20% discount is applicable toward the simultaneous purchase of 12 or more lamps (Intensitron Hollow Cathode lamps or Electrodeless Discharge lamps)

Electrodeless Discharge Lamps

Class: Accessory, Laboratory

Electrodeless Discharge Lamp, for use with Perkin-Elmer Atomic Absorption Spectrophotometers, exchangeable with Hollow Cathode Lamps but requires an accessory power supply

Multi-element Capability

303-6210 Antimony E.D.L.	All $250.00
303-6211 Arsenic E.D.L.	
303-6214 Bismuth E.D.L.	
303-6216 Cadmium E.D.L.	
303-6220 Cesium E.D.L.**	
303-6230 Germanium E.D.L.*	
303-6239 Lead E.D.L.	
303-6244 Mercury E.D.L.	
303-6250 Phosphorus E.D.L.*	
303-6252 Potassium E.D.L.	
303-6258 Rubidium E.D.L.**	
303-6262 Selenium E.D.L.	
303-6269 Tellurium E.D.L.	
303-6271 Thallium E.D.L.	
303-6274 Tin E.D.L.	
303-6275 Titanium E.D.L.	
303-6281 Zinc E.D.L.	

*Requires a nitrous oxide/acetylene flame.
**Cannot be used with the Models 103 or 107.

Warranty: Spectrum: Two (2) years from date of shipment
Intensity and Absorbance: "Will meet or exceed the intensity and absorption specifications to which all new lamps are tested for a period of six (6) months from the date of shipment."

Manufacturer

References: Manufacturer's Specifications

Cost: Price quoted in list under Multiparameter Capability
Discount same as for Hollow Cathode Lamps
EDL Power Supply $1000/1500*
Dual EDL Power Supply 2000/1500*

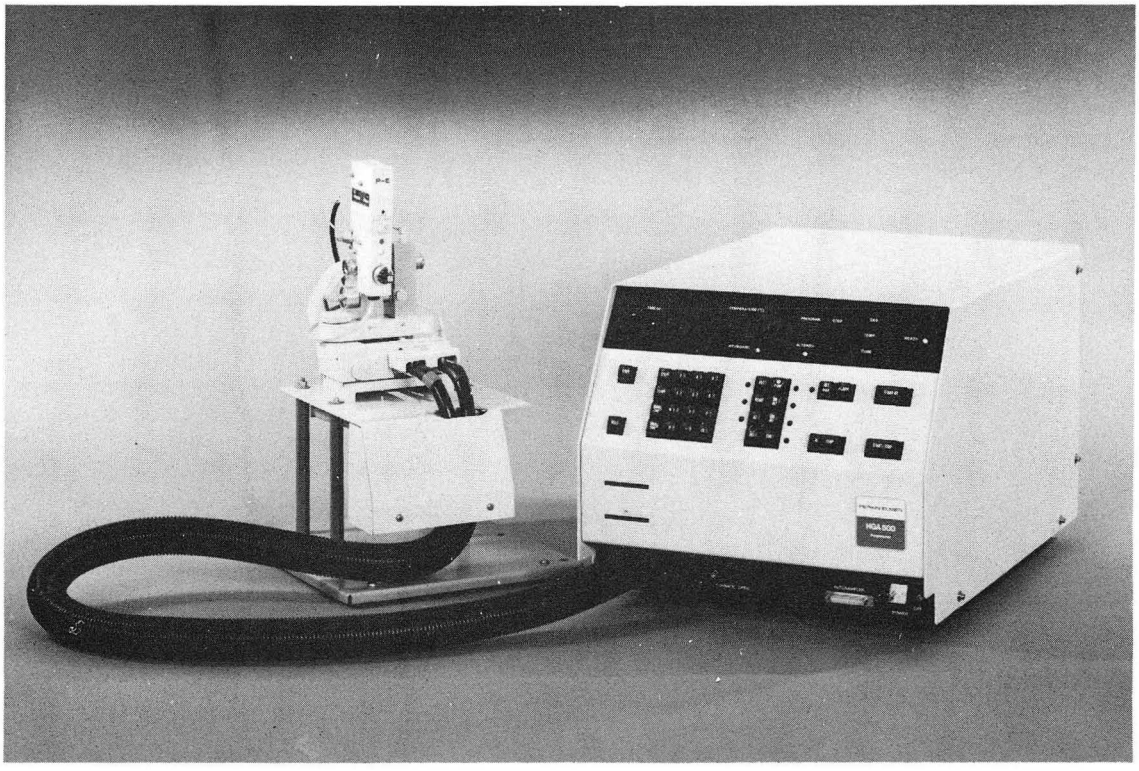
Address:
Perkin-Elmer Corporation
Instrument Division
Norwalk, CT 06852
(203) 762-1000

*Depends upon time of purchase

INSTRUMENTATION
FOR ENVIRONMENTAL
MONITORING

Accessory, Graphite Furnace

Perkin-Elmer Model HGA-500,2200



Class

Accessory, Laboratory

Description

500-microprocessor controlled, Programmable Graphite Furnace, with up to nine steps - 6 analytical programs

2200 - Programmable Graphite Furnace - up to 7 steps (with optional ramp accessory)

Lower Detectable Limit

HGA Minimum Detectable Limits

Element	Absolute ($g \times 10^{-12}$)	Relative 100µℓ sample	Element	Absolute ($g \times 10^{-12}$)	Relative 100 µℓ sample
Ag	0.5	0.005	Li	30	0.3
Al	2	0.02	Mn	1	0.01
As	20	0.2	Mo	7	0.07
Au	10	0.1	Ni	20	0.2
Ba	10	0.1	Pb	5	0.05
Be	3	0.03	Sb	15	0.15
Bi	10	0.1	Se	50	0.5
Cd	0.3	0.003	Si	20	0.2
Co	10	0.1	Sn	30	0.3
Cr	1	0.01	Te	10	0.1
Cu	2	0.02	Ti	50	0.5
Fe	2	0.02	V	20	0.2
In	30	0.3	Zn	0.1	0.001

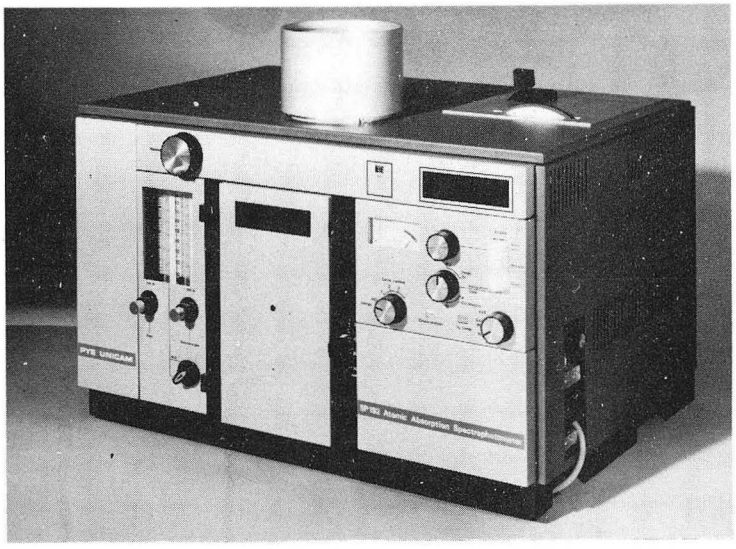
Range	From 10^{-15} grams, depending on element and wavelength
Interferences	Occasional problems from the formation of carbon compounds, from selective volatilization, and from background absorption. Matrix interferences can often be overcome by the method of additions. Use of a background correction system is highly recommended
Sampling	Method: Liquid or solid Volume: From <1 to 100 µℓ
Performance	Accuracy: Dependent upon accuracy of standards Max. Temperature Dry, Ash, Atomize } up to 3000°C in each cycle Programs: Continuously adjustable HGA-500: Nine program steps with selection: - Ramp and hold times (up to 999S) - Temperature (up to 3000°C) - Internal gas flow (0-300 mℓ/min.) - Atomization speed HGA-2200: Three program steps (seven with optional ramp accessory), selection of - Timers: Dry - 0-120 sec. Ash - 0-1200 sec. Atomize - 0-30 sec. - Internal gas flow - Atomization speed
Requirements	Power: 210 - 240V, 15 Amps, 50-60 Hz Weight: HGA-500 programmer - 58 kg HGA-2200 programmer - 41 kg Furnace - 4 kg Dimensions: HGA-500 programmer: 39 cm W × 325 cm H × 57 cm D HGA-2200 programmer: 36 cm W × 41 cm H × 56 cm D Furnace: 12 cm × 17 cm × 12 cm Cooling Water: 1.5 liters/min Inert Gas: Argon or nitrogen, 45 psi (3 kg/cm^2)
Options	AS-1 Auto sampler $4,095/3,695* Pyro coated tubes - package of 50 400 HGA-500: Magnetic card reader for program storage 850 HGA-2200: Ramp accessory 1200/600*
References	Manufacturer's Specifications
Cost	HGA-500 $6,995 HGA-2200 4,500
Address	Perkin-Elmer Corporation Instrument Division Norwalk, CT 06856 (203) 762-1000

*Depends upon time of purchase

INSTRUMENTATION
FOR ENVIRONMENTAL
MONITORING

Atomic Absorption/Emission Spectrophotometers

Pye Unicam SP191/192



Class

Laboratory

Description

Single beam atomic absorption spectrophotometers

Modes of Operation

Atomic absorption, flame emission and concentration

Lower Detectable Limit (examples)

Element	Sensitivity (µg/ℓ)	Detection Limit (µg/ℓ)
Aluminum	500	40
Calcium	20	2
Chromium	40	4
Copper	30	3
Iron	50	7
Magnesium	3	0.5
Potassium	15	3
Selenium	300	100
Zinc	9	1

Range and Sensitivity

% to ppb, photometric range -0.05 to 1.999A

Interferences

Multiparameter Capability

Sampling

Method: Batch or automatic (optional)
Capacity: 50 per batch/250 per hour - auto
Volume: 3.5 - 4.5 mℓ/min, min. size < 0.5 ml
Sample area:

Performance and Specifications

Electronics: Solid state on circuit boards with built-in monitoring points.

Linearity: 2A with curvature correction included
Stability: Good
Scale Expansion: 0.1x - 25x continuously variable
Damping: Not used, generally quiet
Detection: Photomultiplier, S5 spectral response
Integration: 4,10 sec
Zero drift: Auto zero
Readout: Digital display, linear in absorbance and emission, concentration readout, analog and digital electrical output
Background: Included on 192 (corrects within 1% up to 1.5A background) by using closely matched amplifier and time constant; high chopping frequency
HCL exactly match

Monochromator: Ebert mount, 250 mm focal length, aperture is f/8

Grating: 1200 lines/mm, blazed at 250 nm
Dispersion: 3.3 nm/mm slitwidth
Range: 190-770 nm (or optional red detector for Rb, Cs)
Spectral bandpass: Fixed slits giving 0.2, 0.4, 0.8, 1.6 and 4.0 nm bandwidths
Wavelength Accuracy: Not available ca 0.5 nm
Scan speeds: Not available

Gas Control: Inert nebulizer, platinum/iridium capillary, PTFE and Penton coated pre-mix chamber; integral gas controls, flow meters
Oxidant: N_2O, air
Fuel: C_2H_2, H_2
Venting: Chimney available
Burner: All titanium head (optional) or stainless steel
Adjustments: 3 dimensional

Operation

Calibration: By standards
Maintenance: Contracts available
Training required/available: Yes

Requirements

Power: 110VAC/60 Hz or 240V/50Hz, ±10% power supply fluctuations
Dimensions: 68×49×41 cm (without chimney which is 25 cm)
Weight: 55 kg

Features

Single beam operation
Four lamp magazine
Large sample compartment
Digital display
Concentration readout

Options

Digital Printer
Recorder
Mercury cold vapour kit
Auto sample changer
Graphite furnace

References

Manufacturer's Specifications

Cost

Model 191	$ 7500
192	8650

Address

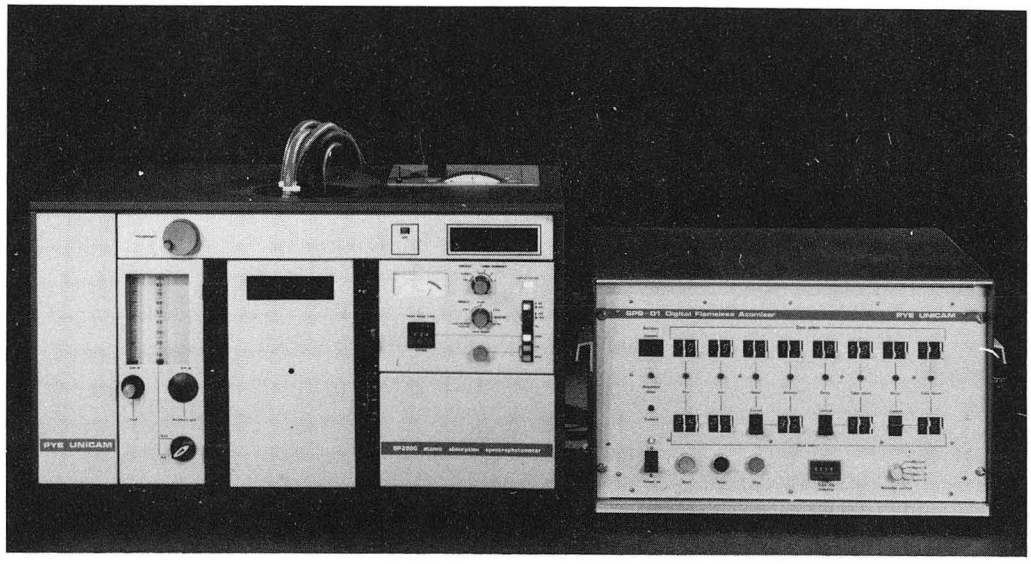
Pye Unicam Division
Philips Electronics Instruments
85 McKee Dr.
Mahwah, NJ 07340
Attn: Mr. Frank Hamm
(201) 529-3800

INSTRUMENTATION
FOR ENVIRONMENTAL
MONITORING

H20-MET
NOTES, AAS
Pye Unicam 2
August, 1978

Atomic Absorption/Emission Spectrophotometer

Pye Unicam SP 2900



Class	Laboratory
Deseription	Double beam atomic absorption spectrophotometer
Modes of Operation	Atomic absorption, flame emission and concentration

Lower Detectable Limit (examples)

Element	Sensitivity µg/ℓ	Detection Limit µg/ℓ	Precision %
Aluminum	300	24	0.15
Arsenic*	170	50	0.25
Barium	230	20	0.30
Bismuth	200	24	0.35
Cadmium	10	2	0.25
Calcium	10	2	0.15
Chromium	40	5	0.20
Cobalt	70	20	0.30
Copper	29	3	0.30
Gold	90	21	0.15
Iron	49	10	0.20
Lead	70	10	0.30
Magnesium	3	0.5	0.25
Manganese	20	3	0.25
Molybdenum	250	40	0.25
Nickel	45	8	0.20
Potassium	15	4	0.20
Silicon	1,100	230	0.35
Silver	30	2.4	0.15
Sodium	7	0.6	0.15
Tin	400	30	0.20
Titanium	1,200	100	0.20
Zinc	9	1.4	0.25

*Measurements made using an Arsenic E.D.L.

Range and Sensitivity	-0.05 - 1.999A
Interferences	
Multiparameter Capability	
Sampling	Method: Batch or optional auto Capacity: In auto mode up to 250/hr. Volume: 3.0 - 4.0 mℓ/min. Minimum required for measurement - 0.5mℓ.
Performance and Specifications	Electronics: Linearity: Curvature correction included Stability: Scale expansion: 0.1x - ~50x continuously variable Damping: Not as time constant Detector: Photomultiplier with S5 response Integration: 4, 10 sec peak area Zero drift: Auto zero circuit Readout: Digital in absorbance, concentration or energy, analog or digital available Background: Deuterium arc (optional) Monochromator: Ebert mount Grating: 1200 lines/mm, f/8 aperture, blazed at 250 nm Dispersion: 3.3 nm/mm slit width, limitng resolution, 0.2 nm Range: 190 - 675 nm, to 852 with red sensitive accessory Slits: 0.2, 0.4, 0.8, 1.6 and 4.0 nm bandwidth Wavelength accuracy: Scan speeds: Not available Gas Control: Integral gas control system, piezo-electric ignition, Penton coated pre-mix spray chamber Oxidant: Air, N_2O Fuel: C_2H_2, H_2 Venting: Recommended Burner: 10 cm slot, stainless steel (titanium optional) Adjustments: Height, angular (with scale) and lateral positions adjustable
Operation	Calibration: By standard solution Maintenance: Little required, maintenance contracts available Training required/available instruction manual supplied
Requirements	Power: 200 VAC (±10% power supply fluctuations), 50/60 Hz Dimensions: Same as 191/192 Weight:
Features	Double beam operation Compact size All mirror optics Digital readout, digital, analog output available Auto zero Peak height, area measurement 0-99.9 seconds 0.1 sec steps 4 lamp turret Concentration calculator
Options	Hollow Cathode Lamps — See Pye Unicam A Electrodeless Discharge Lamps — See Pye Unicam B Deuterium arc corrector — $ 475 190-855 nm photomultiplier Auto sample changer Digital printer Recorder Digital flameless atomizer — $ 4975 See Pye Unicam C Mercury cold vapour analyser kit Hydride kit — 275

References	Manufacturer's Specifications	
Cost	Model 2900	$9475
	2900 with background corr.	9950
Address	Pye Unicam Instruments Philips Electronics Instruments 85 McKee Dr. Mahwah, NJ 07430 Attn: Frank Hamm (201) 529-3800	

Hollow Cathode Lamps
Pye Unicam

Class

Accessory

Description

Hollow Cathode Lamps for use with Pye Unicam Spectrophotometers

Multiparameter Capability

DESCRIPTION	LIST PRICE	DESCRIPTION	LIST PRICE
Aluminum	$130	Neodymium	$180
Antimony	130	Nickel	105
Arsenic	170	Niobium	180
Barium	130	Osmium	300
Beryllium	180	Palladium	155
Bismuth	140	Platinum	155
Boron	130	Potassium	155
Cadmium	130	Praseodymium	180
Calcium	105	Rhenium	180
Caesium	180	Rhodium	180
Cerium	160	Rubidium	180
Chromium	105	Ruthenium	180
Cobalt	105	Samarium	180
Copper	105	Scandium	230
Dysprosium	180	Selenium	155
Erbium	180	Silicon	150
Europium	230	Silver	105
Gadolinium	180	Sodium	155
Gallium	155	Strontium	130
Germanium	180	Tantalum	155
Gold	155	Tellurium	175
Hafnium	180	Terbium	180
Holmium	180	Thallium	130
Indium	130	Thorium	230
Iridium	180	Thulium	130
Iron	105	Tin	130
Lanthanum	180	Titanium	130
Lead	130	Tungsten	130
Lithium	130	Uranium	230
Lutetium	220	Vanadium	130
Magnesium	105	Ytterbium	180
Manganese	105	Yttrium	180
Mercury	130	Zinc	105
Molybdenum	105	Zirconium	130
		Deuterium	175

Manufacturer

Cathodeon Div., Philips Electronics Instruments

Warranty

500 hours normal running or 6 months, whichever is shorter

References

Manufacturer's Specifications

Cost

Listed above under Multiparameter Capability

Address

Pye Unicam Division
Philips Electronic Instruments
85 McKee Dr.
Mahwah, N.J. 07430
(201) 529-3800

Electrodeless Discharge Lamps

Pye Unicam

Class

Accessory

Description

Electrodeless Discharge Lamps for use with Pye Unicam Spectrophotometers

Multiparameter Capability

Element	Price	Element	Price
Arsenic	$250	Selenium	$250
Antimony	250	Tellurium	250
Cadmium	250	Tin	250
Lead	250		

Special Order	Price		
Bismuth	$250	Thallium	$250
Mercury	250	Zinc	250
Phosphorus	325		

Manufacturer

Westinghouse

Warranty

References

Manufacturer's Specifications

Cost

Listed above under Multiparameter Capability

Address

Pye Unicam Division
Philips Electronic Instruments
85 McKee Dr.
Mahwah, N.J., 07430
(201) 529-3800

INSTRUMENTATION
FOR ENVIRONMENTAL
MONITORING

Graphic Furnace Atomizer

Pye Unicam SP9-01, Digital Flameless Atomizer

Class: Accessory

Description: Graphite furnace for use in atomic absorption spectrometry

Lower Detectable Limits

Sensitivities (1% absorption)

Element	Absolute (pg, g×10^{-12})	Relative µg/ℓ	
		50µℓ Sample	10µℓ Sample[a]
Al	26	0.52	2.6
As	85	1.7	8.5
Sb	28	0.56	2.8
Bi	37	0.74	3.7
Cd	1	0.02	0.1
Ca	13	0.26	1.3
Ci	13	0.26	1.3
Co	35	0.70	3.5
Cu	27.5	0.55	2.75
Au	10.3	0.21	1.05
Fe	20	0.40	2.0
Pb	9	0.18	0.9
Mn	4	0.08	0.4
Mo	33*[b]	0.66	3.3
Ni	84	1.7	8.5
Pt	320	6.4	32
Rb	15	0.30	1.5
Se	44	0.88	4.4
Si	270*[b]	5.4	27.0
Ag	3.5	0.07	0.35
Sn	38	0.76	3.8
Ti	660	13.2	66
V	118*[b]	2.4	12.0

a. a 10µℓ sample in the standard volume which has been used in these notes to allow comparison with other instruments.
b. Pyrolytically coated tubes may be needed to obtain these performance figures.

Range: ppb-%

Sampling:
Method: Batch or automated
Volume: 0-50 µℓ
Capacity:
Temperature Controls:

1.	Dry	0.99 sec	0-3000°C
2.	Ash	0.99 sec	0-3000°C
	Delay 1	0-99 sec	—
3.	Atomize	0-9.9 sec	0-3000°C
	Delay 2	0-99 sec	—
4.	Tube Clean	0-9.9 sec	0-3000°C
	Delay 3	0-99 sec	—
5.	Tube Blank	0-9.9 sec	0.3000°C

Performance:
Electronics:
Temperature Control:
Programming: Digital, 5 stages available, 3 delays
Reproducibility
Max. Temperature: 5 stages up to 3000°C
Temperature Control: automatic with manual override
Timers: Up to 99 sec on stages 1,2, 9.9 sec on stages 3,4,5.
Temperature Readout: in °C

Operation:
Calibration: Standards
Training:
Unattended Period:
Maintenance: Contracts available

Requirements:
Power: 220/240V, single phase 50/60 Hz
Weight: 53 kg
Dimensions: 56 cm × 32 cm × 51 cm (w×h×d)

Cooling Water: 0.5 ℓ/min, 0.7-8.4 kg/cm^2
Inert Gas: Argon or nitrogen, 3.0 ℓ/min

Features:
Profile Tube
Digital Operation

References: Manufacturer's Bulletin

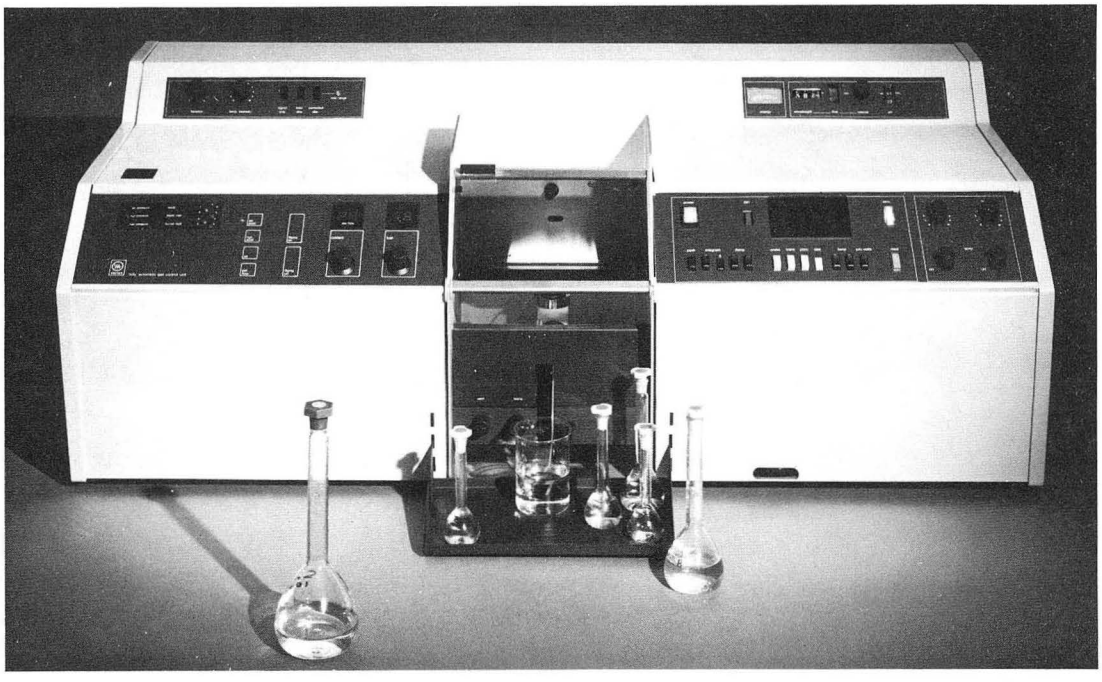
Cost: SP9-01 $ 4995

Address:
Pye Unicam Division
Philips Electronic Instruments
85 McKee Dr.
Mahwah, N.J. 07430
(201) 529-3800

INSTRUMENTATION
FOR ENVIRONMENTAL
MONITORING

Atomic Absorption/Emission Spectrophotometer

Varian Model AA-175



Class	Laboratory
Description	Single beam atomic absorption spectrophotometer with digital readout
Modes of Operation	Atomic Absorption, flame emission

Lower Detectable Limit

AA-175 Sensitivities and Detection Limits

Element	Sensitivity µg/ℓ	Detection limit µg/ℓ	Element	Sensitivity µg/ℓ	Detection limit µg/ℓ
Ag	0.03	2	Hg*	2.5	200
Al*	0.75	20	Ho	0.7	30
As	0.6	200	In	0.2	400
Au	0.1	9	K	0.01	5
B	9.	2,000	La	50.	3,000
Ba	0.2	20	Li	0.02	2
Be	0.02	1	Lu	8.	400
Bi	0.2	50	Mg	0.003	2
Ca	0.015	2	Mn	0.02	3
Cd	0.01	1	Mo	0.3	40
Co	0.05	9	Na	0.003	3
Cr	0.05	5	Nb	20.	3,000
Cs	0.04	6	Nd	6.	2,000
Cu	0.04	2	Ni	0.05	8
Dy	0.7	40	Os	1.5	200
Er	0.5	30	Pb	0.11	15
Eu	0.4	20	Pd	0.1	20
Fe	0.05	6	Pr	20.	9,000
Ga	0.7	50	Pt	1.5	90
Gd	20.	1,000	Rb	0.03	2
Ge	1.5	100	Re	10.	900
Hf	10.	2,000	Rh	0.15	6

AA-175 Sensitivities and Detection Limits (contd.)

Element	Sensitivity µg/ℓ	Detection limit µg/ℓ	Element	Sensitivity µg/ℓ	Detection limit µg/ℓ
Ru	800	90	Ti	1,500	60
Sb	300	30	Tl	300	20
Se*	300	200	Tm	300	26
Si	1,500	200	U	120,000	60,000
Sm	6,500	900	V	750	50
Sn	400	30	W	6,000	500
Sr	40	2	Y	2,500	100
Ta	11,000	2,000	Yb	075	2
Tb	8,000	500	Zn	10	1
Te	300	40	Zr	10,000	1,000

NOTE: The reported values for these elements were measured using recommended flame conditions.

*These elements are best determined using the Model 64 Vapor Generation Kit. Sensitivities are: As, 0.0001; Se, 0.0002 and Hg, 0.0001 µg/ml/EDL sources were used for As and Se.

Sensitivity and Range

Range: ppb to %
Sensitivity and detection limits: (see page 1)

Sampling

Method: Batch or automatic
Capacity: 50 samples with changer; 4 sample/min
Volume: At least 100µℓ per sample

Performance and Specifications

Electronics:

Overall system stability: ±0.5% of transmission for ±10% mains voltage variation
Readout linearity: ±0.1% of full scale deflection
Readout noise: <0.5%T
Scale expansion: 0.3 to 50x
Auto zero: 0.000 Å± 0.002 Å
Detector: R446 photomultiplier
Damping: 03 or 1.5 seconds

Monochromator: 254 mm (Czerny-Turner mount)

Grating: 32×27 mm, 1200 lines per mm
Wavelength range: 185-900 nm
Wavelength accuracy: ±0.2 nm
Wavelength reproducibility: ±0.1 nm
Reciprocal linear dispersion: 2.7 nm/mm
Slit system: Step variable corresponding to 0.2, 0.5, 1.0nm spectral band width (6 nm height) plus 1 extra slit for carbon rod analysis (0.5 nm spectral band width, 3 mm height).

Gas Control: Premix chamber separate fuel oxidant flow meters, two way valve for oxidant selection, electric ignition, safety interlock.

Fuel: C_2H_2, H_2
Oxidant: N_2O, air
Vent: exhaust recommended
Burner: Titanium, single slot (Hi-solids burners)
Adjustment: 3 dimension, scale on angular adjustment

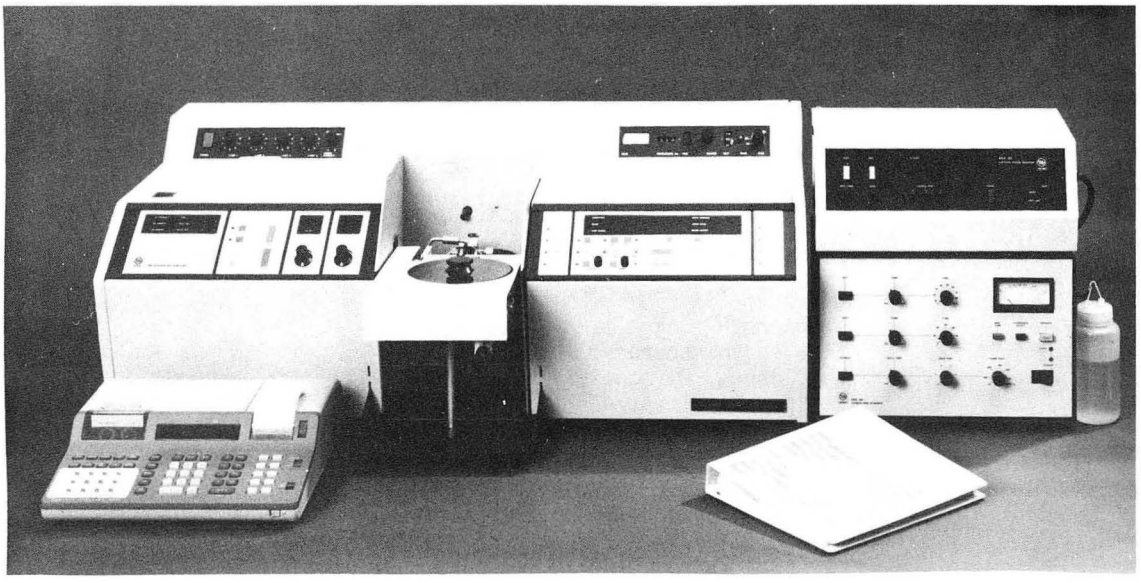
Requirements	Power: 110/115/220/240 volts AC; 50-60 Hz Size: (106 cm × 39 cm × 55 cm) 41 1/2" × 15 1/2" × 31 1/2" Weight: (80 kg) 176 lb shipping weight	
Features	Digital four-figure display for results in absorbance, transmission, or concentration Auto gas control system Simultaneous background correction All-reflective quartz coated optical system Four lamp turret Auto zero Electronic calibration system Peak signal detector Electronic integration Energy indicator High solids burner	
Options	Automatic gas control system	$1800
	Simultaneous background correction	1400
	Automatic sample changer, Model 51	1375
	Carbon rod atomizer, Model CRA-90	See Varian C
	Automatic sample dispenser for CRA-90, Model ASD-53	3400
	Digital printer, Model DP-37	1500
	Programmable Calculator, Model 9815A	4500
	Chart recorder, Model 9176	1095
	Hollow cathode lamps	See Varian A
	Electrodeless discharge lamps	See Varian B
References	Manufacturer's Specifications	
Cost	Model AA-175	$6800-9900
Address	Varian Instrument Division 611 Hansen Way, D-425 Palo Alto, CA 94303 (415) 493-4000 X3201	

INSTRUMENTATION
FOR ENVIRONMENTAL
MONITORING

H20-MET
NOTES, AAS
Varian 2
August 1978

Atomic Absorption/Emission Spectrophotometry

Varian Techtron Model AA-375



Class

Laboratory

Description

Double beam atomic absorption spectrophotometer with digital signal processor and readout.

Modes of Operation

Atomic absorption, flame emission

Lower Detectable Limit

Typical AA-375 Performance (Flame Atomization)

Element (a)	Sensitivity µg/ℓ	Detection Limit µg/ℓ, ppb
As(e)	550	200(b)
Ag	29	3
Ba (n)	280	15
Bi	280	80
Ca (n)	12	1
Cd	15	0.6
Cr	70	6
Co	60	10
Cu	40	2
Fe	50	8
Mo (n)	28	20
Ni	60	6
Pb	130	20
Rh	150	6
Sn (h)	950	90
Zn	9	0.8

(a) Analysed in air-acetylene, unless otherwise indicated.
(b) Using background corrector.
(e) With an EDL
(h) Air-hydrogen flame, using 235.5 nm
(n) Nitrous oxide-acetylene flame.

Range

ppb to %

Sampling

Method: Batch or automatic
Capacity: 50 samples with changer, 4 samples/min
Volume: At least 100 µℓ per sample

Performance and Specifications

Electronics:

Overall system stability: Better than ±0.5% of transmission for ±10% mains voltage variation
Readout linearity: ±0.1% of full scale deflection
Scale expansion: 00.00 to 99.99
Auto zero: 0.000 A
Abs. range: to 2.000
Concentration display: 0.0000 to 9999
Integrate: to 99 secs.
Detector: R446 photomultiplier

Monochromator: 254mm (Czerny-Turner mount)

Grating: 32×27 mm, 1200 lines/mm
Wavelength range: 185-900 nm
Wavelength accuracy: ±0.2 nm
Wavelength reproducibility: ±0.1 nm
Reciprocal linear dispersion: 2.7 nm/mm
Slit system: Step variable corresponding to 0.2, 0.5, 1.0 nm spectral band width (6 mm height) plus 1 extra slit for carbon rod analysis (0.5 nm spectral bandwidth, 2 mm height).

Gas Control

Oxidant: N_2O, air
Fuel: C_2H_2, H_2
Vent: Recommended
Burner: All titanium, single slot
Adjustments: Three dimensional scale on angular adjust.

Requirements

Power: 110/115/220/240 volts AC; 50-60 Hz
Size: 106 cm × 39 cm ×55 cm (41 1/2" ×15 1/2" × 21 1/2")
Weight: 90 kg (208 lb) shipping weight

Features

Digital display for results in absorbance, concentration or emission
Double-beam optical system with all-reflective quartz-coated surfaces
Double or single beam operation
Automatic gas control system
Simultaneous background correction (double or single beam)
Four-lamp turret
Touchbutton keyboard input
Digital calibration, integration
Peak area and peak height retrieval for the same peak, peak signal detector
Automatic calculation of the mean value of a series of readings
Auto zero
Wavelength scanning
Energy indicator

Options

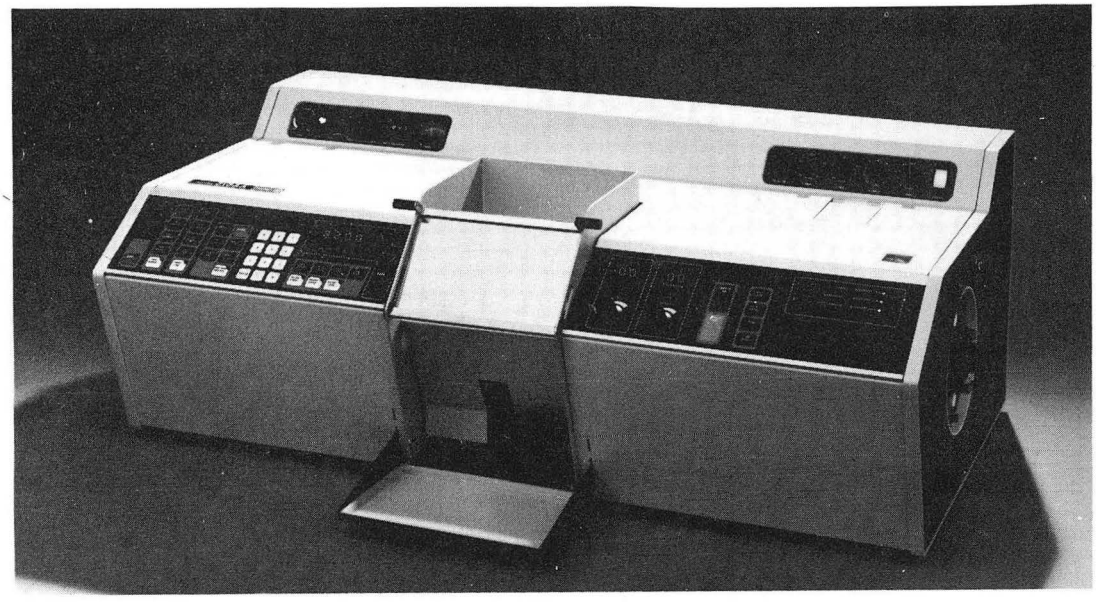
Automatic gas control system	$1800
Simultaneous background correction	1300
Four lamp quadrant	700
Automatic sample changer, Model 51	1375
Carbon rod atomizer, Model CRA-90	4500, See Varian C
Automatic sample dispenser for CRA-90, Model ASD-53	3400
Digital printer, Model DP37	1500
Programmable calculator, Model 9815A	4500
Chart recorder, Model 9176	1095
Hollow Cathode Lamps	See Varian A
Electrodeless Discharge Lamps	See Varian B

References	Manufacturers specifications
Cost	Model AA-375 $8600-12,400
Address	Varian Instrument Division 611 Hansen Way, D-425 Palo Alto, CA 94303 (415) 943-4000, X3201

INSTRUMENTATION
FOR ENVIRONMENTAL
MONITORING

Atomic Absorption/Emission Spectrophotometer

Varian Model AA-575



Class	Laboratory
Description	Microprocessor controlled, double-beam atomic absorption spectrophotometer with digital readout
Modes of Operation	Atomic absorption/flame emission
Lower Detectable Limits	Same as Varian 2 (AA-375)
Range	ppb - % Absorbance: 0-2.1A Concentration: 0-9999
Interferences	Depends upon element, scattering, non atomic absorption
Multiparameter Capability	About 67 elements, sequentially
Sampling	Method: Batch or automated (optional) Volume: At least 100 µl per sample Capacity: 50 samples with changer
Performance	Electronics Linearity: Stability: Scale Expansion: 0.1 to 100x Integration Times: 0.1 to 100 sec Detector: R-446 photomultiplier Zero Drift: Auto zero Readout: Analog, digital, optional parallel BCD and bit-parallel byte-serial Background: Optional, D_2 Monochromator: Czerny-Turner, 254 mm focal length, time-shared Grating: 1200 lines/mm, blazed at 250 mm Range: 185-900 nm Accuracy: ± 0.2 nm

Performance (continued)	Dispersion: 2.7nm/mm Spectral Bandwidth: 0.2, 0.5, 1.0 nm - separate slit for use with CRA-90 Scan Speeds: 6nm/min Resolution: To 0.20nm Gas Control: Manual, automatic optional; safety-interlock for N_2O, gas pressures and flows, liquid trap. Oxidant: Air, nitrous oxide Fuel: Acetylene Vent: Recommended Burner: Same as 775 Adjustments: 3 dimensional, scales on vertical and angular adjustment
Operation	Calibration: Standard solutions, computer handles a zero and three standards, calculates curve Training: Available on request Unattended period Maintenance: Minimal
Requirements	Power: 110/115, 220/240 VAC, 50/50 Hz Weight: 69 kg (152 lb) Dimensions: 106 cm long × 39 cm high × 55 cm deep (41" × 15-1/2" × 21-1/2")
Features	Digital Real time and result processing with an inlet 8-bit microprocessor with 8 k memory

Options

Automatic Sample Changer AS-51	$1375
Carbon Rod Atomizer CRA-90	See Varian C
Automatic Sample Dispenser ASD-53	3400
Hg, As, Se Kit - Model 64	575
DP-37	1500
Programmable Calculator HP9815A	4500
Data Interface kit AA	300
Nebulizers - fixed	175
- variable	285
Background Correction	1300
Automatic Gas Control	1800
Four Lamp Turret	700
Strip Chart Recorder	1095
Hollow Cathode Lamps	See Varian A
Electrodeless Discharge Lamps	See Varian B

References

(1) Manufacturer's Bulletin AA-575, 9/77
(2) Manufacturers Price List
(3) Manufacturer's Representative

Cost: AA-575 — $12,000

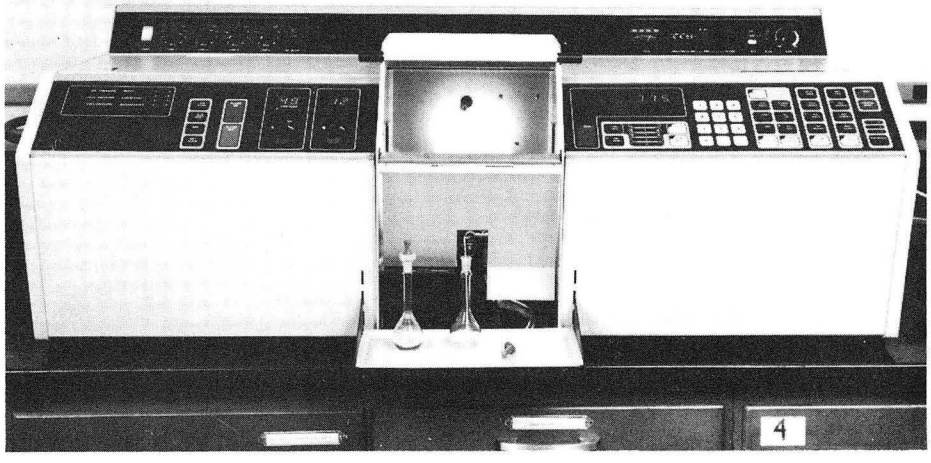
Address

Varian Instrument Division
611 Hansen Way
Palo Alto, CA 94303
(415) 493-8100

INSTRUMENTATION
FOR ENVIRONMENTAL
MONITORING

Atomic Absorption/Emission Spectrophotometer

Varian, Model AA-775 ABQ



Class	Laboratory
Description	Microprocessor controlled, double beam atomic absorption spectrophotometer
Modes of Operation	Atomic Absorption/Flame Emission
Lower Detectable Limits	Same as Varian 2 (AA-375)
Range	Absorbance: 0-2.1 A Concentration: 0-9999 concentration units
Interferences	Depends upon element, scattering, non-atomic absorption
Multiparameter Capability	About 67 elements, sequentially
Sampling	Method: Batch or automated Volume: At least 100μℓ per sample Capacity: 50 samples with charger
Performance	Electronics Linearity: Stability: Scale expansion: 0.001 to 100x Integration Times: 0.1 to 100 sec Detector: R-446 photomultiplier Zerodrift: Auto zero Readout: Analog, digital, IEEE-488 byte-serial bit-parallel with alphanumerics Background correction: Deuterium lamp (Model AA-775 AQ-D_2 lamp, opt.) Monochromator: Czerny-Turner, focal length 330 mm time shared Grating: 1800 lines/mm, blazed at 250 nm Range: 185-900 nm Accuracy: ± 0.2 nm

Performance (continued)

Dispersion: 1.5 nm/mm
Spectral Bandwidth: 0.05, 0.2, 0.5, 1.0 nm - separate slits for use with CRA-90
Scan Speeds: 6 nm/min
Resolution: To 0.05 nm

Gas Control: Automatic safety interlock for N_2O, gas pressures and flows, liquid trap
Fuel: Acetylene
Oxidant: Air, nitrous oxide
Venting: Recommended
Burner: Air/acetylene, titanium single groove head, Pt/Ir nebulizer
Adjustments: 3 dimensional

Operation

Calibration: Standard solutions, computer handles up to 5, calculates curve
Training: Available on request
Unattended period:
Maintenance: Minimal

Requirements

Power: 100/115, 220/240 VAC, 50/60 Hz
Weight: 69 kg (152 lb)
Dimensions: 106 cm L × 39 cm H × 55 cm D (41-1/2" × 15-1/2" × 21-1/2")

Features

Options

Automatic Sample Changer Model-51	$1375
Carbon Rod Atomizer CRA-90	See Varian C
Automatic Sample Dispenser ASD-53	3400
Hg, As, Se Kit, Model 64	575
Digital Printer, DP-38	1650
Nebulizers, fixed	175
variable	285
Background Correction	1300
Strip Chart Recorder	1095
Hollow Cathode Lamps	See Varian A
Electrodeless Discharge Lamp	See Varian B

References

(1) Manufacturer's Bulletin, AA-775, 1/78
(2) Manufacturer's Price List
(3) Manufacturer's Bulletin, Varian at Cleveland 2/78
(4) Manufacturer's Service Manual

Cost

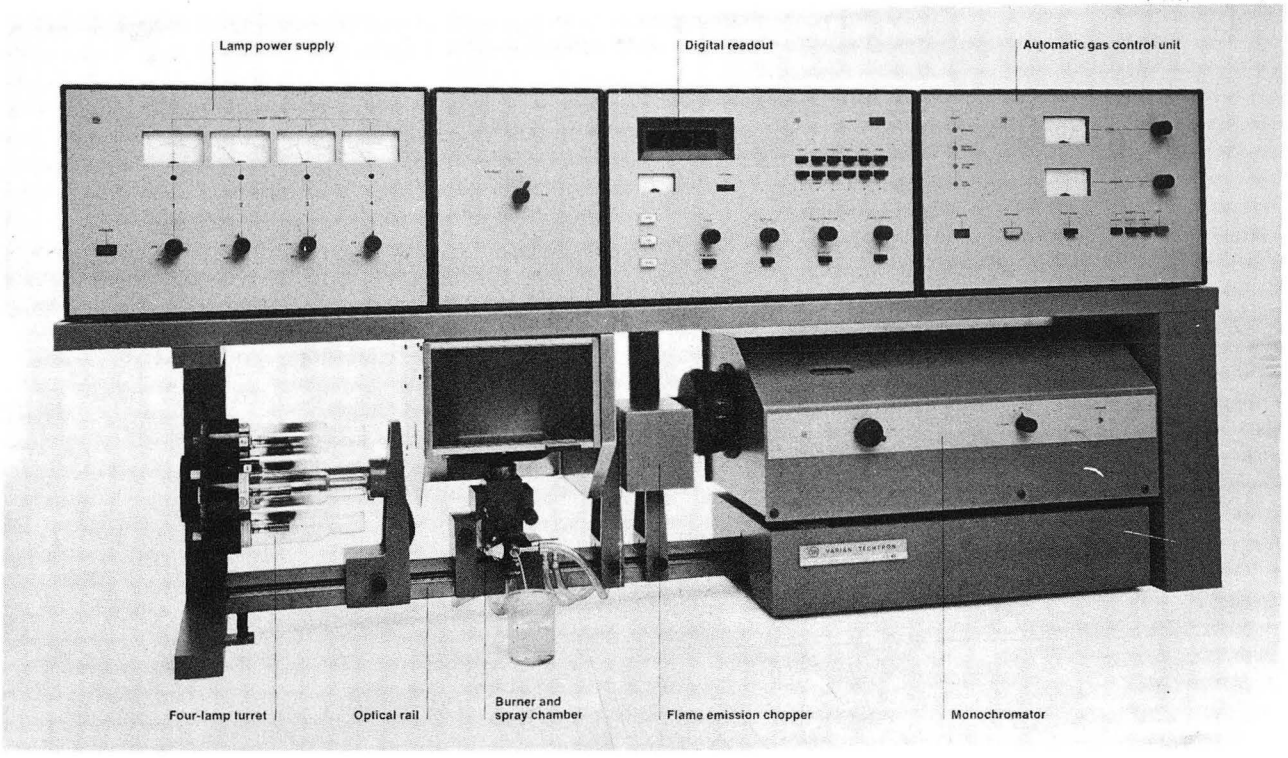
Varian Model AA-775 ABQ	17,250
Model AA-775 AQ	15,950

Address

Varian, Instrument Division
611 Hansen Way
Palo Alto, CA 94303
(415) 493-8100

Atomic Absorption/Emission Spectrophotometer

Varian Techtron Model AA-6



Class	Laboratory
Description	Research grade single beam atomic absorption spectrophotometer
Modes of Operation	Atomic Absorption, flame emission
Lower Detectable Limit	Depends on element -- usually ppb, within a factor of 2 of limit for models 175, 375
Range	ppb to %
Interferences	Light scattering, non-atomic absorption some chemical interferences
Multiparameter Capability	About 67 elements
Sampling	Method: Batch or automated Volume: 4 samples/minute Capacity: At least 100 µl per sample
Performance	Electronics: Linearity: ±1% of full scale division Stability: Better than ±0.5% of transmission for ±10% mains variation Scale Expansion: 0.3 to 50x Detector: R-446 photomultiplier Zero Drift: Automatic zero

Monochromator: 0.5 m Ebert mounting

Grating: 50 × 50 mm, 638 lines per mm
Wavelength Range: 185 to 1000 nm
Resolution: 0.03nm
Dispersion: 3.3 nm/mm
Spectral Bandpass: 0.03 nm to 1.0 nm continuous

Gas Control

Oxidant: N_2O, air
Fuel: C_2H_2, H_2
Vent: recommended
Burner: all Ti single slot head
Adjustments: 3 dimensional, scales on vertical and angular adjustment

Operation

Calibration: Standard solutions
Procedure: Calibration curve; standard addition; internal standard
Training: Available on request
Unattended Period: 20 min. with sample changer
Maintenance: minimal

Requirements

Power: 110/115, 220/240 Vac; 50 to 60 Hz
Weight: 105 kg (230 lb)
Dimensions: 137 cm L × 62 cm H × 28 cm D (55" L × 25" H × 13-1/2" D)

Features

Digital
Recorder
Peak Signal
Digital Printer

Options

Automatic Sample Changer, Model 51	$1375
Carbon Rod Atomizer, CRA-90	4500, See Varian C
Automatic Sample Dispenser, ASD-53	3400
Hg, As, Se Kit, Model 64	575
Digital Printer, Model 37	1500
Hollow Cathode Lamps	See Varian A
Electrodeless Discharge Lamps	See Varian B
Hydrogen continuum lamp (used for background correction)	190
Strip chart recorder 10" - Model 9176	1095
Standard solution of metals 10-20/250	
Simultaneous background correction	2250
Programmable calculator, Model 9815A with interface	4500

References

(1) Manufacturer's bulletin "Model AA-6 Atomic Absorption Spectrophotometer," 1/73.
(2) Manufacturer's price list, July 1978

Cost

AA-6 $13,200 to 16,700

Address

Varian Instrument Division
611 Hansen Way - D-425
Palo Alto, CA 94303
(415) 493-8100 X 3201

INSTRUMENTATION
FOR ENVIRONMENTAL
MONITORING

Hollow Cathode Lamps

Varian Hollow Cathode Lamps

Class: Accessory, Laboratory

Description: Single and multielement hollow cathode lamps for use with Varian atomic absorption spectrophotometers

Multiparameter Capability

Order No.	Element Lamp	Unit Price	Order No.	Element Lamp	Unit Price
56-100001-00	Aluminum	$ 130.00	56-100035-00	Molybdenum	135.00
56-100002-00	Antimony	165.00	56-100036-00	Neodymium	215.00
56-100003-00	Arsenic	190.00	56-100037-00	Nickel	135.00
56-100004-00	Barium	170.00	56-100038-00	Niobium	190.00
56-100005-00	Beryllium	205.00	56-100039-00	Osmium	295.00
56-100006-00	Bismuth	170.00	56-100040-00	Palladium	190.00
56-100007-00	Boron	170.00	56-100041-00	Platinum	215.00
56-100008-00	Cadmium	170.00	56-100042-00	Potassium	185.00
56-100010-00	Calcium	135.00	56-100043-00	Praseodymium	215.00
56-100011-00	Cerium	210.00	56-100044-00	Rhenium	215.00
56-100009-00	Cesium	180.00	56-100045-00	Rhodium	260.00
56-100012-00	Chronium	135.00	56-100046-00	Rubidium	180.00
56-100013-00	Cobalt	135.00	56-100047-00	Ruthenium	215.00
56-100014-00	Copper	135.00	56-100048-00	Samarium	215.00
56-100015-00	Dysprosium	215.00	56-100049-00	Scandium	265.00
56-100016-00	Erbium	215.00	56-100050-00	Selenium	180.00
56-100017-00	Europium	265.00	56-100051-00	Silicon	170.00
56-100018-00	Gadolinium	215.00	56-100052-00	Silver	150.00
56-100019-00	Gallium	190.00	56-100053-00	Sodium	180.00
56-100020-00	Germanium	190.00	56-100054-00	Strontium	180.00
56-100021-00	Gold	190.00	56-100055-00	Tantalum	170.00
56-100022-00	Hafnium	215.00	56-100056-00	Tellurium	180.00
56-100023-00	Holmium	215.00	56-100057-00	Terbium	190.00
56-100024-00	Hydrogen Continuum*	190.00	56-100058-00	Thallium	170.00
56-100025-00	Indium	175.00	56-100060-00	Thulium	240.00
56-100026-00	Iridium	215.00	56-100061-00	Tin	175.00
56-100027-00	Iron	130.00	56-100062-00	Titanium	155.00
56-100028-00	Lanthanum	215.00	56-100063-00	Tungsten	155.00
56-100029-00	Lead	165.00	56-100064-00	Uranium	245.00
56-100030-00	Lithium	165.00	56-100065-00	Vanadium	205.00
56-100031-00	Lutetium	240.00	56-100066-00	Ytterbium	215.00
56-100032-00	Magnesium	130.00	56-100067-00	Yttrium	200.00
56-100033-00	Manganese	140.00	56-100068-00	Zinc	145.00
56-100034-00	Mercury	165.00	56-100069-00	Zirconium	170.00

	Multi-Element Lamps	
56-100070-00	Sodium/potassium multi-element lamp	$ 200.00
56-100071-00	Calcium/magnesium multi-element lamp	190.00
56-100082-00	Cooper/lead/zinc multi-element lamp	240.00

Multi-element Hollow Cathode Lamps are available, consisting of any combination of the following six elements: Iron (Fe); Coablt (Co); Nickel (Ni); Manganese (Mn); Copper (Cu); Chromium (Cr).

56-100072-00	2 Combinations	$ 190.00
56-100073-00	3 Combinations	240.00
56-100074-00	4 Combinations	258.00
56-100075-00	5 Combinations	285.00
56-100076-00	6 Combinations	315.00

Warranty — 4000 millampere-hours

Manufacturer

References — Manufacturers Specification

Cost — Prices quoted in listing under Multiparameter Capability

Address — Varian Instrument Division
611 Hansen Way
Palo Alto, CA 94303
(415) 493-4000

INSTRUMENTATION
FOR ENVIRONMENTAL
MONITORING

Varian Electrodeless Discharge Lamps

Class	Accessory, Laboratory
Description	Electrodeless discharge lamps, Westinghouse, RF frequency
Multiparameter Capability	

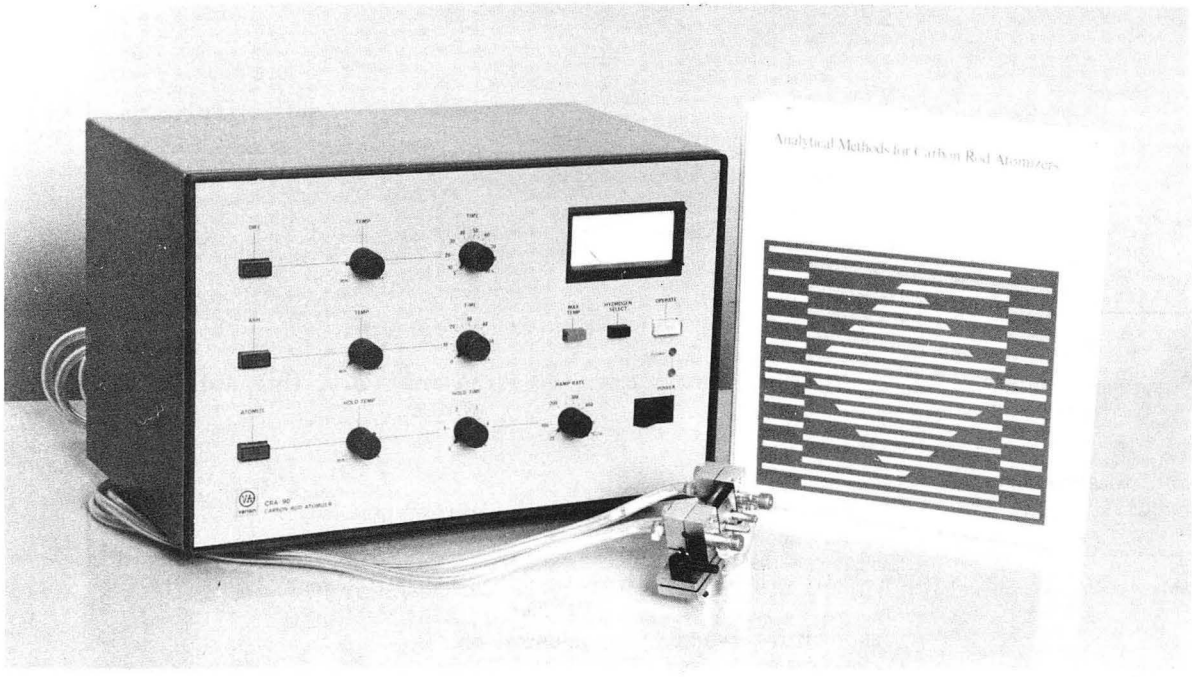
56-100229-00	EDL, Arsenic	$ 200.00	56-100228-00	EDL, Antimony	$ 200.00
56-100231-00	EDL, Cadmium	200.00	56-100230-00	EDL, Bismith	200.00
56-100232-00	EDL, Lead	200.00	56-100237-00	EDL, Tellurium	200.00
56-100233-00	EDL, Mercury	200.00	56-100236-00	EDL, Thallium	200.00
56-100234-00	EDL, Phosphorous	225.00	56-100238-00	EDL, Tin	200.00
56-100235-00	EDL, Selenium	200.00	56-100239-00	EDL, Zinc	200.00

Manufacturer	
Warranty	2500 hours or 2 years
References	Manufacturer's Specifications
Cost	Prices quoted in listing under Multiparameter Capability Power Supply $1500
Address	Varian Instrument Division 611 Hansen Way Palo Alto, CA 94303 (415) 493-4000

INSTRUMENTATION
FOR ENVIRONMENTAL
MONITORING

Accessory Graphite Furnace

Varian CRA-90



Class	Laboratory Accessory
Description	Programmable graphite furnace

Lower Detectable Limit

Element	Sensitivity (µg/ℓ)[a]	Detection Limit (µg/ℓ)[a]
Ag	0.02	0.015
Al	1.5	1.0
As	2.0	0.05
Au	1.0	0.05
Ba	1.5	1.0
Be	0.1	0.1
Bi	0.7	0.07
Ca	0.03	0.03
Cd	0.015	0.01
Co	0.5	0.4
Cr	0.5	0.23
Cs	2.0	2.0
Cu	0.4	0.2
Eu	2.5	3.5
Fe	0.3	0.25
Ga	2.0	1.0
Hg	6.0	6.0
K	0.1	0.1
Li	0.2	0.20
Mg	0.006	0.003
Mn	0.06	0.02
Mo	1.0	0.3
Na	0.02	0.01
Ni	1.0	0.5
Pb	0.4	0.15
Pd	1.4	1.4
Pt	1.0	5.0
Rb	0.6	0.3
Sb	1.0	1.5

Element	Sensitivity	Detection Limit (µg/ℓ)[a]
Se	3.0 (2.0[b])	3.0
Si	3.5	3.5
Sn	0.5	0.5
Sr	0.4	0.4
Tl	0.3	0.3
V	5.0	4.5
Zn	0.01	0.01

a. based on a 10 µℓ sample
b. using EDL

Range

0.01 ppb to %

Sampling

Method: Liquid or solid
Max. Temp: 3000°C
Volume: Up to 50 µℓ
Atomizer configurations: 5 - standard tubes, threaded tubes, standard cups, large volume tubes, perforated cups for air sampling
Capacity: ~ 40 to 90 samples/hour

Performance and Specifications

Accuracy: To better than 1%
Reproducibility: With ASD-53, better than 1% RSD
Linearity:
Relative humidity range: 20% to 90%
Temperature repeatability: Better than ±5% over the full temp. range for ±10% mains voltage variation
Temperature readout: Graduated in °C
Max. temperatures: Dry - 300°C
Ash - 1700°C
Atomize - 3000°C
Timers: Continuously adjustable
Dry - 0 to 90 secs.
Ash - 0 to 60 sec.
Atomize Ramp Rage - 25 to 800°C per sec.
Atomize hold - 0 to 5 seconds
Cooling time: From 2000°C to room temp. in 20 secs.

Requirements

Power: 110/115/208/220/240 volts AC; 50-60 Hz
Size: 387 cm × 266 cm × 241 cm (15 1/4" × 10 1/2" × 9 1/2")
Weight: 35 kg (77 lb) shipping weight
Inert Gas: Argon or N_2, from cylinder at 40-100 kPa (0.4-1.0 kg (cm^2, 6-15 psig)
Cooling water: 2 liters/min
Additional support gas: Has separate H_2 gas input for special applications

Option

Automatic sample dispenser, Model ASD-53

References

Manufacturer's Specifications

Cost

Model CRA-90 $4500 ($4200 with AA purchase)

Address

Varian Instrument Division
611 Hansen Way, D-425
Palo Alto, CA 94303
(415) 593-4000 - X3201

Atomic Emission Instruments with Plasma Sources

Instrument	Plasma	Max. Elements Simultaneous	Polychromator, Grating	Computer, Language	Type, Storage	Cost	Remarks
Applied Research Labs. Model 34000 ICP Plasma Quantometer	RF	60	1m, laser ruled f/31	PDP 11/03, Extended BASIC	Dual floppy disks	$92,166 (10 channels) 113,286 (30 channels)	
Model 34000 ICP Plasma Quantovac	RF	60	1m, laser ruled f/31	PDP 11/03 Extended BASIC	Dual floppy disks	95,966 (10 channels) -117,086 (30 channels)	Vacuum System
Fischer, Jarrell Ash Plasma Atom.Comp.	RF	50	0.75m, f/19	Dedicated mini-computer		Contract Item	
955	RF	30	0.75m, f/19	PDP8, PAL	Tape Cassette	$39,900 (10 channels)	
965	RF	48	0.75m, f/19	PDP8A, PAL	Dual floppy disk	65,000 (15 channels)	Basic back-ground correction, N+1 variable channel
975	RF	48	0.75m, f/19	PDP8A, PAL	Dual floppy disk	95,455 (28 channels)	Basic back-ground correction, N+1 variable channel
1120	RF	48	0.75m, f/19	PDP 11/03L, SAIL	Dual hard disks	116,000 (30 channels)	Mercury profile monitor standard back corr., variable N+1, software
1140	RF	61	0.75m, f/19	DPD 11/04, SAIL	Dual hard disks	145,030 (40 channels)	Mercury profile monitor standard back corr., variable N+1, software

(continued)

Atomic Emission Instruments with Plasma Sources (continued)

Instrument	Plasma	Max. Elements Simultaneous	Polychromator, Grating	Computer, Language	Type, Storage	Cost	Remarks
Fischer, Jarrell Ash (continued)							
1160	RF	61	1m, laser ruled f/31	PDP 11/34, SAIL	Dual hard disks	$206,585 (50 channels)	Mercury profile monitor standard back corr., variable N+1, software
Labtest Equipment							
ICP,V-25	RF	—	1m, f/18, holographic	Dedicated	Dedicated	$ 20,000-50,000	(Depends on # of channels)
ICP310	RF	60	1.5m, holographic	Dedicated	Dedicated	28,000-68,000	
ICP2100, CRT-100	RF	30	1m, holographic	Dedicated	Dedicated	45,000 (10 channels)	
Plasma Scan	RF	Sequential	—	—	—	20,000-35,000 (sequential)	
Spectrametrics							
SpectraSpan III	DC	20	Echelle, 0.75m, f/15	—	—	49,155 (20 channels)	Multiple 20 element cassettes available
SpectraSpan IV	DC	Sequential	Echelle 0.75, f/15	—	—	15,925 (sequential)	

Atomic Emission Spectrophotometer

Model 34000 ICP Plasma Quantovac,
Model 34000 ICP Plasma Quantometer

Class	Laboratory
Description	Computer controlled, inductively-coupled RF plasma emission spectrometer
Modes of Operation	Atomic emission

Typical Lower Detectable Limit:

1 - 1 ppb	1 - 10 ppb	10 - 100 ppb	100 - 1000 ppb
Mg	Ag	Al	K
Ca	B	As	Bi
Mn	Ba	Au	Ge
Sr	Be	Ga	I
	Ce	Gd	In
	Co	Hf	Pr
	Cr	Ag	S
	Cu	In	Te
	Fe	Ir	Th
	Li	La	U
	Ni	Mo	
	V	Nb	
	Yb	P	
	Cd	Pb	
	Zn	Pd	
		Rb	
		Rh	
		Se	
		Si	
		Ta	
		Ti	
		Tl	
		W	
		Y	
		Zr	
		Sb	
		S	
		Na	

Range and Sensitivity: 6 orders of magnitude

Interferences

Multiparameter Capability: Up to 60 elements, simultaneously

Sampling:
Method: batch
Capacity: 40-60 samples/hour, max.
Volume: 2-5 ml/min

Performance and Specifications:

Electronics: Solid state, plug-in circuitry

Detector: Photomultiplier tubes (60 max.)
Integration: performed by computer
Readout: digital from a PDP. 11/03, 64K byte mos memory, dual 512K byte, floppy disk mass storage, 4 digit LED
Terminal: LA-36 DEC writer, II (30 cps); CRT optional

Polychromator: Concave laser intertrometrically ruled, tripartite, aluminum grating, 1 m focal length, using 1st, 2nd and 3rd orders, f/31

Grating: 1080 g/mm blazed at 600 nm
Filters: Narrow bandpass filters for order sorting

	Positive Spectral Order			
	1st order	2nd order	3rd order	4th order
Blaze nm:	600	300	200	150
Reciprocal Linear Dispersion nm/mm:	0.926	0.463	0.309	0.231
Efficiency at Blaze Percent:	71	60	45	28
Wavelength Ranger nm:	340-820	170-410	170-270	170-200
Resolving Power:	43,200	86,400	129,000	172,800

Slits: primary - 15μm
secondary - 35, 50μm

Gas Control: Argon

Purity: 99.995%
Consumption: 40 cfh
Regulator: supplied by manufacturer
Nebulizer: pneumatic, all glass, no adjustment

Source: Inductively-Coupled RF Plasma

Frequency: 27 mHz, ISM band
Oscillator: crystal controlled, frequency multiplier
RF generator output: Model 139010-3 kW
Model 139010-2 kW
Normal operating power: 1.6 kW for aqueous solutions
RF amplier: Air cooled, ground grid, Class AB_2
Modulation on RF waveform: less than 2% P-P
Power level control: closed loop, forward power regulator, 3 presettible levels plus continuous power level adjustment

Operation	Calibration: With standard solutions, computer calculates curve Maintenance: Preventive schedule, 4 calls/yr @ $1500/yr Training required/available
Requirements	Spectrometer: 220 VAC, 50/60 Hz, Power: RF generator: 4KVA, 220 single phase 50/60 Hz, 50A, 8KVA voltage regulator required if fluctuations are greater than ±10% Water: Tap water; 1/4 GPM at 75° F or less Temperature: 14° C - 24° C (65°C - 85° F) Humidity: 20-80% Dimensions: Spectrometer with ICP Source and Sample table: 246 cm W × 91.5 cm D × 140 cm H (97"W × 36" D × 55" W) RF Generator: 61 cm W × 58.5 cm D ×134.5 cm H (24"× 23" × 53") Weight: Air circulation: 700 CFM minimum
Features	Vacuum capability RF inductively coupled argon plasma source Computer control Simultaneous element determinations PdP 11/03 computer Floppy disk DEC Writers ARL Basic extended software Diagnostic instrument checks made at each analysis Variety of elements determined simultaneously
Options	Additional elements to 60 $1000 each SAMI, Scanning accessory for multielement instrumentation (computer controlled scanning primary slit) 1 meter scanning monochromator Computer controlled auto samples - 200 sample capacity Video Display Terminal
References	Manufacturer's Specifications
Cost	Model 34000 Plasma Quartometer 86,766 Model 34000 Plasma Quantovac 90,566 Analytical channels: 10 channels 5,400 30 channels 26,520
Address	Applied Research Labs 9545 Wentworth Street Sunland, CA 91040 Attn: Bryce Hanna, General Product Manager (213) 352-6011

INSTRUMENTATION
FOR ENVIRONMENTAL
MONITORING

Atomic Emission Spectrophotometer

Jarrell-Ash Plasma AtomComp (ICAP)

Class: Laboratory

Description: Emission spectrophotometer using an inductively-coupled argon plasma excitation source

Modes of Operation: Atomic Emission

Lower Detectable Limit

Detection Limits
µg/l (ppb)

Element	Water	Element	Water
Ag	4	La	6
Al	15	Li	3
As	25	Mg*	20
Au	5	Mn	0.5
B	5	Mo	5
Ba	0.2	Na	10
Be	0.3	Nb	20
Bi*	50	Nd	10
Ca*	4	Ni	6
Cd	1	Os	200
Ce	20	P	30
Co	2	Pb	20
Cr	4	Pd	40
Cu	2	PR	30
Dy	2	Pt	30
Eu	1	Re	25
Fe	2	Rh	30
Ga	40	Ru	60
Gd	8	Sb	30
Ge	50	Sc	1
Hg	50	Se	20
In	40	Si	10
Ir	70	Sm	10
K	125	Sn	6

(continued)

Lower Detectable Limit

Detection Limits
µg/1 (ppb)

Element	Water	Element	Water
Sr	0.2	U	75
Ta	50	V	2
Te	20	W	25
Th	25	Y	1
Ti	1	Zn	2
Tl	75	Zr	4

*Note: Data are for normal analytical line, not the most sensitive line.

Range and Sensitivity

ppb to %

Interferences

Spectral interferences primarily

Multiparameter Capability

Up to 50, simultaneously

Sampling

Method: Batch or automated
Capacity: Single sample at one time
Volume: 1 ml/min. 5 ml sufficient

Performance and Specificiations

Electronics:

Stability: ±2% over 3 hours
Detector: Photomultiplier tubes, 1.27 cm × D
Integration: Selectable, commonly 10 sec.
Readout: Digital, comp. controlled individual op-amp analog integrator with multiplexed A/D converter
Background: Dynamic background correction standard

Polychromator: Rowland Circle focal curve, aperture f/19

Grating: 2400 grooves/mm, blazed at 270nm
Dispersion: 705 - 1st order, 5.4 Å/mm; 2nd order, 2.7 Å/mm
Range: 190-500 nm, optionally detects Na (590 nm), Li (670 nm) and K (766 nm)
Spectral bandpass: 0.03 nm (first order)
Entrance slits: 3 mm H × 25 µM W
Exit slits: 50 µM

Gas Control: Argon

Purity: Welding grade
Consumption: 0-5 1/min
Regulator: provided by manufacturer
Nebulizer: pneumatic, cross-flow design
Coolant: flow controlled 0-25 ℓ/min

Source: Inductively-coupled RF plasma

Frequency: 27.12 MHz ± 0.05%
Oscillator:
RF generator output: 2 kW
Ripple: 5% max peak to peak

Computer:

Dedicated minicomputer

Operations

Calibration: Included in software allows 5 standards, with 1-2 conc. per metal
Maintenance: Software to aid in diagnosis; training included with equipment
Training required/available: provided with instrument

Requirements	Power: Spectrometer 110/120 VAC, 50/60 Hz, 1000 VA, single phase RF power supply: 208-240 VAC, 50/60 Hz, 3900 VA, 3 phases Water: 2.1 liters/min (0.5 gal/min) Temperature: 65° - 85°F Humidity: Less than 75% rel. humidity Dimensions: Spectrometer - 177.8 cm L × 85.9 cm W × 129.5 cm H (70.0" L × 338" W × 51.0" H) RF power supply - 61.5 cm L × 64.7 cm W × 162.5 H (24.2"L × 25.5"W × 64.0" H) Weight: Spectrometer - 402 kg (2000 lbs) RF power supply - 364 kg (800 lbs)
Features	Inductively-coupled RF argon plasma source Computer-controlled
Options	Optics and mount for scanning spectrometer for non-programmed elements 190-900 - depends on PMT Auto background correction
References	Manufacturer's Specifications
Cost	Plasma AtomComp, GSA contract item
Address	Jarrell-Ash Division Fisher Scientific Co. 590 Lincoln STreet Waltham, MA 02154 Attn: Marketing Manager, Atomic Emission (617) 890-4300

INSTRUMENTATION
FOR ENVIRONMENTAL
MONITORING

Atomic Emission Spectrophotometer

Jarrell Ash Models 955/965/975

Class	Laboratory
Description	Atomic Emission Spectrometer with inductively-coupled plasma source equipped with PDP-8 series computer
Modes of Operation	Atomic Emission

Lower Detectable Limit

Element	Min. Detect. Limit (ppb)	Element	Min. Detect. Limit (ppb)
Ag	3	Na	5
Al	15	Ni	5
Au	4	P	30
B	5	Pb	16
Ba	0.6	Rh	15
Be	0.6	Sb	20
Cd	1	Sc	0.8
Co	2	Se	25
Cr	4	Si	8
Cu	1	Sr	0.2
Fe	2	Ti	0.7
Li	3	V	3
Mg	0.3	W	15
Mn	1	Zn	1
Mo	7	Zr	3

Range and Sensitivity	ppb to %, 1 ppb to > 200 ppm
Interferences	Depends upon element of concern, spectral primarily
Multiparameter Capability	Model 955: up to 30 elements simultaneously Model 965/975; up to 48 elements simultaneously
Sampling	Method: Batch or automated Capacity: Single sample at a time Volume: 1 mℓ/min, 5mℓ sufficient

Performance and Specifications

Electronics: Solid State

Stability: 3% for over 4 hours
Detectors: photomultipliers (manuf: Hamamatsu)
Integration: user-chosen, typically 10 sec.
Readout: digital, Model 955: TI 733
Models 965/975: LA-36 DEC writer
Background: Model 955: not available
Models 965/975: basic automatic background correction optional
Spectrometer: Rowland Circle - 0.75 m, aperture f/19.
Gratings: 30×40 mm, 2400 grooves/m blazed at 270 nm
Dispersion: 1st order, 5.4 Å/mm, 2nd order, 2.7 Å/mm
Range: 190-500 nm, optionally detects Na(590 nm), Li(670 nm) and K(766 nm)
Entrance Slits: 3mm H × 25 μm wide
Exit Slits: 50 μm
Spectral Bandpass: 0.036 nm (first order)
Accuracy: Mercury profile monitor opt. on 965/975.

Gas Control: Argon

Purity: Welding grade
Plasma: 0-5 ℓ/min
Regulator: Provided by manufacturer
Nebulizer: Pneumatic
Coolant: 0-25 ℓ/min
Consumption: 18 ℓ/min

Source: Inductively-coupled RF argon plasma

Frequency: 27.12 MM_2
Oscillator:
RF generator output: max 2KW
Ripple: < 5% peak to peak

Computer: PDP-8 series using Plasma Analytical Language (PAL) software.
Model: Model 955/965: PDP-8A
Model 975: PDP-8E
Memory: 8K core
Storage devices: Model 955-Tape Cassette
Model 965/975 - dual floppy disc.

Operation

Calibration: Standards, included software allows 5 standards with 1-2 conc. per metal
Maintenance: Software to aid in diagnosis
Training: Provided with instrument

Requirements

Power: Spectrometer: 110/120 VAC, 50/60 Hz, 1 phase
RF Power Supply: 208/240 VAC, 50/60 Hz, 3 phases
Dimensions: Spectrometer - 161 cm L × 86 cm W × 129.5 cm H (63.5" × 35" × 51")
RF Power Supply: - 60 cm L × 66 cm W × 162 cm H (23.5" × 26" × 64")
Weight: Spectrometer 907 kg (2000 lbs)
RF Power Supply: 364 kg (800 lbs)
Temperature: ~65° - 85°
Humidity: Less than 75% rel. humidity

Features

Inductively coupled RF plasma source
PDP-8 series computer
PAL software
8K core memory
975: mercury profile monitor, source projection optics

Options

Multiple channels
Variable wavelength (N+1) channel
Statistics software
Auto sampler
965: mercury profile monitor

Options (continued)

965/975 Read only remote terminals
Auto Tuning module
Automatic Basic background correction
975: multiple sources
two-way remote terminals
storage and retrieval bundle

References

Manufacturer's Specifications

Cost

Base Price (channels not included)

Model 955	$ 34,900
965	41,900
975	54,900
Typical Instruments	
Model 955 - 10 channels	39,900
Model 965 - 15 channels, Basic Auto Bkg. Corr. variable (N+1) channel	65,000
Model 975 - 28 channels, Basic Auto Bkg. Corr. variable (N+1) channel	95,455

Address

Jarrell-Ash Division
Fisher Scientific Co.
590 Lincoln Street
Waltham, MA 02154
Attention: Marketing Manager, Atomic Emission
(617) 890-4300

INSTRUMENTATION
FOR ENVIRONMENTAL
MONITORING

Atomic Emission Spectrometer

Jarrell-Ash Models 1120/1140/1160

Class: Laboratory

Description: Atomic Emission Spectrophotometers with inductively-coupled plasma source equipped with PDP-11 series computer

Modes of Operation: Atomic Emission

Lower Detectable Limit

Detection Limits
µg/l (ppb)

Element	Water	Element	Water
Ag	4	La	6
Al	15	Li	3
As	25	Mg*	20
Au	5	Mn	0.5
B	5	Mo	5
Ba	0.2	Na	10
Be	0.3	Nb	20
Bi	50	Nd	10
Ca	4	Ni	6
Cd	1	Os	200
Ce	20	P	30
Co	2	Pb	20
Cr	4	Pd	40
Cu	2	Pr	30
Dy	2	Pt	30
Eu	1	Re	25
Fe	2	Rh	30
Ga	40	Ru	60
Gd	8	Sb	30
Ge	50	Sc	1
Hg	50	Se	20
In	40	Si	10
Ir	70	Sm	10
K	125	Sn	6

(continued)

Lower Detectable Limit (continued)

Detection Limits
µg/l (ppb)

Element	Water	Element	Water
Sr	0.2	U	75
Ta	50	V	2
Te	20	W	25
Th	25	Y	1
Ti	1	Zn	2
Tl	75	Zr	4

*Note: Data are for normal analytical line, not the most sensitive line.

Range and Sensitivity

ppb to %

Interferences

Spectral interferences primarily

Multiparameter Capability

Model 1120: 48 maximum simultaneously
Model 1140/1160: 61 maximum simultaneously

Sampling

Method: Batch or automated (opt.)
Capacity: Single sample at a time
Volume: 1 mℓ/min, 5 mℓ sufficient

Performance and Specifications

Electronics: Solid State

Stability: 3% for over 4 hours
Detectors: Photomultipliers (manuf. Hamamatsu)
Integration: User's preference, typically 10 sec.
Readout: Digital, LA-36 DEC writer
Background: Advanced automatic background correction (opt.)

Spectrometer: Rowland Circle - 0.75 m, aperture f/19

Grating: 30×40 mm, 2400 grooves/mm, blazed at 270 nm
Dispersion: 1st order 5.4 Å/mm, 2nd order 2.7 Å/mm
Range: 190-500 nm, optionally detects Na(590 nm), Li(670 nm) and K (766 nm).
Entrance Slits: 3mm H, 25 W
Exit Slits: 50
Spectral Bandpass: 0.03 nm (first order)
Accuracy: mercury profile monitor, standard

Gas Control: Argon

Purity: Welding grade
Plasma: 0-5 ℓ/min
Coolant: 0-25 ℓ/min
Regulator: provided by manufacturer
Nebulizer: Pneumatic
Argon Consumption: 18 ℓ/min

Source: Inductively-coupled RF Argon Plasma

Frequency: 27.12 MHz
Oscillator:
RF generator output: max 2KW
Ripple: <5% peak to peak

Computer: PDP-11 series, using Sophisticated Analytical Interactive language (SAIL)
Model: Model 1120 - PDP-11/03L
Model 1140 - PDP-11/04
Model 1160 - PDP-11/34
Memory: Model 1120/1140 - 28K MOS
Model 1160 - 32K MOS
Mass Storage Devices: Dual hard disks

Operation

Calibration: Standards, included software allows up to 7, blank subtraction, dilution factors, auto standardization, and autocalibration (opt. std.)
Maintenance: Software to aid in diagnosis
Training: Provided with instrument

Requirements

Power: Spectrometer: 110/120 VAC, 50/60 Hz 1 phase
RF Power Supply: 208/240 VAC, 50/60 Hz, 3 phases
Dimensions: Spectrometer: 161 cm L × 86 cm W × 129.5 cm H (63.5" × 34" × 51")
RF Power Supply: 60 cm L × 66 cm W × 162 cm H (235" × 26" × 64")
Weight: Spectrometer 907 kg (2000 lbs)
364 kg (800 lbs)
Temperature: ~65° - 85°
Humidity: Less than 75% relative humidity

Features

Inductively-coupled RF Plasma Source
PdP-11 Series Computer
SAIL Software, operating on DEC RSX-11M OS
Mercury profile monitor
Basic and Advanced Statistics software

Options

Number of channels
Variable wavelength channel
Multiple sources (available 1979)
Two-way remote terminals
Autotuning module
Spectrum scanning
Higher level languages
Advanced storage and retrieval (SARA)
Advanced automatic background correction
Advanced Blank Subtraction (BIAS)
Correlation software
Source listings
1140/1160: RSX/11M Class A Licence

References

1160: Additional memory up to 128 K

Cost

Base Price (channels NOT included)

Model 1120	$ 71,500
Model 1140	79,500
Model 1160	89,500

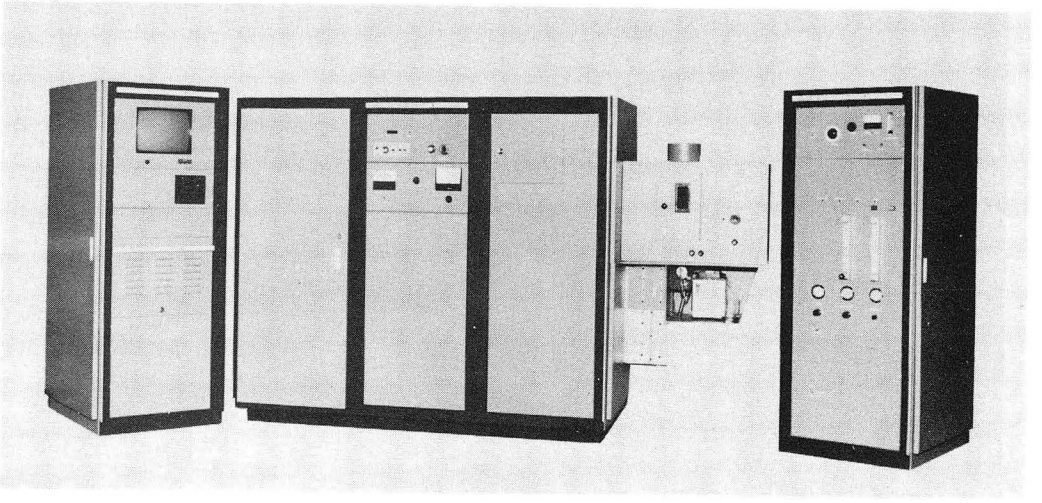
Typical Systems

Model 1120, 30 channels, Adv. Bkg. corr., variable wavelength channel software	116,000
Model 1140, 40 channels, Adv. Bkg. corr., BIAS software, SCAN software, UT52 remote	145,030
Model 1160, 50 channels, Adv. Bkg. corr., variable wavelength, Fortran, OS Class A license, SARA software, BIAS software, SCAN software, correlation software, UT52 remote, source listings, 64K MOS extra memory	206,585

Address

Jarrell Ash Division
Fisher Scientific Co.
590 Lincoln Street
Waltham, MA 02154
(617) 890-4300
Attention: Marketing Manager, Atomic Emission

Atomic Emission Spectrometers
Labtest Model ICPV-25, ICP 310 and ICP 2100 with CRT-1000 Display



Class: Laboratory

Description: Modular Inductively-coupled RF argon plasma atomic emission spectrometers

Modes of Operation: Atomic Emission

Lower Limit of Detection

	Detection Limit µg/ℓ		
Metal	ICP V-25[a]	ICP 310[b]	ICP 2100[c]
Aluminum	7	20	10
Antimony		70	60
Arsenic		40	20
Barium		5	5
Beryllium	0.02	5	5
Bismuth		100	100
Boron	5	30	5
Cadmium	5	20	2
Calcium	0.2	1	1
Carbon		100	100
Cerium		20	20
Chromium		6	6
Cobalt	6	5	5
Copper	1	3	3
Erbium		20	20
Europium		9	9
Gadolinium		20	20
Gallium		50	50
Germanium		10	10
Gold		100	5
Indium		500	500
Iridium		100	100
Iron	3	3	3
Lanthanium		10	10
Lead		50	50
Lithium		1000	1000
Magnesium	0.05	0.2	0.2

Lower Limit of Detection (continued)

Metal	Detection Limit µg/ℓ ICPV-25[a]	ICP310[b]	ICP2100[c]
Manganese	0.2	3	3
Mercury		50	200
Molybdenium		60	5
Neodynium		20	20
Nickel		10	10
Palladium	—	—	—
Phosphorous		100	30
Platinium		150	20
Potassium		27,000[d]	100
Praeseodynium		30	30
Rhodium		20	20
Rubidium		30	30
Ruthenium		5000	5000
Samarium		50	50
Selenium	50	80	80
Silicon		30	30
Silver		10	5
Sodium		1	1
Strontium		1	1
Tantalum		20	20
Terbium		50	50
Tellurium		200	200
Thallium		1000	1000
Thorium		50	50
Tm		20	20
Tin		500	70
Titanium		10	5
Tungsten		130	50
Uranium		1000	80
Vanadium		5	5
Ytterbium		6	6
Yttrium		10	10
Zinc		10	10
Zirconium		10	5

a. Analyses performed by City Chemistry Department, Brisbane, Australia Provided by the manufacturers.
b. Analyses, performed and provided by the manufacturer on Test Solutions.
c. Valves obtained from water leached from ashed plant tissue. Analyses performed by the Australia Dept. of Agriculture at Perth; values provided by the manufacturer.
d. Not the best line is used.

Range and Sensitivity

4-6 orders of magnitude

Interferences

Multiparameter Capability

V-25- 48 Elements, simultaneously
310 - 60 elements, simultaneously
2100- 30 elements, simultaneously
Scanning monochromator (option) - sequential

Sampling

Method: Batch
Capacity: 1 at a time
Volume: 15 ml

Performance and Specifications

Electronics: Solid State

Detectors: Photomultiplier tubes
Readout: Readout Data Aquistion and Display system - 24K Random Access memory, expendable to 48K RAM, 2K programmable read only memory, cathod ray tube display with interface

Performance and Specifications (continued)

Background Correction: Special baffling, no optics between entrance and exit slits other than grating

Polychromator - V-25: 1 meter focal length, f/18,Paschen-Runge mount, in vacuum weldment (gauge displays operating vacuum, may be operated with inert gas or air).

Grating: 2160 lines/mm
Dispersion: 4.6 Å/mm
Range: 160 - 430 nm
Slits: Primary - 20μ
Secondary - 75μ

Polychromator - ICP 310: 1.5 meter focal length, Paschen Runge mount

Grating: Holographic, 1200 lines/mm, blazed at 300 nm
Dispersion: 1st order - 5.6 Å/mm,
Range: 190 - 690 nm
Slits: Primary: 20 micron
Secondary: 40, 75 150 microns
Alignment Check: Mercury monitor

Polychromator - ICP 2100: 1 meter focal length , Paschen-Runge mount

Grating: Holographic, 2160 lines/mm, blazed at 200 nm
Dispersion: 1st order - 4.6 Å/mm, 2nd order - 2.3 Å/mm
Range: 187.5 - 455 nm (optional scanning monochromator - 180-900 nm)
Slits: Primary: EDM shaped 20μ width
Secondary: 40, 75, and 150μ as required
Alignment Check: Mercury monitor

Monochromator: 350 mm focal length, f/6,8 (optional)

Grating: 1180 lines/mm
Dispersion: 20 Å/mm
Range: 200-800 nm, with N_2 purge (185-1000 nm)
Slits:
Wavelength accuracy:
Scan Speeds: 0.05 to 20 Å/second, externally programmable

Gas Control: All glass torch, argon

Purity: Welder's grade
Consumption: 33 cfh
Regulator: Provided in cooling and sample streams
Nebulizer: All glass torch and nebulizer

Source: Inductively-coupled RF argon plasma

Frequency: 27.12 MHz
RF generator output: 2 kW
Modulation of RF waveform: less than 2%

Operation

Calibration: Included in software, 2 standards
Maintenance: Check points for servicing in spectrometer
Training Avail./required: Provided with instrument

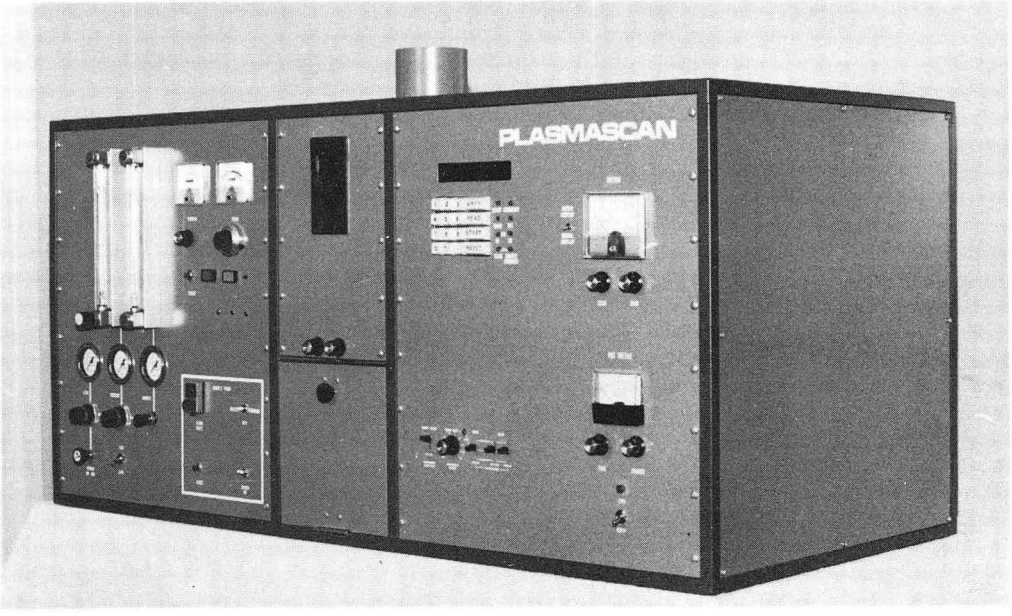
Requirements

Power: Spectrometer:
RF Power Supply: 240 VAC, 50/60 Hz, 30 amps
Water: Self Contained
Temperature: 72° ± 5°F
Humidity: Below 60% relative humidity
Dimensions: Spectrometer:
RF generator: 71 cm × 61 cm × 56 cm (32" × 24" × 22")
Weight: Shipping weight - 2100 lbs.

Features	RF Plasma source Computer control Digital display, CRT display Simultaneous element determinations Modular systems	
Options	Printer	$ 8000 (if installed instead of the CRT-1000)
	Scanning monochromator (180-900 nm) V-25 ICP, vacuum spectrometer Model ICP 310 spectrometer Model ICP 2100 spectrometer Model ICP 71 direct reading spectrometer	$40,000-80,000
	CRT 1000 Readout Transsource (R) Excitation Source Nebulizers: Cross flow Concentric Class Ultrasonic	
References	Manufacturer's Specifications	
Cost	Model ICPV-25 Price Range	$25,000-50,000
	Model ICP 310	28,000-68,000
	Model ICP 2100 with CRT readout and ten DMT's	45,000
Address	Labtest Equipment Company Subsidiary: Systron Donner Corp. 11828 LaGrange Ave. Los Angeles, CA 90025 (213) 478-2518	

Atomic Emission Spectrometer

Labtest Equipment, Plasmascan Model 700



Class	Laboratory
Description	Sequential, atomic emission spectrometer with inductively coupled plasma source
Modes of Operation	Atomic Emission
Lower Limits of Detection	
Range and Sensitivity	4-6 orders of magnitude
Interferences	
Multiparameter Capability	Multielement, sequentially
Sampling	Method: batch Capacity: 1 at a time Volume: ca 15 ml
Performance and Specifications	Electronics: Solid state Detectors: PMT's Readout: Readout data acquisition and display system, Programs stored in PRPM, 4K variable data in RAM, 1K, optional up to 64K Background Correction Monochromator: Modified Czerny-Turner - f16.8 at 200 nm Grating: 1180 lines/m blazed at 250 nm Range: -1000 nm, first order Dispersion: 2.0 nm/mm at exit slit Slits: Manual, continuously variable from 5 to 2000μ Stray light: 0.1% or better Resolution: Better than 0.1 nm

Gas Control:

Source: Inductively - coupled RF Argon Plasma

Frequency: 27.12 MHz
RF Generator Output: 2 KW
Modulation of RF Waveform: 1.0% forward power regulator

Operation

Calibration: Included in solftware
Maintenance:
Training Avail./required: Provided with instrument

Requirements

Power: Spectrometer
RF Power Supply: 200-260 VAC, 50-60 Hz, 15 amps; provides: 17.5KHz, 3000 VDC, 1A
Water: self contained
Temperature: 21°C ± 5°
Humidity: below 60%
Dimensions: Height 60 cm, depth 60 cm, width 125 cm
Weight: 160 K

Features

RF Plasma Source
Scanning Monochromator
LED display
Model 1000C, Computer-Date Acquisition System

Options

Printer Model 43 TTY
Nebulizers: Cross Flow
Concentric Class
Ultrasonic
Automatic Sampler for 50 samples

References

Manufacturer's Specifications

Cost

PlasmaScan, Model 700 manual control	$ 20,000
- With microprocessor controlled scanning line peaking and visual readout	35,000

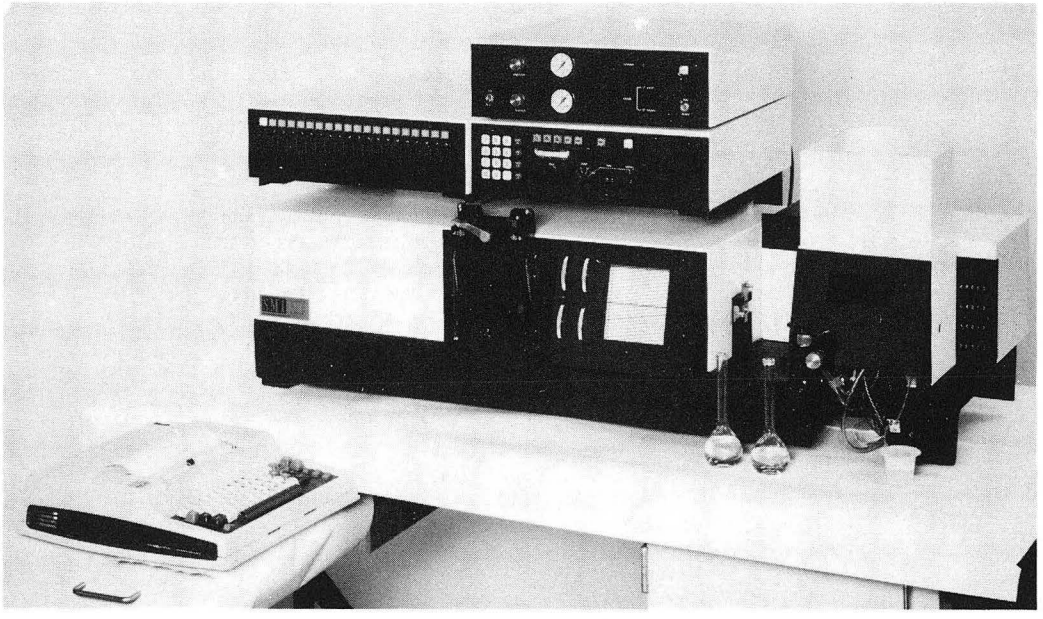
Address

Labtest Equipment Company
Subsidiary: Systron Donner Crop.
11828 LaGrange Ave.
Los Angeles, CA 90025
(213) 478-2518

INSTRUMENTATION
FOR ENVIRONMENTAL
MONITORING

Atomic Emission Spectrophotometer

SpectraSpan III



Class	Laboratory
Description	Computer controlled, dc plasma atomic emission spectrophotometer using an echelle grating
Modes of Operation	Atomic Emission
Lower Limit of Detection	SPECTRASPAN ATOMIC EMISSION INSTRUMENTATION

Typical Detection Limits
(All Concentrations in µg/ℓ)

Element	
Ag	1.0
Al	1.0
B	2.5
Ba	1.0
Be	0.5
Bi	50.0
Ca	1.0
Cd	2.0
Co	2.0
Cr	4.0
Cu	1.0
Fe	10.0
Li	5.0
Mg	1.0
Mn	1.0
Mo	5.0
Na	1.0
Ni	10.0
P	50.0
Pb	30.0
Si	10.0
Sr	.5
V	5.0
Zn	2.0

Range and Sensitivity

Interferences

Multiparameter Capability: 20 elements simultaneously, or sequential
interchangable optical cassettes for multiple analytical programs

Sampling: Single sample at one time, uptake approx. 3 mℓ/min

Performance and Specifications:

Electronics:

Detector: Photomutiplier tubes R292, R274, R368
Integration: optional routine on microcomputer
Zero drift: standard routine on microcomputer
Readout: digital display with optional printer
Background: optional routine on microcomputer

Polychromator: Modified Czerny Turner with Echelle grating and 30° prism for order separation, 0.75 m focal length
Grating: 79 grooves/mm
Dispersion: 200 nm, 0.61 Å/mm
400 nm, 1.22 Å/mm
800 nm, 2.44 Å/mm
Range: 190-800 nm
Aperture: f/15

Gas Control: Argon

Purity: welder's grade
Consumption: approx. 7 liter/min.
Regulator: included
Nebulizer: pneumatic
Venting: recommended

Source: Spectrajet III dc argon plasma jet in a Y configuration

Output: Current: 14 amps non-adjustable
Voltage: 100V maximum
Normal operating power: 115V, 50/60

Operation:
Calibration: with standards, standard routine on micro-computer
Maintenance: diagnostics standard routine in microprocessor
Training: available

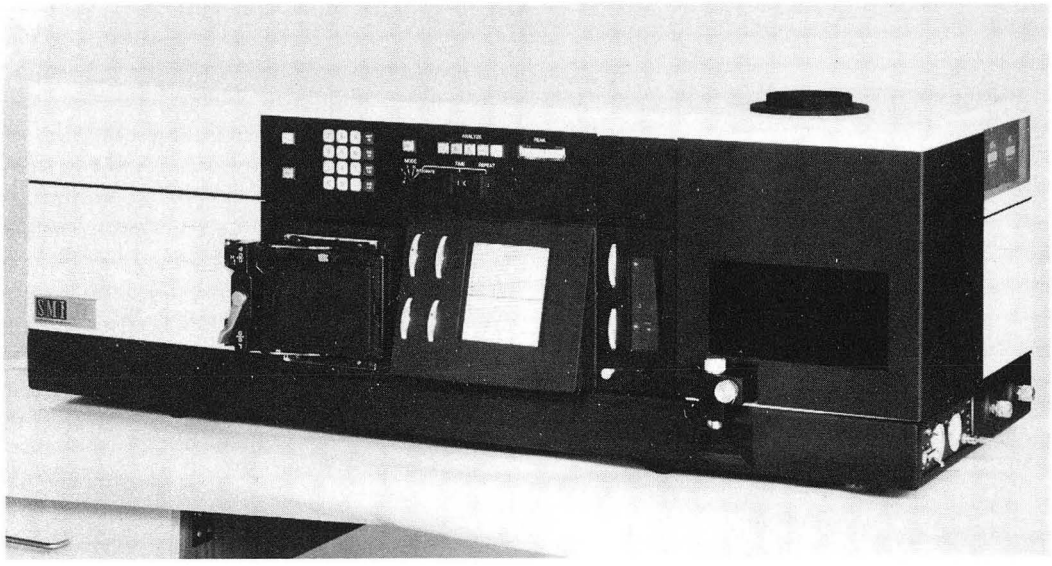
Requirements:
Power: Spectrometer and Source: 115V, 50/60 Hz, 20 amp
Water:
Temperature: standard analytical laboratory conditions
Humidity: standard analytical laboratory conditions
Dimensions: 122 cm L × 45.7 cm W × 76 cm H (48"L × 18" W × 30" H)
Weight: 350#

Features:
Echelle Grating
Micro-computer controlled
Multiple routines
Photographic, sequential, multielement analysis, dc plasma source - spectra jet (3) - Y configuration
20 element simultaneous determination
multiple optical cassettes for multiple analytical programs

Options	Photographic attachment	$ 1375
	Sequential measurement cassette	575
	Additional multi-element cassettes with 20 elements	4500
References	Manufacturer's Specifications	
Cost	SpectraSpan III with 20 element multichannel system (without options)	49,155
Address	Spectrametrics Incorporated 204 Andover Street Andover, MA 01810 (617) 475-7015	

Atomic Emission Spectrophotometer

SpectraSpan IV



Class	Laboratory
Description	Microprocessor controlled, dc plasma sequential atomic emission spectrophotometer utilizing an echelle grating
Modes of Operation	Atomic Emission
Lower Detectable Limit	SPECTRASPAN ATOMIC EMISSION INSTRUMENTATION

Typical Detection Limits
(All Concentrations in µg/ℓ)

Element	
Ag	1.0
Al	1.0
B	2.5
Ba	1.0
Be	0.5
Bi	50.0
Ca	1.0
Cd	2.0
Co	2.0
Cr	4.0
Cu	1.0
Fe	10.0
Li	5.0
Mg	1.0
Mn	1.0
Mo	5.0
Na	1.0
Ni	10.0
P	50.0
Pb	30.0
Si	10.0
Sr	.5
V	5.0
Zn	2.0

Range and Sensitivity

Interferences

Multiparameter Capability: Single samples at one time, sequential elements

Sampling:
Method: sequential
Volume: 3 mℓ/min

Performance and Specifications:

Electronics:
Linearity:
Stability:
Damping:
Detector: photomultiplier tubes, R292, R-274, R368
Integration: standard routine in microprocessor
Zero drift: standard routine in microprocessor
Readout: digital
Background: optional routine on microcomputer

Monochromator: modified Czerny-Turner mounting with echelle grating (0.75 m focal length) and 30° quartz prism for order separation
Grating: 79 grooves/mm
Dispersion: 200 nm: 0.61 Å/mm; 400 nm:1.22 Å/mm; 800 nm: 2.44 Å/nm
Range: 190-800 nm
Spectral bandpass: entrance and exit slits adjustable

Gas Control: Argon
Purity: Welder's grade
Consumption: approx. 7 liter/min.
Regulator: included
Nebulizer: pneumatic

Source: Spectrajet III dc argon plasma jet
Ignition power: push button
Operating power: 14 amps - 100V maximum
Input power: 115 V, 50/60 Hz, 20 amp.

Operation:
Calibration: By standards
Maintenance: Diagnostics standard routine in microprocessor
Training required/available: available

Requirements:
Power Spectrometer and Source: 115V, 50/60 Hz, 20 amp.
Dimensions: 122 cm L × 47 cm W × 46 cm H (48"L × 18 1/4"W ×18" H)
Weight: 225#
Temperature: standard analytical laboratory conditions
Humidity: standard analytical laboratory conditions

Features:
Echelle grating prism order separator
dc Argon plasma source
Microprocessor based readout system
Adjustable entrance and exit slits

Options:

Photographic attachment	$ 1000
Polaroid camera back	100
Printer	2000
Mercury lamp	220

References	Manufacturer's Specifications	
Cost	SpectraSpan IV	$ 15,925.00
Address	Spectrametrics, Incorporated 204 Andover Street Andover, MA 01810 (617) 475-7015	

TABLE OF
ULTRAVIOLET VISIBLE ABSORPTION INSTRUMENTATION

Instrument	Beams	Wavelength Range (nm)	Wavelength Accuracy	Cost	Remarks
American Instrument Co.					
DW-2a™	Double beam	200-825	Within 0.2nm	$25,000	Dual wavelength, scanning, digital
Fluorocolorimeter	Single beam	300-700 (200-750, opt.)	—	1,750	Filter photometer, manual meter readout
Bausch and Lomb					
Mini 20	Single beam	400-800	± 3nm @ 546nm	545	Meter readout, manual, portable
Spectronic® 20	Single beam, ratio recording	340-600 (340-900, opt.)	2.5 nm	690	Meter readout, manual
Spectronic® 70	Single beam, ratio recording	325-925	1.0 nm	—	Meter readout, manual
Spectronic® 88	Single beam, ratio recording	325-925	1.0 nm	1,755	Meter readout, manual
Spectronic® 100	Single beam, ratio recording	325-925	1.0 nm	2,895	Digital, manual
Spectronic® 710	Single beam, ratio recording	200-1000	1.0 nm	3,850	Digital, manual
Spectronic® 400 Series	Single beam, ratio recording	325-925 200-1000	1.0 nm	—	Digital, automated, semiautomated
Spectronic 21 Series					
UV-D	Single beam, ratio recording	200-1000	Better than 2 nm	2,260	Meter readout
UV-M	Single beam, ratio recording	200-1000	Better than 2 nm	1,950	Digital
DV	Single beam, ratio recording	340-1000	Better than 2 nm	1,745	Digital
MV	Single beam, ratio recording	340-1000	Better than 2 nm	845	Meter readout

(continued)

TABLE OF
ULTRAVIOLET VISIBLE ABSORPTION INSTRUMENTATION
(continued)

Instrument	Beams	Wavelength Range (nm)	Wavelength Accuracy	Cost	Remarks
Bausch and Lomb (cont'd)					
Spectronic 200 (Shimadzu)	Double	200-800	± 0.5 nm	$ 6,000	Scanning, meter readout
Spectronic 210 (Shimadzu)	Double	200-900	± 0.5 nm	7,500	Scanning, digital
Beckman					
Model 24	Double	340-700 (190-1000, opt.)	± 0.5 nm	4,580	Digital, scanning
Model 25	Double	190-700 (190-1000, opt.)	± 0.5 nm	6,730	Digital, scanning
Model 26	Double	190-900 (190-1000, opt.)	± 0.5 nm	7,300	Digital, scanning
Model 34	Double	340-700 (190-700, opt.)	± 0.5 nm	5,200	Digital, scanning
Model 35	Double	190-700	± 0.5 nm	7,400	Digital, scanning
Model 3600	Double	190-900	± 0.25 nm	11,025	Digital, scanning, recording, holographic grating
Model 5230	Double beam, ratio recording	190-800	± 0.5 nm	14,000	Recording, scanning and digital, single monochr., holographic grating
Model 5240	Double beam, ratio recording	190-3000	± 0.5 nm (190-800 nm)	21,350	Recording, scanning and digital, single monochr., holographic grating
Model 5260	Double beam, ratio recording	190-800	± 2.5 nm (800-3000 nm)	15,750	Recording, scanning and digital, double monochr.
Model 5270	Double beam, ratio recording	190-3000	± 0.1 nm (190-800 nm) ± 0.5 nm (800-3000 nm)	27,300	Recording, scanning and digital, double monochr.

(continued)

TABLE OF
ULTRAVIOLET VISIBLE ABSORPTION INSTRUMENTATION
(continued)

Instrument	Beams	Wavelength Range (nm)	Wavelength Accuracy	Cost	Remarks
Brinkman					
Probe Colorimeter					
Model PC/600	Probe	420-800 (selected)	Std. interference filters	$ 795 without filters	Analog meter display, field or lab.
PC/600D	Probe	420-800 (selected)	Std. interference filters	1,395 without filters	Digital, field or lab.
PC/1000	Probe	420,470,520,545 620,650	Std. interference filters	1,095-1,295	Analog meter, field or lab.
GCA/MacPherson					
700 Series, modular System					
701-D	Single beam	185-1000 (4000 opt.)	0.1 nm	6,435	Modular system
707-D	Double beam	185-1000 (4000 opt.)	0.1 nm	8,575	Modular system
721-D	Double beam via alternating cell	185-1000 (4000 opt.)	0.1 nm	6,925	Modular system
Gilford					
StasarI	Single beam	300-700	± 2 nm	2,150	Digital, manual
StasarII	Single beam	300-700	± 2 nm	2,850	Digital, manual
StasarIII	Single beam	300-700	± 2 nm	3,750	Digital, manual
Model 250	Single beam	184-800	± 0.5 nm (180-400 nm) ± 1.0 nm (400-800 nm)	6,700	Digital, modular
Model 252-1	Single	200-800	0.1 nm - UV 0.4 nm - Vis	4,400	Updating system for Beckman® DU
252-1	Single	200-800	0.1 nm - UV 0.4 nm - Vis	4,400	Updating system for Beckman® DU-2

(continued)

TABLE OF
ULTRAVIOLET VISIBLE ABSORPTION INSTRUMENTATION
(continued)

Instrument	Beams	Wavelength Range (nm)	Wavelength Accuracy	Cost	Remarks
Perkin-Elmer					
Model 55	Single	300-810 nm (190-900 nm)	± 1 nm	$ 3,700	Digital, manual
Model 200	Double	190-900	± 0.5 nm	6,250	Digital, scanning
Model 550	Double	315-800 (190-800, opt.)	± 0.5 nm	5,150	Digital, scanning
Model 340	Double	190-2600	Better than 0.2 nm (UV-vis) 1 nm (NIR)	26,400	Microprocessor controlled, double monochromator, recording, scanning
Model 552	Double	190-750 (190-900, opt.)	± 0.5 nm	7,400	Recording, scanning, microprocessor controlled
Model 554	Double	190-900	± 0.5 nm	13,950	Recording, scanning, microprocessor controlled
Model 555	Double	190-900	± 0.5 nm	15,500	Recording, scanning, microprocessor controlled with premonochromator
Model 557	Double beam, dual wavelength	190-900	± 0.4 nm	31,350	Microprocessor controlled, scanning, recording, analog or digital
Model 571	Double	190-750 (190-900, opt.)	± 0.5 nm	9,500	Scanning, recording, high resolution
Model 572	Double	190-750 (190-900, opt.)	± 0.5 nm	11,980	Scanning, recording, high resolution
Model 575	Double	190-900	± 0.5 nm	11,000	Scanning, recording, high resolution
Model 576	Double	190-900	± 0.5 nm	12,500	Scanning, recording, high resolution

(continued)

TABLE OF
ULTRAVIOLET VISIBLE ABSORPTION INSTRUMENTATION
(continued)

Instrument	Beams	Wavelength Range (nm)	Wavelength Accuracy	Cost	Remarks
Perkin-Elmer (cont'd)					
Coleman Junior-JuniorII, 6/20 6/35	Single	335-825	± 1 nm @ 610 nm	$ 1,050	Manual, meter or galvanometer readout
JuniorIIA	Single	335-825	± 1 nm @ 610 nm	1,180	Manual, meter of galvanometer readout
JuniorIII	Single	335-825	± 1 nm @ 610 nm	1,210	Manual, meter of galvanometer readout
Model 35	Single	335-825	± 1 nm @ 365, 436, 546 & 630 nm	1,400	Digital
Model 295	Single	400-700	± 1 nm @ 585 nm	605	Meter readout, manual
Pye Unicam					
SP6-200	Single	325-1000	Within 1 nm	1,995	Meter readout, manual
SP6-300	Single	325-1000	Within 1 nm	2,350	Digital, manual
SP6-400	Single	200-1000	Within 1 nm	2,350	Meter readout, manual
SP6-500	Single	200-1000	Within 1 nm	2,725	Digital, manual
SP8-100	Double	190-900	± 0.5 nm	8,950	Scanning, digital, recording
SP8-200	Double	185-950	± 0.5 nm	—	Microprocessor controlled, digital, scanning, recording

(continued)

TABLE OF
ULTRAVIOLET VISIBLE ABSORPTION INSTRUMENTATION
(continued)

Instrument	Beams	Wavelength Range (nm)	Wavelength Accuracy	Cost	Remarks
Shimadzu					
Model UV 100-01	Single	325-1000	± 2 nm	$ 1,660	Meter readout, manual
Model UV 100-02	Single	200-1000	± 2 nm	2,200	Meter readout, manual
Model UV 110-01	Single	325-1000	± 2 nm	2,360	Digital, manual
Model UV 110-02	Single	200-1000	± 2 nm	2,900	Digital, manual
Model UV 140-01	Double	325-1000	± 0.1 nm	2,500	Meter readout, manual
Model UV 140-02	Double	200-1000	± 0.1 nm	2,850	Meter readout, manual
Model UV 150-01	Double	325-1000	± 0.1 nm	3,200	Digital, manual
Model UV 150-02	Double	200-1000	± 0.1 nm	3,550	Digital, manual
Model UV 200S	Double	190-900	± 0.3 nm	6,000	Scanning, meter readout
Model UV 210A	Double	190-900	± 0.3 nm	7,500	Scanning, digital
Technicon					
AutoAnalyzerII	–	–	–	$12,045	One channel
				15,155	One channel, digital
				17,485	Two channels
				22,515	Two channels, digital
				23,530	Three channel
				30,380	Three channels, digital

(continued)

TABLE OF
ULTRAVIOLET VISIBLE ABSORPTION INSTRUMENTATION
(continued)

Instrument	Beams	Wavelength Range (nm)	Wavelength Accuracy	Cost	Remarks
Technicon (continued)					
MonitorIV	–	–	–	Contract	AutoAnalyzer
Turner					
Model 330	Single	320-710 (210-1000, opt.)	± 2 nm	780	Meter readout, manual
Model 350	Single	320-710 (210-1000, opt.)	± 2 nm	940	Meter readout, manual
Model 380	Single	320-710 (210-710, opt.)	± 2 nm	1,725	Digital, manual
Varian					
Model 634UV	Double	190-900	± 0.5 nm	5,450	Manual, digital
Model 634S	Double	190-900	± 0.5 nm	5,950	Scanning, digital
Cary Model 17D	Double	186-2650 (186-3000, opt.)	± 0.4 nm	31,995	Scanning, double (grating & prism) monochromator & digital, recording
Cary Model 219	Double	187-875	± 0.2 nm	12,995	Direct, ratio recording, recording, scanning, double-pass monochromator
SuperScan 1 BE	Double	200-900	± 0.2 nm	9,975	Digital, scanning
SuperScan 2	Double	200-900	± 0.2 nm	9,250	Digital, recorder, scanning
SuperScan 3	Double	200-900	± 0.2 nm	7,620	Digital, recorder, scanning

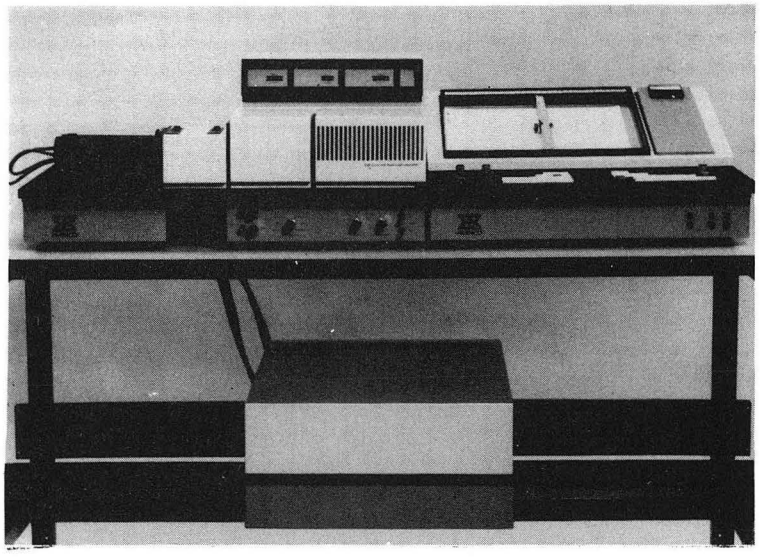
(continued)

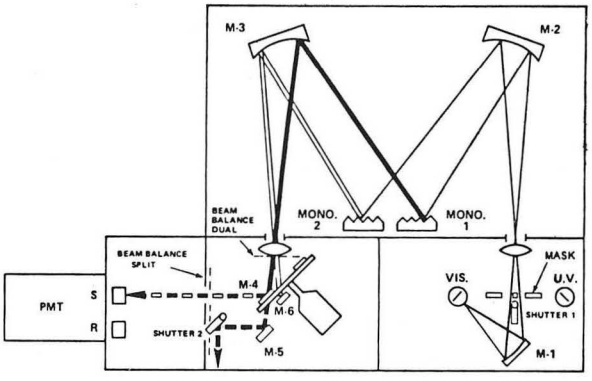
TABLE OF
ULTRAVIOLET VISIBLE ABSORPTION INSTRUMENTATION
(continued)

Instrument	Beams	Wavelength Range (nm)	Wavelength Accuracy	Cost	Remarks
Carl Zeiss					
DM 4	Double	190-850	± 0.5 nm	$ 7,173	Digital, scanning (opt.) ratio recording
PM 2 DL	Single	200-850	± 1 nm	1,606-1,730	Digital
PM 6 P, PM	Single	200-850	± 0.5 nm	7,967,–	Digital, scanning
PM 6 T	Single	200-850	± 0.5 nm	4,935	Digital, scanning
PM 6 K	Single	200-850	± 0.5 nm	5,129	Digital, scanning
PM 6 KS	Single	200-850	± 0.5 nm	7,270	Digital, scanning

Ultraviolet-Visible Spectrophotometer

American Instruments, DW-2a™





Class	Laboratory
Description	Double beam, dual wavelength, dual wavelength scanning ultraviolet-visible spectrophotometer (200-825 nm)
Modes of Operation	Double beam, dual wavelength Absorbance, Transmittance, First derivative, kinetics
Lower Detectable Limit	ppb to %, depends on chemical method and path length
Range	ppb to % - depends on chemical method and path length
Interferences	Depends on chemical method
Multiparameter Capability	Colorimetric, turbidimetric, kinetics, spectrophotometry
Sampling	Method: Batch Volume: 3 mℓ standard, other with accessories Temperature Control: Yes, removable quartz diffuser plate Maximum Cell Length: 100 mm Turbidity Position: Yes

Performance and Specifications

Electronics:

Linearity: DW-2a-linear from -0.6A to 3.0A
Photometric Stability: At 550 nm, 3nm bandpass -< 0.0004A/hr
Photometric Accuracy: ± 0.002A deviation from standard with NBS filter 3

Noise: Full scale ordinate sensitivity of 0.005, maximum level will be 0.0002A at 550nm with 3nm bandpass
Scale Expansion: 2.0, 1.0, 0.5, 0.2, 0.1, 0.05, 0.02, 0.01, 0.005A full scale 100%, 50%, 25%, 10%, 5%, 2.5%, 1% T full scale
Detector: PMT (photomultiplier) with S-20 response
Base line flatness: - ± 0.0025A over range (200-825)
± 0.00025/2 with MIDAN accessory
Zero Drift: ± 0.00025/hr
Readout: Recorder DW-2a - electrostatic, autoscan
External Output: DW-2a analog and digital
Warm Up: 1 hr normal/max. 1 1/2
Response: 50 msec, 185 msec, 2.2 sec at 0.005A, 0.01A, 0.02A
0.5 msec, 5 msec, 140 msec for all other ranges

Optical System: 2 modified Czerny Turner monochromators

Grating: 600 grooves/mm, blazed at 300nm
Wavelength Range: 200-825 nm
Wavelength Accuracy: Within 0.2 nm
Wavelength Reproducibility: Within ± 0.1 nm
Resolution: Bandpass 0-17 nm in 0.02 increments, digital readout; < 0.3 nm measured at half peak of D_2 486 nm line
Slits:
Dispersion: 5.5 nm/mm
Scan Speeds: Manual or auto, 0.1, 0.5, 1.0, 2.0, 5, 10, 20 nm/sec or 100, 50, 20, 10, 5, 2, 1, and 0.5 sec/in.
Stray Light: < 0.2% at 200 nm
Light Source: Deuterium and tungsten iodide
Power Supply: DW-2a - 30 watts
Optical Chopper: Two speed, operates at 250 Hz in normal mode and at 1000 Hz in kinetic mode

Operation

Calibration: Standards, calibration filter supplied
Training: Required - about 4 hours
Maintenance: Monitor electronic circuits at 16 points, factory and field service
Unattended Period: Possible with autoscan

Requirements

Power: 115 VAC, 50/60 Hz, 700 watts
Weight: Optical Assembly - 75 kg (170 lbs), Recorder - 48 kg (110 lbs) power supply - 57 kg (130 lbs)
Dimensions: Optical Unit and Recorder - 153 cm W × 76 cm D × 61 cm H (5'×2.5'×2')
Power Supply: 76 cm × 61 cm × 46 cm H (2.5'×2'×1.5')
Temperature: Normal lab. conditions
< 85°C

Features

Double-beam, dual beam operation
Absorbance, transmittance, first derivative kinetics modes

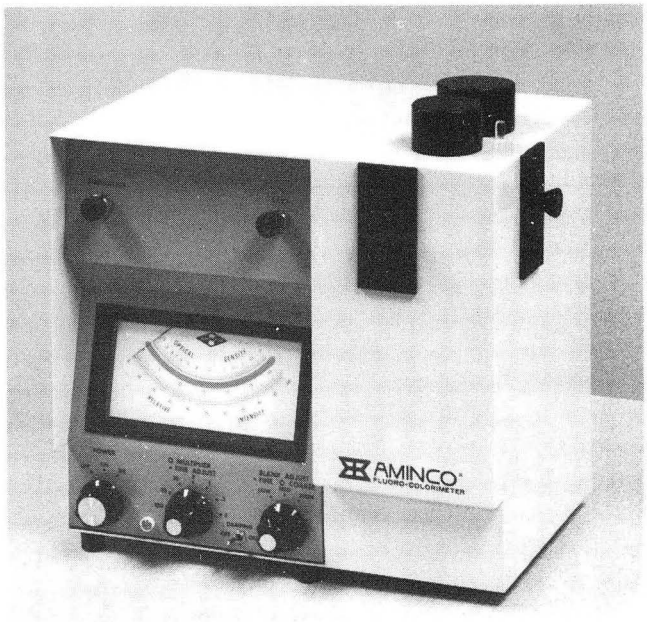
Options

Anaerobic Cell	$ 1150
Stopped-Flow	3690
Lower Temperature	852
Oxygen Electrode	845
Long Path Cell Holder	160
Solid Sample	2120
Filter Holder	83
1 × 2 cm Cell Holder	207
Infrared	900
Variety of Cells	63-126
Total Fluorescence Accessory	1320
Digital Readout	990

Options (continued)	DASAR® Data Aquisition, Storage and Retrieval System	$7875
	DASAR® Interface	1500
References	Manufacturer's Specifications	
Cost	DW-2a	$25,000
Address	American Instrument Company Division of Travenol Lab 8030 Georgia Avenue Silver Spring, MD 20910 (301) 589-1727	

Visible, Absorbance, Fluorescence Spectrometer

Aminco Fluorocolorimeter



Class	Laboratory
Description	Single beam fluorimeter-colorimeter
Modes of Operation	Absorbance, Transmittance, optical density
Lower Detectable Limit	Depends upon element and chemical method used
Range	0-100 relative fluorescence, 0-100%T, 0-2A
Interferences	Depends on metal and chemical method used
Multiparameter Capability	Colorimetry, Fluorimetry, Turbidimetry, Nephelometry
Sampling	Method: Batch, automation option (fluoro, nephel, applications) Volume: Various Temperature Control: Optional Maximum Cell Length: 75 mm Turbidity Position: Yes
Performance and Specifications	Electronics: Linearity: N/A Photometric Stability: N/A Photometric Accuracy: N/A Noise Level: N/A Scale Expansion: 7 steps - 100, 30, 10, 3, 1, 0.3, 0.1 full scale Detector: Photomultiplier Tube, Type 931B (many others opt.) Zero Drift: N/A Readout: Meter, in optical density, relative intensity External Output: Analog 0-50 mV, 0-1 volt Response: 300 microseconds, 2 seconds

Performance and Specifications (continued)	Optical System: Filters: Primary - Corning 7-60; secondary - Wratten 2A, others, optional Wavelength Range: 300-700 nm (200-750 nm opt.) Scan Speeds: Not available Stray Light: N/A Lamp: GE No. F4T4/BL, 4 watt. others opt.
Operation	Calibration: With standards Training: Minimal Maintenance: Minimal Unattended Period: None
Requirements	Power: 115 VAC, 50/60 Hz Weight: 20 lbs (packed) Dimensions: 8 1/2" D × 7 1/2" W × 14" H Temperature: Ambient Lab
Features	Low Cost, Multipurpose
Options	Variety of lamps, detectors, filters Digital Readout and Printout Flow Cells ATP determination adapter Micro Cells Recorders Sample changer Constant temperature sample holders
References	Manufacturer's Specifications
Cost	Fluorocolorimeter $1750
Address	American Instrument Company Division of Travenol Laboratories 8030 Georgia Avenue Silver Spring, MD 20910 (301) 589-1727

INSTRUMENTATION
FOR ENVIRONMENTAL
MONITORING

Spectrophotometer Bausch & Lomb Spectronic ® Mini 20

Class	Field
Description	Portable, battery powered single beam near UV-visible spectrophotometer, colorimeter (400-800 nm)
Modes of Operation	Transmission, overlays for absorbance, concentration
Lower Detectable Limit	Depends on chemical method and cell path length. Limits in the parts per billion range can be achieved.
Range	ppb to percent - depends on chemical method and pathlength
Interferences	Depends on chemical method
Multiparameter Capability	Spectrophotometric, colorimetry, nephelometry
Sampling	Method: Batch, 0.5 in test tubes, flat bottom cuvettes, 10 mm or 25 mm rectangular cuvettes

Minimum Volume of Solution:

Cuvette	Min. Vol.
1/2" test tube	1.3 ml
1/2" flat bottom cuvette	1.8 ml
10 mm square	1.6 ml
25 mm long path	3.2 ml

Temperature control: No
Path length: 1 mm to 25 mm
Turbidity position: Optional; a nephelometer attachment is available for the Mini 20.

Performance

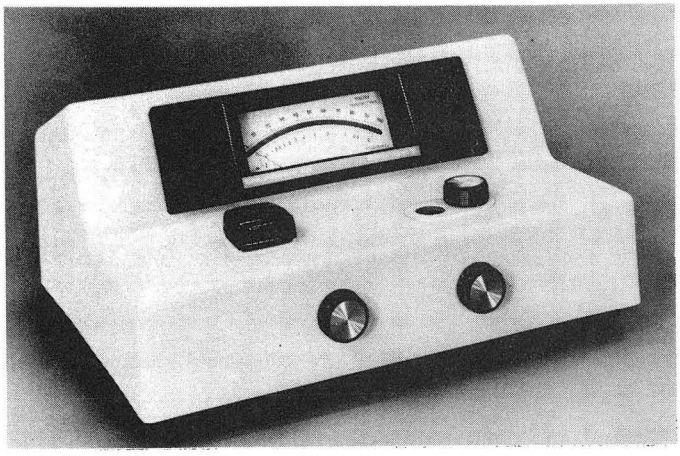
Electronics:

Meter Linearity: ±2 T
Stability: N/A
Photometric Accuracy:
Scale Expansion: None
Detector: Photo Resistor
Zero Suppression: No

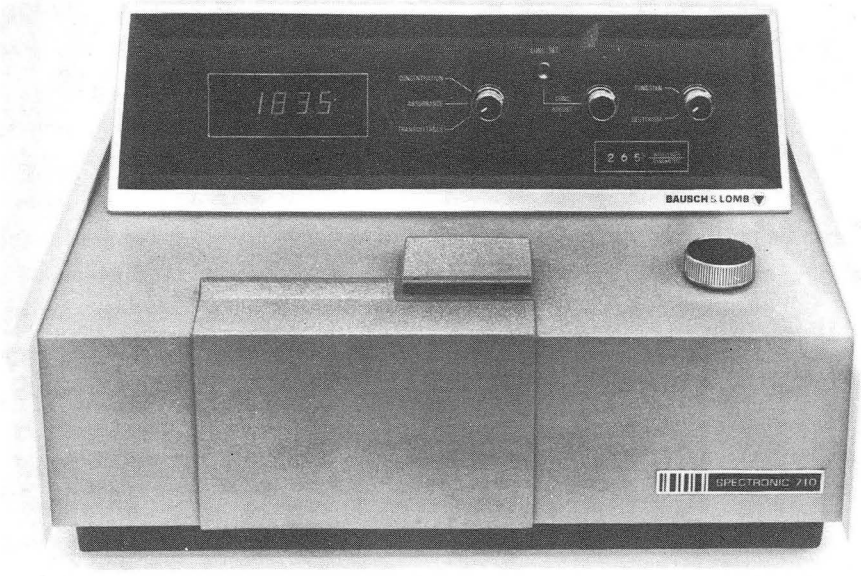
Performance (continued)	Noise: Readout: Meter in % T External Output: 0.5V (analog) Warm-Up: 10 seconds
	Optical System Grating: 600 grooves/mm Dispersion: Wavelength Range: 400-800 nm Wavelength Accuracy: ± 3nm at 546 nm Wavelength Reproducibility: 1 nm Resolution: 20 nm bandwidth Slits: Scan Speeds: Not available Stray light: Light source: Tungsten bulb Power supply: Battery included
Operation	Calibration: Standard samples Training: Manual available Unattended Period: Not automated Maintenace: Sample compartment is removable and waterproof. One year warranty.
Requirements	Power: Battery operated 3 hours of continuous use or 115 VAC, 50-60 Hz, or 230 VAC, 50-60 Hz, or 12 Vdc (automobile cigarette lighter) adapters Weight: 0.45 kg (1 lb) Dimensions: 15 cm × 9 cm × 5 cm (6 in. × 3.5 in.× 2 in.) Temperature: Operation - 0°C to 40°C Storage - 40°C to 66°C
Features	Field use instrument, rechargeable Single beam spectrometer Field carrying case, Instrument carrying case Sampling flexibility Light Weight Readout in transmission, overlays for absorbance, concentration
Options	Chart Recorder
References	Manufacturer's Specifications
Cost	Spectronic Mini 20 Suggested Price $ 545
Address	Bausch & Lomb, Inc. Analytical Systems Division 820 Linden Avenue Rochester, N.Y. 14625 (716) 385-1000

Colorimeter/UV-Visible Spectrometers

Bausch and Lomb, Spectronic ® 20, 70, 88, 100, 710 and 400 Series



Spectronic 20



Spectronic 210

Spectronic 100

Class

Laboratory

Description

Single/beam ratio recording, UV-visible spectrophotometers

Manual Instruments

Spectronic ® 20: Meter readout, 340-600 nm (900 nm, optional)
70,88: Meter readout, 325-925 nm
100: Digital, 325-925 nm
710: Digital 200-1000 nm

Automated and Semi Automated Instruments - 400 Series

400-2- Model 100 Spectrophotometer and printer
400-3- Model 100 Spectrophotometer, printer, and auto sampler
400-4- Model 100 Spectrophotometer, printer, auto sampler and diluter-pipettes
400-UV-Series (400 UV-2,3,4) as in the 400 Series but using the Model 710 spectrophotometer

Modes of Operation

Absorption, transmittance, optical density (88, 100 and 710 concentration)

Lower Detectable Limit

Depends on chemical method and path length. Limits in the part per billion range can be achieved

Range

ppb to %	20	70	88	100	710
Absorbance	0-2A log	0-2A log	0.-2A linear	0-2A linear	0-2A linear
Transmittance	0-100%	0-100%	0-100%	0-100%	0-100%
Concentration			0-100C	0-2000C	0-2000C

Interferences

Depends on chemical method

Multiparameter Capability

Spectrophotometric, turbidimetric, color, reflectance

Sampling

Method: Batch or semi automatic
Volume of sample versus cell size:
Spectronic 20: 1.25 cm (0.5")-3mℓ; 1.90 cm (0.75")-5 mℓ; 2.54 cm (1.0")-8 mℓ; microcuvette - 0.2 mℓ
Spectronic 70, 88, 100, 710

	Path Length	Min.Vol.
Test Tubes	10mm	2.5 mℓ
	20mm	10.0 mℓ
Short Path Cuvettes	1mm	0.02 mℓ
	2mm	0.04 mℓ
	5mm	1.0 mℓ
Cuvette	10mm	2.0 mℓ
Long Path Cell	50mm	14.2 mℓ
	100mm	28.4 mℓ

Capacity: 5 samples/min with semi automatic flow through
Turbidity position: No
Temperature control: Optional on 70, 88, 100, 700, 710

Performance and Specifications

Electronics: Solid State, integrated circuitry

Linearity:

Instrument #	20	70	88	100	710
Meter	± 1%	0.7%	0.7%		
Electronic		0.2%	0.2%		
Digital	—		—	0.2%	0.2%
Photometric:					
near 0A	—				
near 0.5	—		0.025	0.002A	0.002
near 1.0A	—		0.025	0.004A	0.005
near 1.5A	—		0.055	0.009A	0.008

Stability:

Instrument #	Zero Drift	100% Drift
20	1% full scale	
70,88,100,710	0.2%/day	0.2%/hour

Photometric Accuracy

Spectronic 20: Better than 2.0%T
Spectronic 70: 0.5%T
Spectronic 88: 0.5%T, 0.005A
Spectronic 100: 0.1%T, 0.001A
Spectronic 710: 0.5%T, 0.005A near 6.4A

Noise Level	%T	Near 0A	Near 1.0A	Near 1.5
20				
70	0.1%	0.001A		
88	0.1%	0.1%	0.001A	0.010A
100	0.1%	0.1%	0.001A	0.004A
710	0.1%	0.1%	0.001A	0.004A

Scale Expansion: 20, 70-not available
88,100,700,710: - 3x in concentration
Detector: 20, 70, 88, 100, - phototubes
710 - 1 phototube, 1 solid state
Zero Suppression:
Readout:

Instrument #	Form	A	%T	Conc.
20,70	meter	log	lin.	——
88	meter	lin	lin.	lin.
100,710	digital	lin	lin.	lin.

External Output: 20 standard - not available
20 (regulated), 70,88, 0-1 Vdc (nominal) analog
100,710 - 0-2 Vdc (nominal), analog
BCD (710-RTLBCD) Logic $0 \leq 0.4$ Vdc,
logic ≥ 0.8 Vdc

Warm Up: Less than 15 min.
Response:

Optical System

Grating: 20 - 600 grooves/mm blazed at 500 nm
70,88,100,710 - 1200 grooves/mm blazed at 300 nm
Dispersion:

Optical System (continued)

Wavelength Range: 20 - 340-600 m,. tp 900 nm with filter and phototube accessory
70,88,100 - 325-925 nm
710 - 200-1000
Wavelength Accuracy: 20-2.5 nm; all others - 1.0 nm
Wavelength Reproducibility: 20-1.0 nm; all others - 0.2 nm
Wavelength Precision: 710 - better than 0.3 nm
Scan Speeds: Not available
Stray Light: 0.5% (20 - over entire range; 70,88,100 @ 340 nm, 710 @ 220 nm)
Resolution: 20 - 20 nm
70,88,100 - 8 nm
710 - 2 nm
Slits:
Light Source: 20, 70, 88, 100 - tungsten
710 - deuterium (200-360), tungsten (360-950 or 1000)
Power Supply: Built-in

Operation

Calibration: Standard samples
Training: Manual available
Unattended Period: Not completely automatic
Maintenance: Minimal (20 - liquids can be drained out of bottom of sample compartment), service centers throughout U. S. Warranty, service contract available

Requirements

Power: 20 standard (115 VAC) 60 Hz, 40 watts
All Others: 100, 115, 220, 240 VAC, 50/60 Hz, 90-100 watts depending on model

Dimensions and Weight

Instrument #	Width	Depth	Height	Weight
20	42.5 cm (17")	38.8 cm (15 1/2")	25 cm (10")	8.2 kg (18 lbs)
70,88	43 cm (17")	34 cm (13.5")	25 cm (10")	15.9 kg (35 lbs)
100	43 cm (17")	34 cm (13.5")	25.4 cm	17.2 kg (38 lbs)
710	43 cm (16.25")	39.4 cm (13.25")	(8.25")	18.6 kg (41 lbs)

Features

Single beam, ratio recording spectrometer
Easy to use
Adaptable sampling (70, 88, 100, 710)
Meter Readout (20,70,88)
Digital Readout (100, 710)

Options (70,88,100,700,710)

10" strip chart recorder
Single sample compartment
Multiple sample compartment
Semi automatic flow through compartment
Automatic cell positional
DR-37 digital readout
Thermo regulated multiple sample holder

References

Manufacturer's Specifications

Cost

Spectronic® 20 (regulated)	690
Spectronic® 88	1755
Spectronic® 100	2895
Spectronic® 710	3850

Address

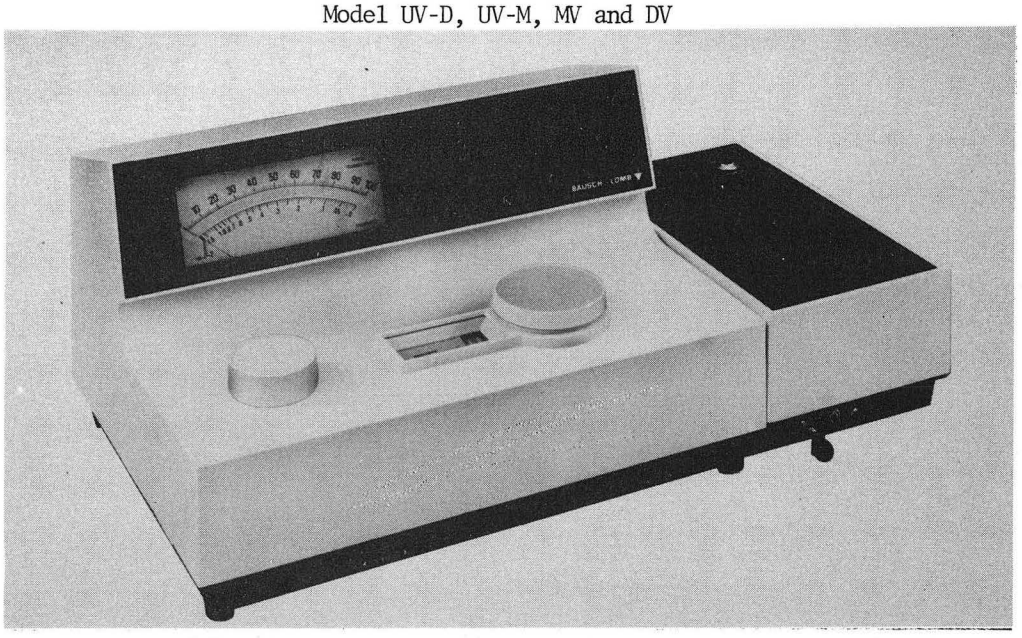
Bausch and Lomb, Inc.
Analytical Systems Division
820 Linden Avenue
Rochester, N.Y. 14625
(716) 385-1000

INSTRUMENTATION
FOR ENVIRONMENTAL
MONITORING

Ultraviolet/Visible Spectrophotometer, Colorimeter

Bausch & Lomb, Spectronic ® 21 Series

Model UV-D, UV-M, MV and DV



Class	Laboratory
Description	A series of spectrophotometers with UV, visible or visible ranges and digital or meter readout Model UV-D- digital, 200-1000 nm UV-M- meter, 200-1000 nm DV - digital 340-1000 nm MV - meter, 340-1000 nm
Modes of Operation	Digital Models (UV-D and DV) linear transmittance, absorbance and concentration Meter Model (UV-M,MV) linear transmittance, nonlinear absorbance
Lower Detectable Limit	Depends on chemical method, metal and path length
Range	Absorbance: 0-2A Transmittance: 0-100% Concentration: DV,UV-D,: 0-2000C
Multiparameter Capability	Spectrophotometry, colorimetry
Sampling	Method: Batch Cells: Cuvettes, test tubes, semimicro-standard volume, flow through, multiple cell position Temperature: thermostat Pathlength: 1-25 mm available
Performance and Specifications	Electronics: Solid state, plug-in circuit boards Photometric linearity: Better than 0.2%T (0.0002 near 0.5A) Stability: Auto Zero T Photometric accuracy: 0.3% (0.003A near 0.4A) Noise: < 0.001A near 0.004 Scale expansion: Detector: Solid state photodetector Zero Suppression Readout: UV-D, DV-digital, linear in A, %T and concentration UV-M,-MV meter, %T and A available

Performance and Specifications (continued)

External Output: UV-D, DV - BCD and Analog (0-1 Vdc)
UV-M,MV Analog 0-1 V

Warm Up:
Response:

Optical System:

Grating:
Dispersion
Wavelength range: UV-D, UV-M-200-1000 nm
DV-340-1000 nm
Wavelength accuracy: Better than 2 nm
Wavelength reproducibility:
Spectral Slit Width: 10 nm
Stray Light: DV, MV - < 0.3%T at 340 nm
UV-D. VV-M- < 0.3%T at 220 nm

Operation

Calibration: Standard solutions
Training: Manual available
Unattended Period: Not completely automatic
Maintenance: Minimal

Requirements

Power: 110/115, 220/240V, 50/60 Hz
Dimensions: DV,MV - 36.8 cm W × 26.7 cm D × 21.6 cm H
UV-D, UV-M- 50.8 cm W × 26.7 cm D × 21.6 cm H
Weight: DV,MV- 7.5 kg
UV-D, UV-M- 10 kg

Features

Large sample handling capabilities with general purpose sample compartment

Options

Strip Chart Recorder
Data Processor

References

Manufacturer's Specifications

Cost

Spectronic® 21, spectrophotometer

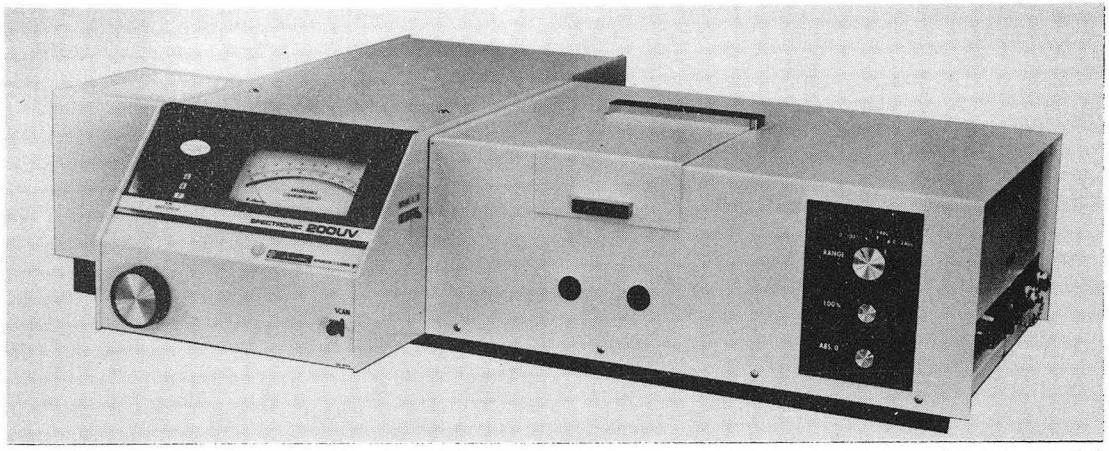
Model UV-D	$2260
Model UV-M	1950
Model DV	1745
Model MV	845

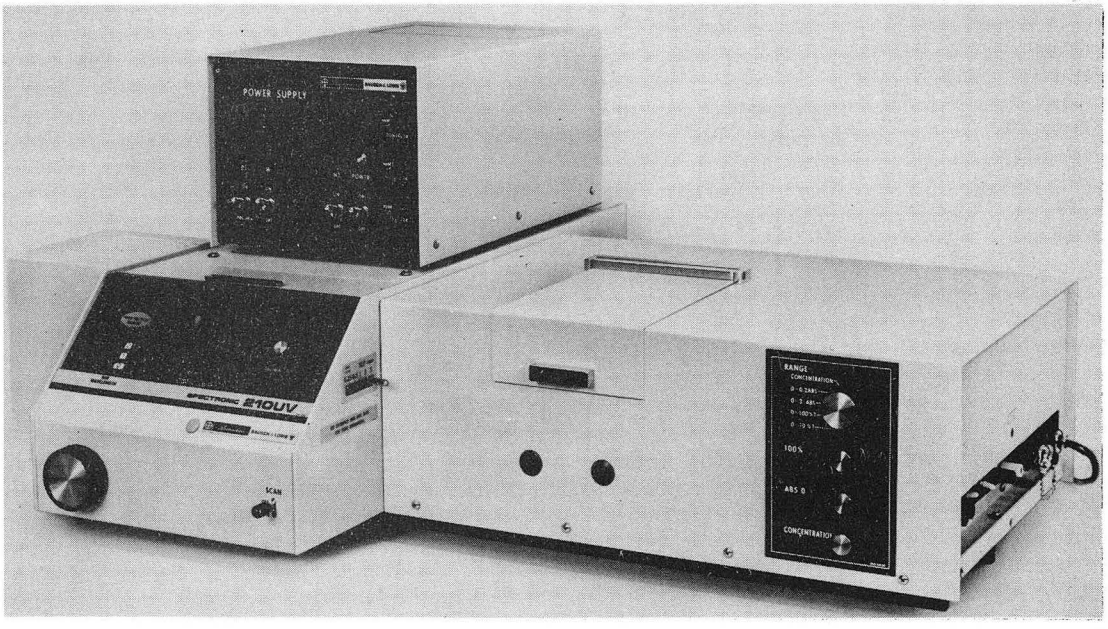
Address

Bausch and Lomb, Inc.
Analytical Systems Division
820 Linden Avenue
Rochester, N.Y. 14625
(716) 385-10000

Ultraviolet/Visible Spectrophotometer

Bausch & Lomb/Shimadzu Spectronic ® 200, 210





Class	Laboratory
Description	Double beam UV-visible spectrophotometer manufactured by Shimadzu Model 200-meter, 200-800 nm Model 210-digital, 200-900 nm
Modes of Operation	Model 200-absorbance, % transmission Model 210-absorbance, % transmission, concentration
Lower Detectable Limit	Depends on chemical method and cell pathlength
Range	Absorbance: Model 200 - 0-2.00A, 0-1.00 (linear) Model 210 - 0-2.00A, 0-0.2A (linear) Transmittance: Model 200 - 0-100%T (linear) Model 210 - 0-100%T, 0-10% (linear) Concentration: Model 210 - 0-1999, selectable decimal point
Interferences	Depends upon chemical method

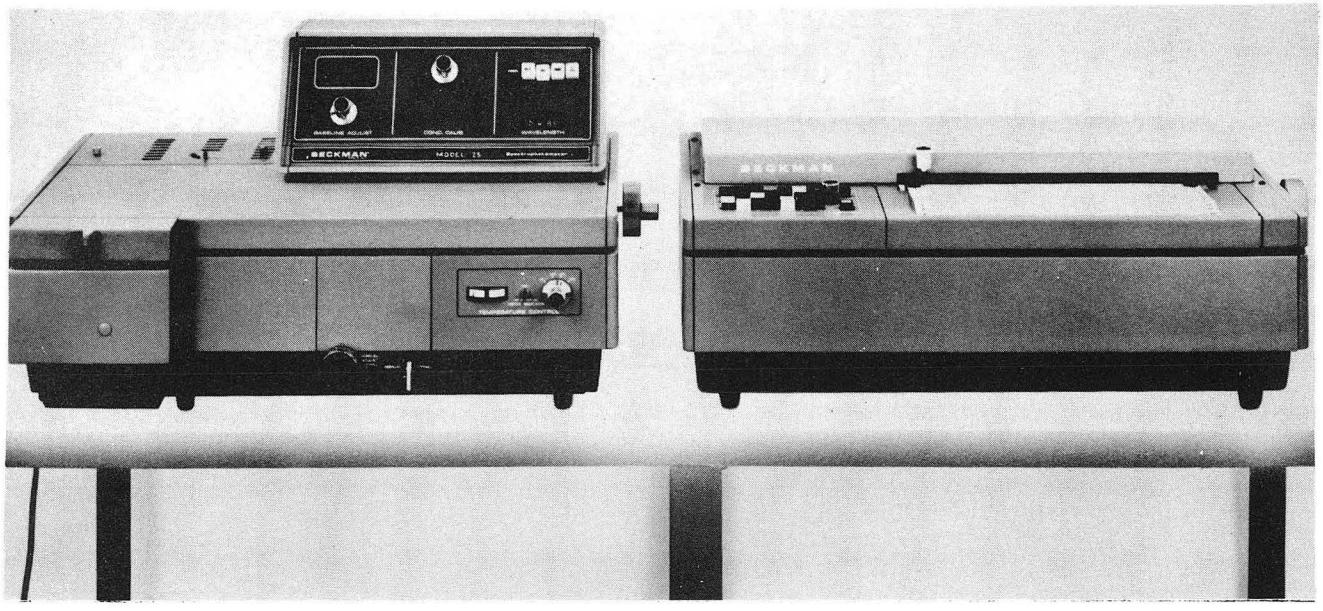
Multiparameter Capability	Molecular absorption, turbidity, reflectance
Sampling	Method: Batch or semi-automatic Volume: Dependent upon sample cell used Compartment: 11 cm W, 17 cm D, 13.5 cm H Maximum Optical Path Length of Cell: 100 mm Temperature Compensation: Water jacket cells or constant temperature cell holders
Performance and Specifications	Electronics: Solid state Linearity: Stability: Better than 0.005 A per day Scale Expansion: Via accessory recorder Detector: R-446 photomultiplier Photometric Accuracy: ±0.005 (at 0.4 Abs) Noise level: Photometric Reproducibility: ±0.2%T Span Drift: Baseline flatness, ±1.0% Zero Suppression: Readout: Model 200-meter, scales in absorbance and %Transmittance Model 210-digital, readout in absorbance, %Transmittance, and concentration External Output: Model 200 - 0.1 Vdc, analog Model 210 - 0.1 Vdc, analog and digital (BCD) Warm Up: Response Time: Optical System: Czerny-Turner mount, monochromator Grating: 1200 lines/mm, blazed at 200 nm Dispersion: Scan Speeds: 60, 120, 240, 480 nm/min (30 nm/min optional) Stray Light: 0.1%T @ 220 nm Lamps: Deuterium - 190-400 nm; Tungsten - 390-900 nm (800 with Model 200) Slit Width: 0.25, 0.5, 1.0, 2.0 nm (5.0 nm or Model 210) Wavelength Range: Model 200 - 200-800 nm Model 210 - 200-900 nm Wavelength Accuracy: ± 0.5 nm Wavelength Reproducibility: ± 0.2 nm
Operation	Calibration: Didymium and 10% neutral density filters Procedure: Manual Training: Operators' Manual Unattended Period: Manual Operation Maintenance: 1-year warranty, service contract available
Requirements	Power: 120 VAC, 60 Hz, 300 watts Weight: 56.7 kg (125 lbs) Dimensions: Spectrometer - 85 cm W, 60 cm D, 21 cm H (33.4" × 26.6" × 8.2") Power Supply - 21 cm W, 35 cm D, 17 cm H (8.2" × 13.7" × 6.7")
Features	Double beam, scanning UV-VIS spectrophotometer
Options	T-Y flatbed recorder 4-place turret cell holder Opal glass attachment Cylindrical cell holder Constant temperature cell holder DP-110 data processor Reflectance sphere Baseline compensator
References	Manufacturer's Specifications

Cost	B & L/Shimadzu 200UV meter Model	$6000
	B & L/Shimadzu 210UV, digital Model	7500
Address	Bausch and Lomb, Inc. Analytical System Division 820 Linden Avenue Rochester, N.Y. 14625 (716) 385-1000	

INSTRUMENTATION
FOR ENVIRONMENTAL
MONITORING

Ultraviolet/Visible Spectrophotometers

Beckman, Models 24, 25 and 26



Class	Laboratory
Description	Double beam ultraviolet-visible spectrophotometer (digital) Model 24 - 340-700 nm (190-1000 optional) Model 25 - 190-700 nm (190-1000 optional) Model 26 - 190-900 nm (190-1000 optional)
Modes of Operation	Double beam, absorbance, transmittance, concentration
Lower Detectable Limit	1 - 10 ppb
Range	0-2.00 Absorption; 0-8000 concentration, 0-100%T
Interferences	Depends on the method used
Multiparameter Capability	Spectrophotometric, colorimetric, turbidimetric (optional) kinetics
Sampling	Method: Automatic, sipper accessory (1 ml vol) Volume: 4 mℓ Capacity: 6-10 samples/minute Temperature controlled sample compartment: (optional) Fixed temperatures: 30°C, 32°C, 37°C Accuracy: ±0.25°C Control: ± 0.1°C Maximum Cell Length: 5 cm Turbidity Position: No
Performance	Electronics: Solid state Linearity: linear to 2A Stability: 0.6004 A/hr, zero drift 0.0004A/hr. Photometric Accuracy: 0.5% or 0.001A Scale Expansion: 0.1A, full scale Detector: Photomultiplier tube Zero Suppression: at 1.9A will suppress ≯ 0.010A

Performance (continued)

Readout: Digital
External Output: Digital, analog
Noise Level: ± 0.005A peak to peak
Warm Up: 1 hour in A
Response: Fixed 4 sec.

Optical System

Grating: 1200 lines/mm, blazed at 250 nm
Dispersion: 2.7 nm/mm
Wavelength Range: Model 24, 340-700, 190 nm optional
Model 25, 190-700, 900 with red sensitive PMT
Model 26, 190-900
Wavelength Accuracy: ± 0.5 nm
Wavelength Reproducibility: ± 0.25 nm
Slits: Model 24 fixed @ 0.8 nm wide by 1.5 nm high
Model 25-26 manual adjust. -0.05 to 2.0 mm
2 programs - normal, wide (3x normal)
Resolution: Model 24 - Better than 4 nm throughout
Model 25/25 - Better than 0.2 nm throughout
Scan Speeds: 100, 50, 20 and 5 nm/mm
Stray Light: <0.1% (Model 24 @ 370nm, Model 25, 26 @ 220 nm)
Light Source: Deuterium, Tungsten
Power Supply:

Operation

Calibration: Standard samples
Procedure: Manual provided
Training: Requires about 1 week
Unattended Period: Overnight
Maintenance: 21 sales and service centers in the U.S.

Requirements

Power: 115 VAC ±15 V, 50/60 Hz, 2 amps; 230 VAC ± 30 V, 50/60 Hz, 2 amps
Weight: 31.75 kg (70 lbs)
Dimensions: 61 cm L, 40.6 cm D, 35.6 cm H (24" × 16" × 14")

Features

Double beam scanning UV-visible spectrophotometer
Common optics
Model 24, fixed slit, Model 25, 26 programmed slit
Digital

Options

Heated Sipper,	Model 24 HS	$ 5,820.00
	Model 25 HS	7,970.00
	Model 26 HS	8,540.00
Kinetics System	Model 24K	10,180.00
	Model 25K	12,330.00
	Model 26K	12,900.00
Scanning System	Model 24S	6,410.00
	Model 25S	8,560.00
	Model 26S	9,130.00

References

Manufacturer's Bulletin 7244-C

Cost

Model 24	$ 4,580.00
Model 25	6,730.00
Model 26	7,300.00

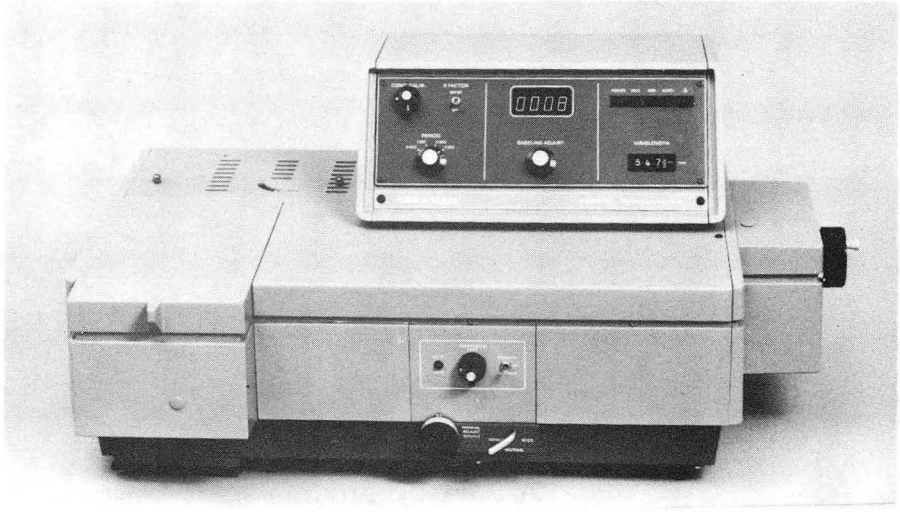
Address

Beckman Instruments, Inc.
Campus Drive and Jamboree Blvd.
Irvine, CA 92664
Attn: UV Product Line
(714) 833-0751

INSTRUMENTATION
FOR ENVIRONMENTAL
MONITORING

Ultraviolet/Visible Spectrophotometer

Beckman Models 34, 35



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Class	Laboratory
Description	Double beam, single beam, scanning, digital ultraviolet visible spectrophotometers Model 34 340-700 nm; 190-700 (opt.) Model 35 190-700 nm
Modes of Operation	Single beam, double beam, gel scan (opt.), 1st, 2nd deriv. (opt.) concentration
Lower Detectable Limit	Depends upon element, chemical method and pathlength
Range	Absorbance: 0-3A Transmission:
Interferences	Depends on chemical method, metal
Multiparameter Capability	Spectrophotometry, colorimetry, kinetics
Sampling	Method: Manual or automatic Volume: depends on system - 0.9 mℓ - 2 mℓ Capacity: depends on system - up to 175 samples Temperature control: Accessory Maximum cell length: 5 cm Turbidity position: No
Performance and Specifications	Electronics: Solid state Linearity: linear to 3.5A Photometric stability, ± 0.25% or 0.001 which ever is greater from 0-2.0A Photometric accuracy: ± 0.5% of value or 0.001A which ever is greater, from 0-2.0A Scale expansion: 0.02, 0.05, 0.1, 0.2, 0.5, 1.0 and 2.0A full scale Time constant: 0.5, 1, 2, 4 sec. Noise level:

Performance and Specifications (continued)	Zero Suppression: -0.25 to 2.0A Readout: digital External Output: BCD Warm Up: Optical System: Grating: 1200 lines/mm; blazed at 250 nm Dispersion: Wavelength Range: Model 34 - 340-700 nm Model 35 - 190-700 (-900 nm, opt.) Wavelength accuracy: ± 0.5 nm (190-700 nm), ± 1.0 nm (700-900 nm) Wavelength reproducibility: ± 0.25 nm Slits: Model 34 - fixed at 0.8 mm W, 1.5 mm high Model 135 - two programs, normal and wide (3x normal), adjustable from 0.05 - 2.0 nm Spectral bandpass: Model 34 - 2 nm Model 35 - 0.125 - 5 nm Resolution Stray light: Model 34 - < 0.1% at 370 nm Model 35 - < 0.1% at 220 nm Scan speeds: 1, 5, 20, 50, 100, 250 nm/min
Operation	Calibration: Standard solutions Training: Manual available Maintenance: 21 sales and service centers throughout U.S. Unattended period: overnight
Requirements	Power: 120 ± 10% VAC, 50/60 Hz; 240 ± 10% VAC, 50/60 Hz Weight: 31.75 kg (70 lb) Dimensions: 61 cm × 40.6 cm × 35.6 cm
Features	Programmed slits Digital readout Time constant selection Absorbance over range Digital readout Double beam, single beam operation
Options	Choice of Sipper System Kinetic System Series B Shelf saver 1st and 2nd derivative Model 701 printer/calculator 3 115T Printer Gel scan Temperature readout control Four position sample changer Column chromatography kit Wavelength programmer, density gradient kit
References	Manufacturer's Bulletin
Cost	Model 34 $5200 Model 35 7400
Address	Beckman Instruments Campus Drive and Jamboree Blvd. Irvine, CA 92664 Attn: UV Product Line (714) 833-0751

INSTRUMENTATION
FOR ENVIRONMENTAL
MONITORING

Ultraviolet/Visible Spectrophotometer

Beckman Model 3600

Class	Laboratory
Description	Digital, double beam, UV-visible, recording spectrophotometer
Modes of Operation	Absorbance, transmittance, concentration, 1st or 2nd derivative
Lower Detectable Limit	Depends upon chemical technique, element
Range	Absorbance: 0-3A Transmittance: 0-200%T Concentration: To 9999 Ca
Interferences	Depends upon element, technique
Multiparameter Capability	Spectrophotometry, colorimity, turbidimeter, kinetics
Sampling	Method: Manual or automated Volume: Capacity: Temperature control: (optional) Fixed temp. 30°C, 32°C, 37°C Maximum cell length: 5 cm Turbidity Position: No
Performance and Specifications	Electronics: solid State Linearity and accuracy: linear to 3.5A Photometric stability: Scale expansion: 0.02, 0.05, 0.1, 0.2, 0.5, 1.0 or 2A Detector: Photomultiplier tube Photometric accuracy: 0.001A Noise level: 0.0002A @ 500nm and 0A Zero suppression: -0.25 - 2A Readout: Digital, recorder External Output: Analog digital Response: 0.5, 1, 2, 4 sec Warm Up:

Performance and Specifications (continued)

Optical System:

Grating: Holographic grating
Wavelength range: 190-900 nm
Wavelength accuracy: ± 0.5nm (190-700nm), ±1.0nm (700 to 900)
Wavelength reproducibility: ± 0.25nm
Resolution: 0.125 - 5.0 mm bandpass
Slits: 0.05 to 2.0 mm (manually selected)
or programmed normal and wide (3x).
Scan speeds: 1, 5, 20, 50, 100, 250 nm/min
Recorder speeds: 11 speeds, from 25.4 mm/min to 25.4 mm/hour
Stray Light: 0.1% @ 200nm
Light Source: Deuterium, tungsten lamps with auto change over

Operation

Calibrations: With standard solutions, k factor
Training: Manual available
Maintenance: 21 sales and service centers throughout U.S.
Unattended Period: Overnight

Requirements

Power: 120 ± 10% VAC, 50/60 Hz; 240 ± 10% VAC, 50/60 Hz
Dimensions: Spectrophotometer 61 × 40.6 × 35.6 cm, recorder 66.1 × 38 × 29.2 cm
Weight: 51.45 kg (113.5 lb) total

Features

Double beam, common optics, holographic grating
Wavelength programmer

Options

Data Printer	$ 1600-1680
Kinetics sampler	1200
Gel scanner	1600
Heated and unheated flow cells	125 - 240
Auto sampler	3770
Column chromatography system	540
Temperature control accessories	445 - 960

References

Manufacturers Bulletin 7324 and Price List

Cost

Model 3600 — 11,025

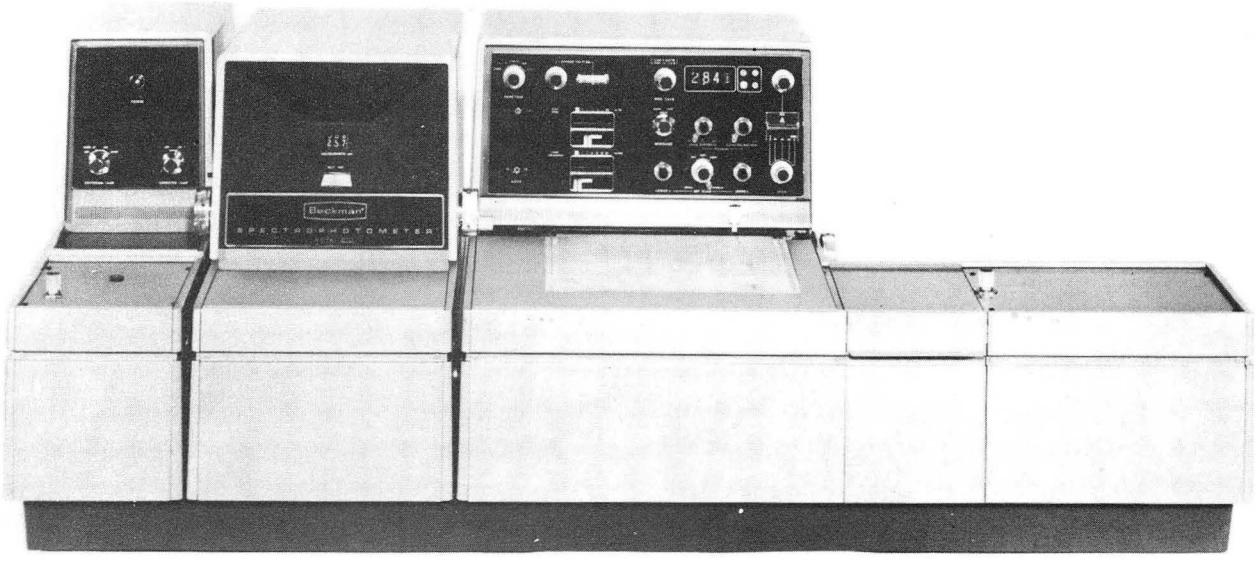
Address

Beckman Instruments
Campus Drive and Jamboree Blvd.
Irvine, CA 92664
Attn: UV-Product Line
(714) 833-0751

INSTRUMENTATION
FOR ENVIRONMENTAL
MONITORING

Ultraviolet/Visible Spectrophotometer

Beckman, 5230, 5240, 5260, 5270



Class	Laboratory
Description	A series of double beam, ratio recording UV-visible-NIR spectrophotometers with high flexibility 5230, 5260 - 190-800 nm 5240, 5270 - 190-3000 nm
Modes of Operation	Single beam, double beam Absorbance, % transmittance, concentration, derivative (1st and 2nd)
Lower Detectable Limit	1 - 10 ppm depends upon element, chemical method and pathlength
Range	Absorbance: 0 - 3 A Transmission: 0-100% T
Interferences	Depends upon chemical method, metal
Multiparameter Capability	Spectrophotometry, colorimetry, turbiditimetric, kinetics
Sampling	Method: Automatic or manual Volume: 4 mℓ Capacity: 10 samples/minute Temperature control: constant temperature, cell holder accessory Maximum cell length: 100 mm Turbidity position: accessory
Performance and Specifications	Electronics: Solid state Linearity and accuracy 0.003A at 1.0A; 0.005A at 2.0A, 0.030 at 3.0A Photometric Stability: 0.0005A/hour, zero drift, 0.005 A-/day Scale expansion: Normal absorption: 0.1, 0.5, 1.0, 2.0, 3.0, Var A, conc. expanded abs. 0.01, 0.02, 0.05, 0.1, .1, .2, Var A, conc. % transmittance - 10.20, 50, 100, 200; VAC derivative 0.1, 0.02, 0.05, 0.10, 0.20 Detector: 190-800 nm photomultiplier tube (and on), 800-3000 nm, PbS detector

Performance Specifications (continued)

Photometric accuracy:
Noise level: 0.01A P-P 2.0A, 340 nm, 3 nm bandwidth
Zero suppression: to 2.9A
Readout: Recorder readout in absorbance, transmittance, concentration, first derivative, 2nd derivative
External Output: Analog, digital (BCD)
Warm Up:
Response: (period control) 0.5, 1, 2, 4, 8 seconds

Optical System: 5230, 5240 single monochromator
5260, 5270 double monochromator
Gratings: 5230: single holographic grating blazed at 250 nm
5240: single holographic grating, blazed at 250 nm, 1200 nm
5260: double monochromator, gratings blazed at 250 nm, 1200nm
5270: double monochromator, gratings blazed at 250 nm, 1200 nm
Wavelength Range: 5230, 5260 - 190 to 800 nm
5240, 5270 - 190 - 3000 nm
Wavelength Accuracy: 5230 - ± 0.5 nm (190-800 nm)
5240 - ± 0.5 nm (190-800), ± 2.5 nm (800-3000)
5260 - ± 0.1 nm (190-800 nm)
5270 - ± 0.1 nm (190-800 nm), ± 0.5 nm (800-3000)

Wavelength Reproducibility:
Resolution: 5230 - better than 0.2 nm (190-800 nm)
5240 - better than 0.2 nm (190-800 nm), 1.2 nm (800-3000 nm)
5260 - better than 0.05 nm (190-800 nm)
5270 - better than 0.05 nm (190-800 nm), 0.3 nm (800-3000 nm)
Slits: Manual 0.005 to 7.0 nm or programmed
Scan Speeds: 190-800 nm: 4, 2, 1, 1/2, 1/4, 1/8, 1/16, 1/64 nm/sec
800-3000 nm: 16, 8, 4, 2, 1, 1/2, 1/4, 1/16 nm/sec
Short Speeds: 190-800 nm: 1, 2, 5, 10, 20, 50, 100 nm/in
800-3000 nm: 4, 8, 20, 40, 80, 200, 400 nm/in
Stray Light: 5230 - < 0.1% @ 220 nm, 370 nm
5240 - < 0.1% @ 220, 370, and 1690 nm
5260 - < 0.001% @ 210-690 nm, 0.1% at range limits
5270 - < 0.0001% @ 240-500 nm, 0.001% 210-690 nm
< 0.01% @ 1690 nm, 0.1% @ range limits
Light Source: Deuterium and Tungsten Lamp

Operation

Calibration: Standard samples
Training: Manual available, requires two weeks
Maintenance: 21 sales and service centers throughout U.S.
Unattended Period: Overnight

Requirements

Power: 120, 240 VAC, 50/60 Hz
Dimensions: 5230, 5240 - 56 cm D × 147 cm L × 56 cm H (22" × 58" × 22")
5260, 5270 - 61 cm D × 158 cm L × 56 cm H (24" × 62" × 22")
Weight: 5230 - 106 kg (235 lbs)
5240 - 113 kg (250 lbs)
5260 - 124 kg (275 lbs)
5270 - 131 kg (290 lbs)

Features

Double beam, single beam operation
Rep scan included

Options

4 position kinetic sampling	
Gel scanning	$ 1620
Reflectance	1210 - 7100
Microsampling	from 113.
Auto sampler	4700 - 6000
Sipper accessory, unheated	1120
Sipper accessory, heated	1530
Fluorescence attachments	870

References

Manufacturer's Bulletin

Cost	Model 5230	$ 14,000
	Model 5240	21,350
	Model 5260	15,750
	Model 5270	27,300

Address

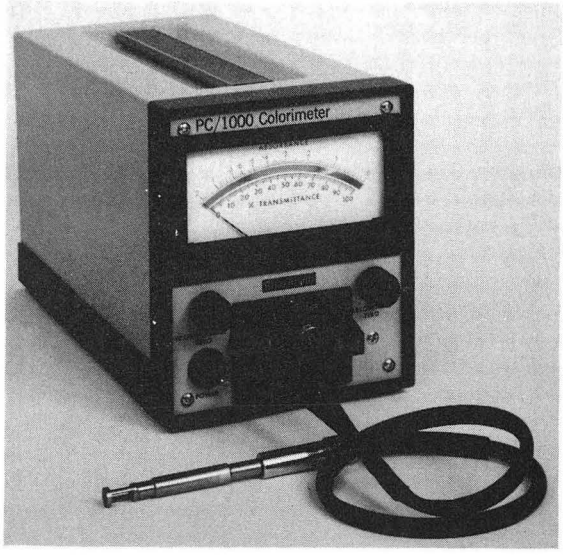
Beckman Instruments
Campus Drive and Jamboree Blvd.
Irvine, CA 92664
Attn: UV Product Line
(714) 833-0751

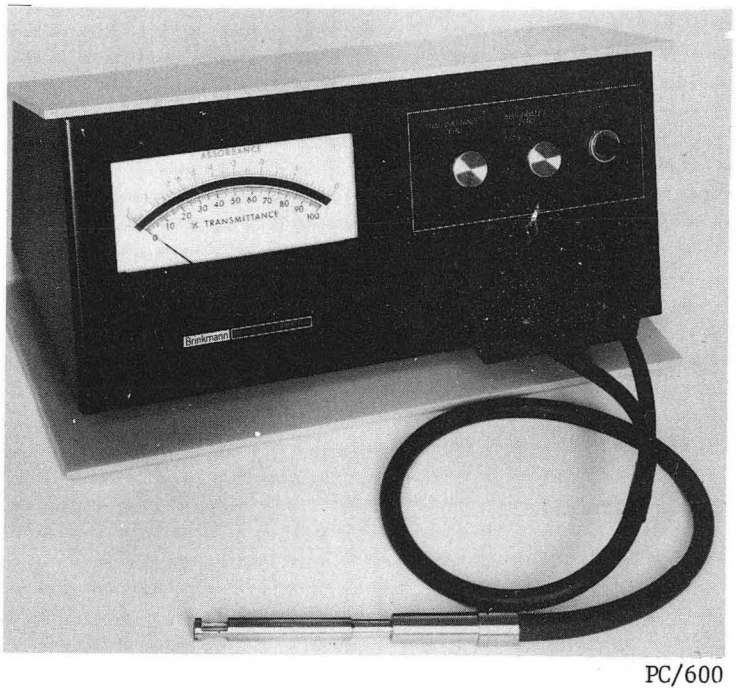
INSTRUMENTATION
FOR ENVIRONMENTAL
MONITORING

Brinkmann Probe Colorimeter Model PC/1000W

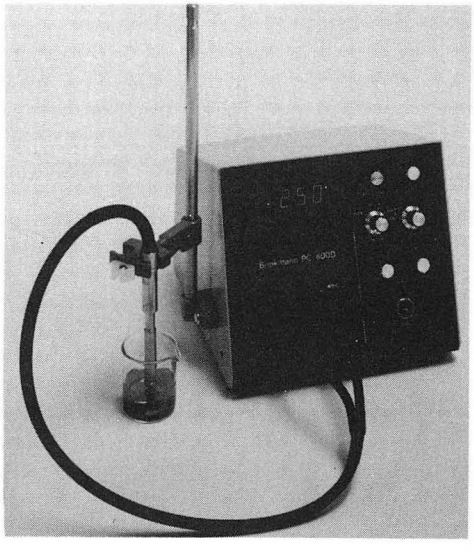
PC/600 and PC/600D

PC/1000





PC/600



PC/600D

Class	Laboratory or field
Description	Probe Colorimeter
Modes of Operation	Concentration (PC/600D only), absorbance, transmittance
Lower Detectable Limit	Arsenic: 10µg or greater (545nm) Total Hardness: 10-400 mg (520nm)
Range	0-100%T, 0-1.999A
Interferences	Depends on metal and chemical method
Multiparameter Capability	Arsenic, CrVI, iron, selenium, total hardness, silica, turbidimetry biological applications

Sampling

Method: Batch or continuous flow
Volume: 1 ml. and up
Capacity: 4/min
Maximum Cell Length: 10 cm, 2 cm standard

Performance and Specifications

Electronics:

Linearity: Within 3%
Photometric Stability: 3%T/day, short term 0.2%T
Scale Expansion: None
Detector: Photocell - phase modulated amplifier
Readout: 600 and 1000 - analog meter
600D - digital display
Output: 100 mV analog
Warm Up: None

Optical System:

Filters: Model 600 and 600D - 420-800nm selected
Wavelength Range: Model 600 and 600D - 420-800nm selected
Model 1000W - 420, 470, 520, 545, 620, 650nm
Wavelength Accuracy: Standard interference filters
Wavelength Repeatability: Standard interference filters
Resolution: 20nm

Operation

Calibration: Standard Samples
Training: Instruction Manual
Maintenance: Regional Service Centers
Unattended Period: 24 hours

Requirements

Power	PC/600 D	PC/600	PC 1000
115 volts, 50/60 Hz	9VA	4.5VA	8.5 VA
Weight (L×W×H)	7 3/4 lbs	6 3/4 lbs	6 1/2 lbs
Dimensions	7 5/8×7 7/8×6 3/4"	12×5 3/4×6"	11 1/2×5 1/2×6 1/2"

Features

Probe Colorimeter

Options

Digital readout and printout (incl. in PC/600 D)

References

Manufacturer's Bulletin BR-362 B

Cost

Model 600 (without filters)	$ 795
Model 600D (without filters)	1395
Model 1000	1095 - 1295

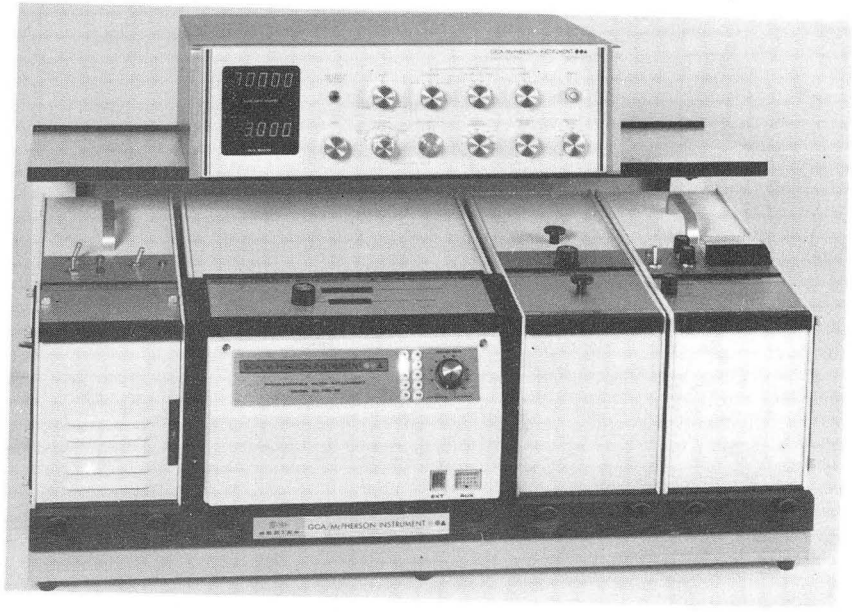
Address

Brinkmann Instruments
Cantiague Rd.
Westbury, N.Y. 11590
(516) 334-7500

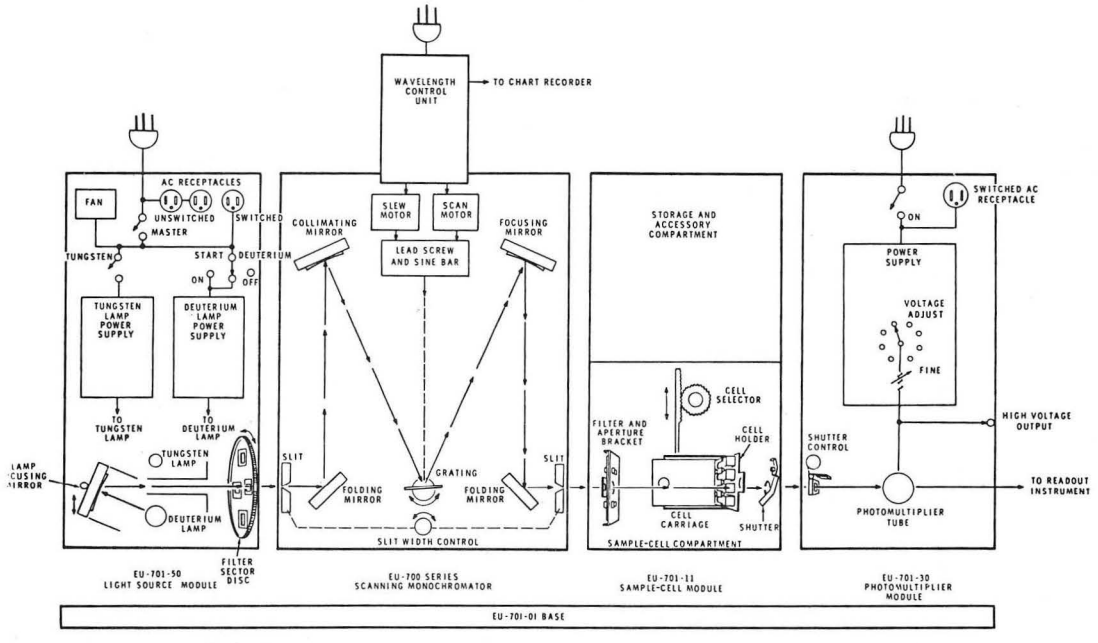
INSTRUMENTATION
FOR ENVIRONMENTAL
MONITORING

Ultraviolet/Visible Spectrophotometer

GCA/McPherson Instruments, 700 Series, Modular UV-Visible Spectrophotometers
701-D, 707-D and 721-D



Block Diagram Of The 701 Spectrophotometer



Class — Laboratory

Description — A modular system of UV-visible spectrophotometers. All three include the following components: Light source (EU 701-50), Detector (EU 701-30), monochromator (EU 700), and the controller and Readout System (E11 700-32). The various instruments are made by changing the sample compartment. All range from 185 to 1000 nm (4000 nm optional)
Model 701-D - Single beam (701-11 Sample chamber)
Model 707-D - Double beam (707-11 Sample chamber)
Model 721-D - Double beam via alternating cell (721-11 sample chamber)

Modes of Operation	Single beam (all three), double beam (707-D, 721-D) Absorbance % Transmission, concentration, intensity kinetics (optional-marketed as Model 707-K), difference
Lower Detectable Limit	Depends upon element, chemical method and pathlength
Ranges	Absorbance: -0.3 to + 3.000 Abs % Transmittance: 0-100% Concentration: 0-5000 units
Interferences	Depends upon metal and chemical method used
Multiparameter Capability	
Sampling	Method:
Performance and Specifications	Electronics: Digital Electronics Linearity: Stability: Zero Drift ± 0.001A/hour Photometric Accuracy: ± 0.002 Abs @ 1 Abs, ± 0.01 Abs @ 2 Abs, ± 0.03 Abs @ 3 Abs Noise Level: ± 0.001 Abs Scale Expansion: 0-0.1A, 0-5A, 0-1.0A, 0-2.0A, -0.3 - + 0.7A; 0-10, 0-50 0-100%T Detector: IP28A Photomultiplier (R372) Zero Suppression: ± 1.2 Abs. Readout: Digital, and chart recorder, discrete-sampling - time averaged External Output: Analog and digital (BCD) Warm Up: 30 min. Response: 30 Abs/sec. Optical System: EU 700-Monochromator module Czerny-Turner Mount with 0.35m focal length - digital controlled Grating: 1200 grooves/mm, blazed at 250nm, 48 × 48mm Dispersion: 2 nm/mm Wavelength Range: 185 nm to 1000 nm (4000 nm-opt.) Wavelength Accuracy: 0.1 nm Wavelength reproducibility ± 0.005 nm Slits: Continuously variable between 2-2000μ Resolution: 0.1 nm Scan Speeds: Stepping rates from 0.0005 to 2 nm/sec Stray Light:< 0.1% @ 220 nm Light Source: Dual deuterium/tungsten Power Supply: Integral
Operation	Calibration: Standard Samples Traing: From Instruction Manual Unattended Period: Any Maintenance: Periodic checks of operating parameters
Requirements	Power: 115 VAC Weight: } Depends upon particular system Dimensions: } Temperature: Ambient laboratory
Features	Modular System
Options	Gratings: 600 lines/mm, blazed at 1μ, 0.2 nm resolution 4 nm/mm dispersion; Range - 185 to 2000 nm 300 lines/mm, blazed at 2.5μ, 0.4 nm resolution, 8 nm/mm dispersion; Range - 185 to 4000 nm

Options (continued)	Sample Models: 705-11 Gel Scan (if entire instrument purchased 705-D) 707-12: kinetics (if entire instrument purchased 707-K) 750-11: stopped flow 735 Data Control and Aquisition System - interface to a Monroe Calculator 701-65 Sample turntable for automatic sampling 701-60 Sampler 205-11 Strip Chart Recorder (23 speed)	
References	Manufacturer's Bulletin	
Cost	Model 701-D - Model 707-D - Model 721-D -	$6435 8575 6925
Address	GCA/McPherson Instruments 530 Main Street Acton, MA 01720 (617) 263-7733	

INSTRUMENTATION
FOR ENVIRONMENTAL
MONITORING

Visible Spectrophotometers

Gilford, Stasar I, II, and III

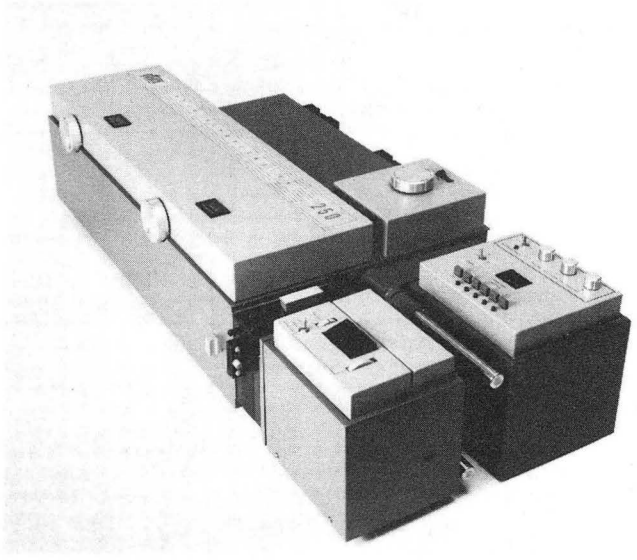
Class	Laboratory
Description	Digital single beam visible spectrophotometer with numerous systems for automated procedures
Modes of Operation	Single beam Absorbance concentration
Lower Detectable Limit	Depends upon metal, method and pathlength
Range	Absorbance: 0-2A Concentration - 0000 to 6000
Interferences	Depends upon metal and method used
Multiparameter Capability	Spectrophotometry, colorimetry
Sampling	Method: Batch, or automated (II,III), III aspiration system Volume: Minimum aspirated - 500 µℓ Maximum Path length: 1 cm Capacity: II and III - rapid sampling cuvette 25, 30 32 and 37°C Temperature Control: Built in on Stasar III 25, 30 32 and 37°C Turbidity Position: N/A
Performance and Specifications	Electronics: Linearity: Maximum deviation less than ±0.005A Photometric Stability: (Drift) better than 0.005A Photometric Accuracy: ±0.01A Noise Level: Better than 0.001A at 0A, reads directly 0.002A at 2A variable from 0-2A Scale Expansion: Detector: PMT Readout: Digital, Recorder External Output: Parallel BCD, pos. 5V logic, standard TTL Zero Suppression: Set

Performance and Specifications (continued)	Response: Less than 0.5 seconds Warm Up: 1/2 hour Optical System: Grating: Wavelength Range: 340-700 nm Wavelength Accuracy: ± 2 nm Wavelength Reproducibility: ± 0.5 nm Resolution: (Spectral Bandwidth) - 8 nm Slits: To achieve 8 nm Stray Light: Less than 0.3% at 340 nm Scan Speeds: Manual Light Source: Tungsten Lamp Power Supply: Integral
Operation	Calibration: Dual calibration standard included on II, III Training: Maintenance: Unattended Periods:
Requirements	Power: 115 ± 10%/230 ± 10% VAC, 50/60 Hz, 70 watts Weight: 14.9 kg Dimensions: 20.3 cm H × 41.9 cm W × 35.2 cm D Temperature: Operation - 20-40°C, storage - 0-50°C
Features	
Options	Recommended for Stasar 1 - Dual Calibration Standard $75 (included with Stasar II, III)
References	Manufacturer's Specifications
Cost	Stasar I $2150 Stasar II 2875 Stasar III 3750
Address	Gilford Instrument Laboratories, Inc. 132 Artino Street Oberlin, OH 44074 (216) 774-1041

INSTRUMENTATION
FOR ENVIRONMENTAL
MONITORING

Ultraviolet-Visible Spectrophotometer

Gilford Model 250



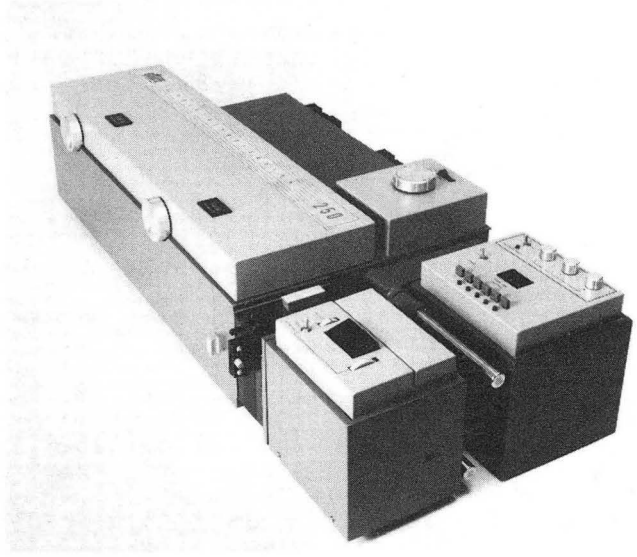
Class	Laboratory
Description	Modular, digital Single beam ultraviolet-visible spectrophotometer with standards for calibration.
Modes of Operation	Single beam, absorbance, concentration
Lower Detectable Limit	Depends upon element, chemical method and pathlength
Range	Absorbance: 0-3A Concentration: 0.000 to 9.000
Interference	Depends upon element and chemical method
Multiparameter Capability	Spectrophotometry, colorimetry, Kinetics, gel scanning
Sampling	Method: Batch or automatic, 4 positions Maximum cell length: 10 cm (opt.), 10 mm standard Temperature control: Integral dual flooding thermo-plates Turbidity Position: No
Performance and Specifications	Electronics: Linearity: ± 0.0075 max. deviation Photometric Stability: 0.005A per hour Photometric Accuracy: ±1.0% max. error Noise Level: 0.001A at 1.5A Scale Expansion: Any 0.1A increment can be expanded to full scale Detector: PMT Readout: Analog and digital Analog - 2 volts DC per A unit External Ouput: Digital - 4 character 4 bits per ch., parallel BCD, positive 5 volt logic (TTL) Zero Suppression: Up to 2.9A

Performance and Specifications (continued)	Response: Warm Up: Optical System: Littrow Mount Prism: Fused silica Wavelength Range: Monochromator: 180-999 nm Photometer Electronics: 184-800 nm Wavelength Accuracy: ± 0.5 nm, 180-400 nm, ± 1.0 nm, 400-800 nm Wavelength Reproducibility: 0.5 nm Resolution: 0.001A Slits: 0.000-2.000 mm, variable Stray Light: < 0.1% at 210 nm Scan Speeds: Optional Light Source: D_2 and tungsten lamps Power Supply: Integral
Operation	Calibration: Standards provided, using NBS standard filters Training: Instrument Manual Maintenance: Service centers Unattended periods:
Requirements	Power: 105-125/210-250 VAC, 50/60 Hz, 2.2 amps Weight: Spectrophotometer: 761 lbs. Power supply: 18 lbs. Dimensions: 36.5" W × 17.5"D × 9.5"H 17" W × 7.75" D × 6.75" H Temperature: Ambient Laboratory + 15°C to + 40°C
Features	
Options	Automatic Programmer Gel Scanners Thermoprogrammer Wavelength Programmer Rapid Sampler Density Gradient Scanner
References	Manufacturer's Bulletins
Cost	Model 250 $6700
Address	Gilford Instrument Laboratories, Inc. 132 Artino Street Oberlin, OH 44074 (216) 774-1041

INSTRUMENTATION
FOR ENVIRONMENTAL
MONITORING

Ultraviolet-Visible Spectrophotometer

Gilford Model 250



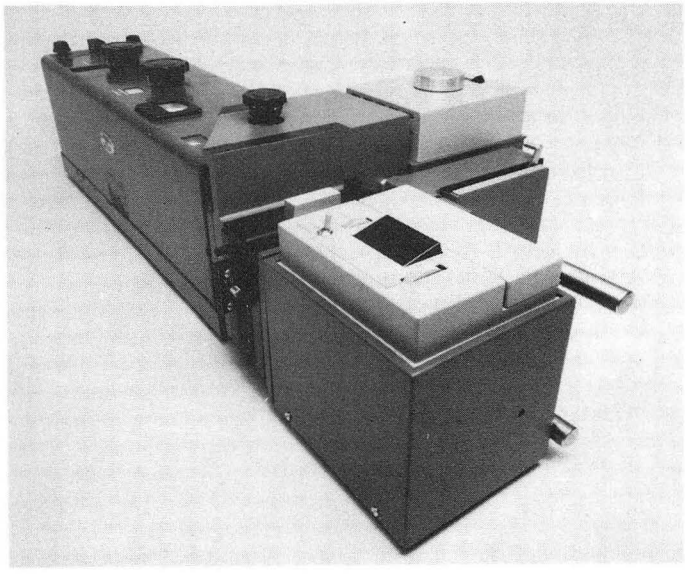
Class	Laboratory
Description	Modular, digital Single beam ultraviolet-visible spectrophotometer with standards for calibration.
Modes of Operation	Single beam, absorbance, concentration
Lower Detectable Limit	Depends upon element, chemical method and pathlength
Range	Absorbance: 0-3A Concentration: 0.000 to 9.000
Interference	Depends upon element and chemical method
Multiparameter Capability	Spectrophotometry, colorimetry, Kinetics, gel scanning
Sampling	Method: Batch or automatic, 4 positions Maximum cell length: 10 cm (opt.), 10 mm standard Temperature control: Integral dual flooding thermo-plates Turbidity Position: No
Performance and Specifications	Electronics: Linearity: ± 0.0075 max. deviation Photometric Stability: 0.005A per hour Photometric Accuracy: ±1.0% max. error Noise Level: 0.001A at 1.5A Scale Expansion: Any 0.1A increment can be expanded to full scale Detector: PMT Readout: Analog and digital Analog - 2 volts DC per A unit External Ouput: Digital - 4 character 4 bits per ch., parallel BCD, positive 5 volt logic (TTL) Zero Suppression: Up to 2.9A

Performance and Specifications (continued)	Response: Warm Up: Optical System: Littrow Mount Prism: Fused silica Wavelength Range: Monochromator: 180-999 nm Photometer Electronics: 184-800 nm Wavelength Accuracy: ± 0.5 nm, 180-400 nm, ± 1.0 nm, 400-800 nm Wavelength Reproducibility: 0.5 nm Resolution: 0.001A Slits: 0.000-2.000 mm, variable Stray Light: < 0.1% at 210 nm Scan Speeds: Optional Light Source: D_2 and tungsten lamps Power Supply: Integral
Operation	Calibration: Standards provided, using NBS standard filters Training: Instrument Manual Maintenance: Service centers Unattended periods:
Requirements	Power: 105-125/210-250 VAC, 50/60 Hz, 2.2 amps Weight: Spectrophotometer: 761 lbs. Power supply: 18 lbs. Dimensions: 36.5" W × 17.5"D × 9.5"H 17" W × 7.75" D × 6.75" H Temperature: Ambient Laboratory + 15°C to + 40°C
Features	
Options	Automatic Programmer Gel Scanners Thermoprogrammer Wavelength Programmer Rapid Sampler Density Gradient Scanner
References	Manufacturer's Bulletins
Cost	Model 250 $6700
Address	Gilford Instrument Laboratories, Inc. 132 Artino Street Oberlin, OH 44074 (216) 774-1041

INSTRUMENTATION
FOR ENVIRONMENTAL
MONITORING

Ultraviolet/Visible Spectrophotometer Modernization Systems

Gilford Model 252-1, 252-2



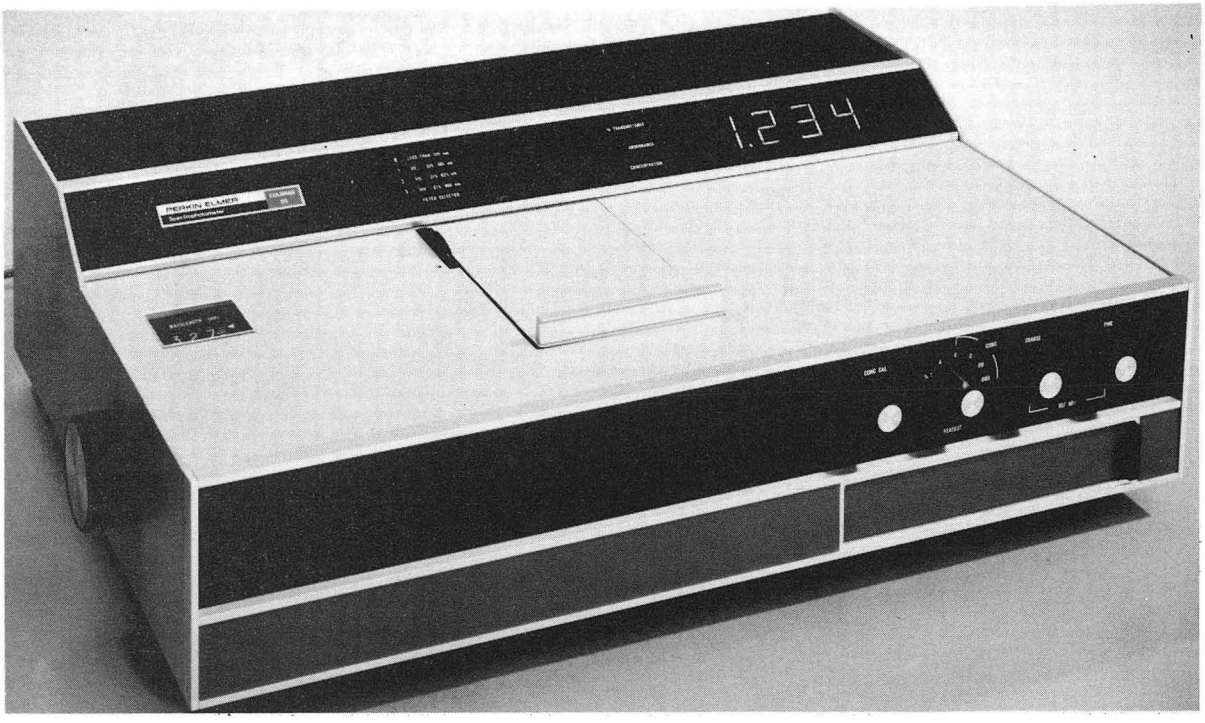
Class	Laboratory
Description	Up dating system using a Beckman DU(252-1) or DU-2 monochromator (252-2 nm)
Modes of Operation	Single beam, absorbance, concentration
Lower Detectable Limit	Depends upon element, chemical method and pathlength
Range	0-3A (linear)
Interferences	Depends upon method and element
Multiparameter Capability	Spectrophotometry, colorimetry
Sampling	Method: 4 position manual available, also automatic Volume: Capacity: Maximum cell length: 10 cm Temperature Control: Thermoplates standard Turbidity Position: No
Performance and Specifications	Electronics: Solid State Linearity: ±0.0075 max deviation Photometric Stability: Long term 0.005A/hr Photometric Accuracy: ±1.0% max error Noice Level: < 0.001A at 1.5A Scale Expansion: 0.1A can be expanded to full scale Detector: Photomultiplier Readout: Digital External Output: Analog: 2Vdc, digital (BCD), TTL Zero Suppression: Up to 2.9A Response: 100 msec Warm Up: 1/2 hour

Performance and Specifications (continued)	Optical System: Beckman DU ® (252-1) DU-2 ® (252-2) monochromator Prism: Fused silica Dispersion: Nonlinear with wavelength Wavelength Range: 200-800 nm Wavelength Accuracy: 0.1 nm UV, 0.4 nm VIS Wavelength Reproducibility: Better than 0.05 nm UV, 0.2 nm VIS Resolution: 0.001A Slits: 0.000 to 2.000 mm, variable Stray Light: Less than 0.2%T Scan Speeds: Not available Light Source: D_2 and tungsten lamp Power Supply: Supplied
Operation	Calibration: With standard samples or filters (optional) Training: Instrument Manual Maintenance: Service centers Unattended Periods:
Requirements	Power: 105-125 VAC, 50/60 Hz, 1.8 amps Weight: Model 222 (60 lbs) Model 252 (94 lbs) Dimensions: Temperature:
Features	System for updating Beckman DU ® , DU ® -2 monochromators
Options	Temperature Control thermoelectric; thermospacers standard Gel Scanner Auto Cuvette positioner 10 cm manual cuvette positioner Rapid Sampler Automatic Programmer Thermoprogrammer
References	Manufacturer's Bulletin
Cost	Model 252-1 $ 4400 Model 252-2 4400
Address	Gilford ® Instrument Laboratories, Inc. 132 Artino Street Oberlin, OH 44074 (216) 774-1041

INSTRUMENTATION
FOR ENVIRONMENTAL
MONITORING

Ultraviolet/Visible Spectrophotometer

Perkin-Elmer, Model 55



Class	Laboratory
Description	Single beam, digital UV-visible spectrophotometer, 300-810 nm (190 nm (optional), 900 nm (optional))
Modes of Operatoin	Single beam Absorbance, % transmittance, concentration
Lower Detectable Limit	Depends on path length element and chemical treatment
Range	Absorbance: -0.3 to 3 A Transmittance: 0-200% T Concentration: 0.1 to 20X
Interferences	Depends on element and chemical method
Multiparameter Capability	Spectrophotometry, colorimetry, turbidimetry
Sampling	Method: Batch and semiautomatic, 5 sample holder Volume: 2-4 mℓ Capacity: 2 samples/minute Temperature Control: 25, 30, 32, and 37°C Path Length: 10, 20, 50 or 100 mm, Turbidity Position: No
Performance	Electronics: Solid state, modular circuit boards Linearity: 0.2% T per 8 hours Stability: 0.005 A per 8 hours (zero drift) Optical Accuracy: Scale Expansion: Noise Level

Performance (continued)

Detector: Photomultiplier
Zero Suppression:
Readout: Digital (4 digits)
External Output: 50 mV per 100% T or 1A, BCD, Bufford, TTL compatible, (+) true logic
Warm Up: Maintains power to electronics while source off
Response: 1 sec to reach 98% of final value

Optical System: Littrow mount monochromator

Grating: 1440 lines/mm
Dispersion:
Wavelength Range: 30-800 nm, 190 nm optional
Wavelength Accuracy: ± 1 nm
Wavelength Reproducibility: ± 0.2 nm
Resolution: 2 nm bandpass
Slit Width:
Scan Speeds: Not available
Stray Light: 0.1% at 340 nm
Light Source: Quartz-iodine, deuterium
Power Supply:

Operation

Calibration: Standard samples
Procedure: Manual provided
Training:
Unattended Period:
Maintenance: Service centers in the U.S.

Requirements

Power: 115 VAC + 15%-10%, 60 Hz, 150 watts
230 VAC + 15%-10%, 50 Hz, 150 watts
Weight: 25 kg (55 lbs)
Dimensions: 58.4 cm W × 41.0 cm D × 17.1 cm H (23" × 16.5" × 6.75")
Temperature: 15-40°C

Features

Single beam digital UV-VIS spectrophotometer

Options

UV Accessory, Model 204 (includes D_2 lamp and power supply)	$ 665
Automatic Sampler, Model 200	745
Digital Printer, Model 5-050	1970
Chart Recorder Model 56	1475
Enzyme Calculator	1690
Print Timer	475
System Controller	745
Sample Programmer, Model 48	2020
Microflow Cells	130-270

References

Manufacturer's Bulletin

Cost

Model 55 $3,700

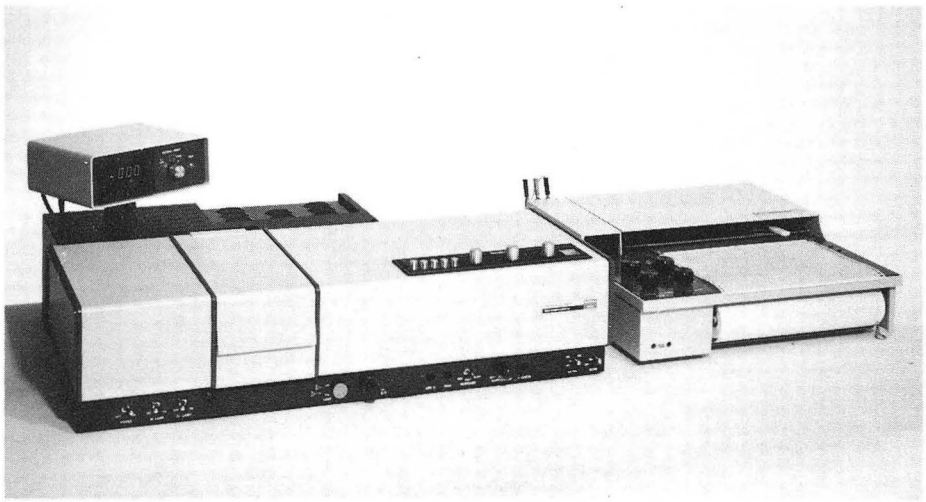
Address

Perkin-Elmer Corporation
Coleman Instruments Division
2000 York Road
Oak Brook, IL 60521
(312) 887-0770/242-4050

INSTRUMENTATION
FOR ENVIRONMENTAL
MONITORING

Visible, Ultraviolet/Visible Spectrophotometer

Perkin Elmer Model 200/550



Class	Laboratory
Description	Double beam, digital, scanning UV-visible, visible spectrophotometers: Model 200 - 190-900 nm Model 550 - 315-800 nm
Modes of Operation	Double beam Absorbance, % transmittance, concentration, first or second derivative (optional)
Lower Detectable Limit	Depends upon pathlength and method employed
Range	Absorbance: 0-3A % Transmittance: 0-100% Concentration: 0.1 to 10X
Interferences	Depends upon metal and chemical method
Multiparameter Capability	Spectrophotometry, colorimetry
Sampling	Method: Batch Volume: Capacity: Temperature Control: Thermostated cells opt. Maximum Cell Length: 100 mm Turbidity Position: Optional integrating sphere for turbid samples
Performance and Specifications	Electronics: Solid state, integrated modular circuitry Linearity Photometric Stability: Model 200-0.0005A/hr at 340 nm, 2 nm slit Model 550 - < 0.001A at 0A/8 hrs after warmup Photometric Accuracy: Model 200: within the accuracy of NBS reference material 930 (±0.5%T) from 0-1A Model 550: ±0.3%T, ±0.005A (at 1A) Noise Level: < 0.0005A (Model 200 at 300 nm, slow, 2nm slit; Model 550 at 0A and 500nm)

Performance and Specifications (continued)

Scale Expansion: Model 200: 0-2A, 0-3A, 2x, 5x, 10x, 20x and 50x
Concentration: 0.1 to 10x
Model 550: 1x to 50x, conc. 1x to 10x
Detector: Photodetector
Readout: Model 200, digital, recorder Model 550 digital only
External Output: Analog: 50 mV for 100%T (analog 0-1V)
Digital: BCD, TTL compatible
Zero Suppression: To 3A or 100%T
Response: Model 200-0.5, 2, 5 sec
Model 550-1, 5 sec

Optical System

Grating: Model 200- 32×30 nm; 1440 lines/mm
Dispersion:
Wavelength Range: Model 200 - 190 to 800 nm
Model 550 - 315 to 800 nm (190 nm with UV accessory)
Wavelength Accuracy: ± 0.5 nm
Wavelength Reproducibility: ± 0.2 nm
Resolution: Model 200 - 0.2 to 4 nm, continuously variable
Model 550 - 2 nm
Slits:
Stray Light: < 0.1% at 220 nm, < 0.05% at 340 nm
Scan Speeds: Model 200 - 30, 60, 120, 240 nm/min
Model 550 - 20, 120 nm/min
Light Source: Tungsten iodide, deuterium, auto change over
Power Supply:

Operation

Calibration: Standard samples
Training: Minimal
Maintenance: Minimal
Unattended Period:

Requirements

Power: 115, 2-6, 220, 230V, 50/60 Hz, 150A
Weight: 33 kg (75 lb) without recorder
Dimensions: 66.5 cm W × 50.5 cm D × 18.0 cm H
Temperature:

Features

Double beam, UV-VIS spectrophotometer
Digital readout

Options

UV Accessory	$ 590
Model 550 recorder	750
Automatic sampling accessory	745
Flowcells	170-270
Automatic sample changer	
Programmable dispenser	2210
Enzyme calculator	1690
BCD Data Output	160
Digital Printer	1970
Auto Zero	270

References

Manufacturer's Specifications

Cost

Model 200	$6250
Model 550	5150

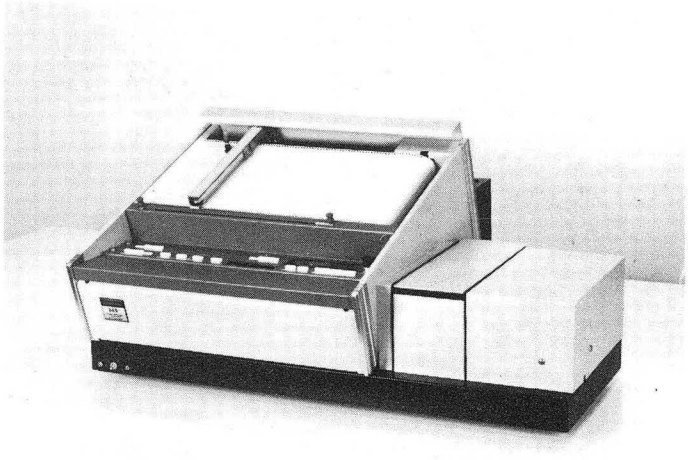
Address

Perkin Elmer Corporation
Coleman Instruments Division
2000 York Road
Oak Brook, IL 60521
(312) 887-0770/242-4050

INSTRUMENTATION
FOR ENVIRONMENTAL
MONITORING

Ultraviolet/Visible Spectrophotometer

Perkin-Elmer Model 340



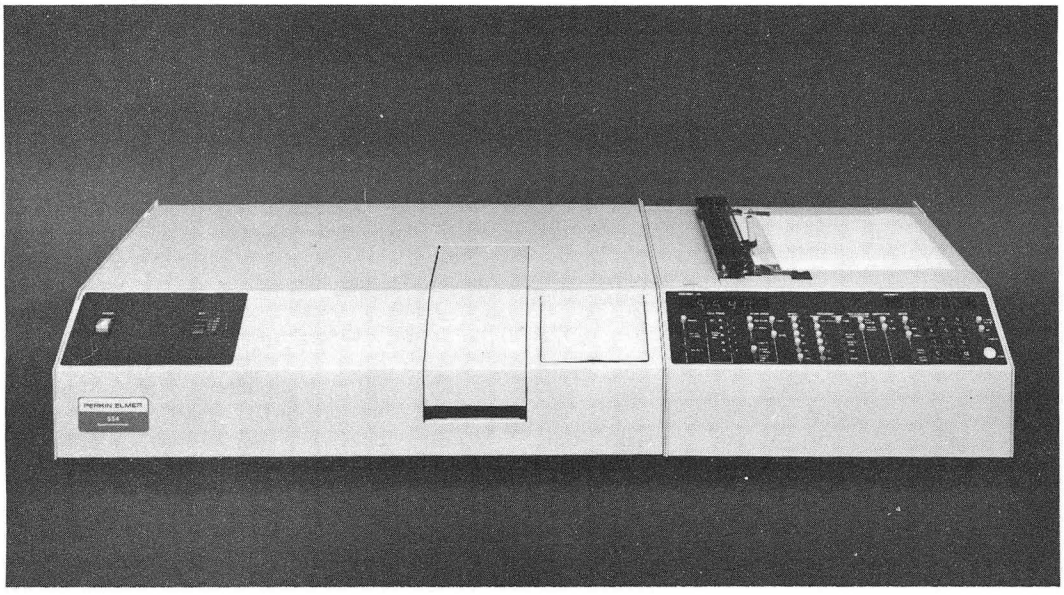
Class	Laboratory
Description	Microprocessor-controlled, double monochromator UV-VIS-NIR Spectrophotometer
Modes of Operation	Double beam, absorbance, % transmittance, concentration, Rep scan
Lower Detectable Limit	Depends on element path length and chemical treatment
Range	Absorbance: -0.3 ~4A % Transmittance: 0-200%
Interferences	Depends upon element and chemical method
Multiparameter Capability	Spectrophotometry, colorimetry, turbidimetry
Sampling	Method: Batch and semiautomatic P2 Volume: 2-4 mℓ Capacity: Temperature Control: Path Length: Turbidity Position: Optional Integrating Sphere for Turbid Samples
Performance and Specifications	Electronics: Solid State Linearity: Photometric Stability: Baseline, 0.0004A/hr Photometric Accuracy: Better than ±0.003A at 1A (930 filters NBS) Scale Expansion: 20, 5, 2, 1, 0.5x Noise Level: Detector: PMT R928 (UV-VIS), PbS (NIR) Readout: Flatbed x-y recorder External Output: Zero Suppression: Over entire scale, by 0.01A steps Response: 0.5, 1.5 and 5 sec Warm Up:

Performance and Specification (continued)	Optical System: Double monochromator, 1st - Littrow prism, 2nd - Littrow, dual grating Prism: Quartz (1st monochromator) Gratings: (2nd monochromator) 1440 lines/mm - (UV-VIS) 600 lines/mm (NIR) Wavelength Range: 190-2600 nm Wavelength Accuracy: Better than 0.2 nm, UV-VIS; 1 nm (NIR) Wavelength Reproducibility: Better than 0.1 mm (UV-VIS), 0.5 nm in NIR Resolution: Better than 0.15 mm (UV-VIS) Slits: NIR servo controlled, UV-VIS, manual or auto Stray Light: < less than 0.0002% at 300 nm Scan Speeds: 0.6, 1.2, 3.6, 12, 30, 60 , 120, 300 min/full scale Light Sources: D_2, tungsten Power Supply:
Operation	Calibration: Training: Maintenance: Unattended Periods:
Requirements	Power: 300 VAC, 50/60 Hz Weight: 110 kg Dimensions: 95 cm W × 74 cm D × 47 cm H Temperature:
Features	Standard Rep Scan Double monochromator Manufactured by Hitachi
Options	
References	Manufacturer's Bulletins
Cost	Model 340: $26,400
Address	Perkin-Elmer Corporation Coleman Instruments Division 2000 York Road Oak Brook, IL 60521 (312) 887-0770/242-4050

INSTRUMENTATION
FOR ENVIRONMENTAL
MONITORING

Ultraviolet/Visible Spectrophotometer

Perkin-Elmer Models 552, 554, 555



Class	Laboratory
Description	Microcomputer controlled, double beam recording ultraviolet visible spectrophotometers Model 555: As above, but with a premonochromator
Modes of Operation	Absorbance, transmission, concentration, 1st and 2nd derivative (optional on 552 - standard on 554, 555)
Lower Detectable Limit	Depends on element, chemical method and pathlength
Range	Absorbance: -0.3A - 3A % Transmission: 0-200%T Concentration: 000.1 to +9999
Interferences	Depends on element and chemical method
Multiparameter Capability	Spectrophotometry, colorimetry, turbidimetry, reflectance (optional)
Sampling	Method: Batch or automated (optional) Volume: Standard with micro options Capacity: Temperature Control: Optional Maximum Path Length: 10 cm Turbitity Position: Optional Integrating Sphere for Turbid Samples
Performance and Specifications	Electronics: Microcomputer Control Photometric Linearity: Photometric Accuracy: ± 0.005A Photometric Stability: < 0.0005A @ 0A, 340nm, 4nm slit Noise: 0.0004A @ 500nm, 0A, 5 sec, 5 sec response, 4nm, peak to peak over 3 min. Scale Expansion: 0.001A over entire scale Zero Suppression: -0.299A to 2.999A

Performance and Specifications (continued)

Response: Model 552: 0.5, 2, 5 sec ±10% for full scale deflection
Model 554, 555: 0.2, 0.5, 1, 2, 4, 7, 10 sec
Detector: Photomultiplier
Readout: Digital readout, recorder (optional on 552, standard on 554, 555)
External Output: Analog recorder

Optical System: Model 552, 554: Single monochromator
Model 555: Dual monochromator

Grating: 1440 lines/mm, blazed at 288nm
Wavelength Range: Model 552: 190-750nm, optional to 900nm
Model 554, 555: 190-900nm
Wavelength Accuracy: ± 0.5nm
Wavelength Reproducibility: ± 0.2nm
Resolution: 0.25, 1.0, 2.0 and 4.0nm bandpass
Slits: To achieve the above resolution

Stray Light: Model 552: <0.1% @ 220nm, 0.05% @ 340nm, 2nm and 2 sec response
Model 554: 0.1% @ 220, 340 and 370nm
Model 555: 0.008% @ 220nm, and 0.001% @ 340, 370nm

Scan Speeds: Model 552: 5, 20, 60, 120, 240, 480nm/sec
Model 554, 555: 5, 15, 30, 60, 120, 240nm/min
Light Source: Tungsten bromide and deuterium auto change
Power Supply:

Computer: Model 552: Motorola 6800 Microcomputer
Model 554 and 555: Two Rockwell PPS4 Microprocessors

Operation

Calibration: With standard solutions
Training: Minimal
Maintenance: Minimal
Unattended:

Requirements

Power: 115/230V ± 10% VAC, 50/60 Hz
Weight:
Dimensions:
Temperature:

Features

Model 554/555: Rep scan, cycle timer
Wavelength Programmer
Auto background corrector
Auto 0A and 100%T

Options

Model 552:
Thermoelectric Temperature Control
X-Y Recorder
Specular Reflectance
Rep Scan (standard on 554, 555)
1st and 2nd Derivatives
Model 554/555: Printer sequences - specular reflectance

References

Manufacturer's Bulletins

Cost

Model 552	$ 7,400
Model 554	13,950
Model 555	15,500

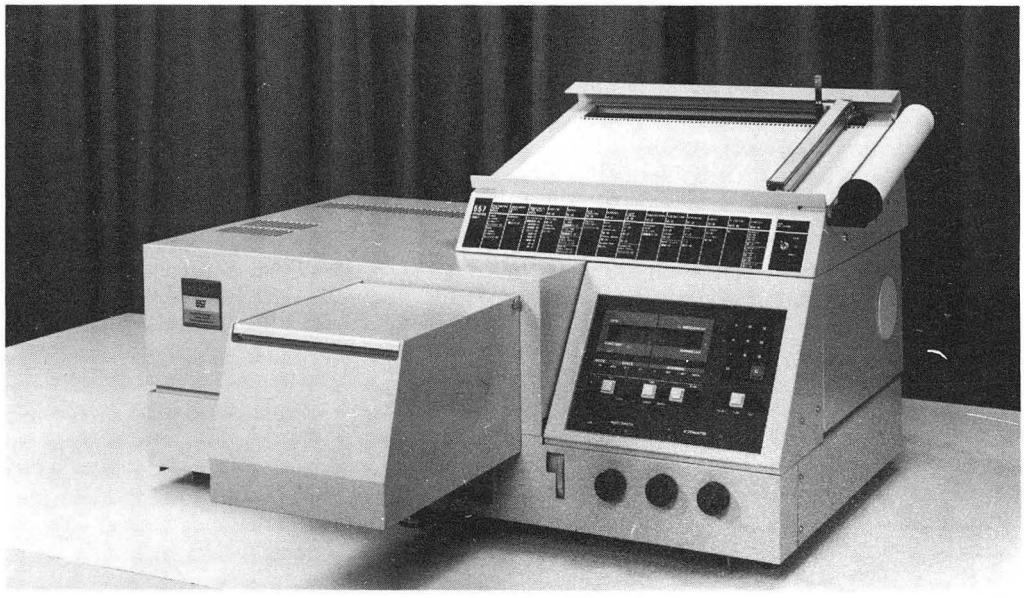
Address

Perkin Elmer Corporation
Coleman Instruments Division
2000 York Road
Oak Brook, IL 60521
(312) 887-0770

INSTRUMENTATION
FOR ENVIRONMENTAL
MONITORING

Ultraviolet/Visible Spectrophotometer

Perkin-Elmer Model 557



Class	Laboratory
Description	Microprocessor controlled Double beam, dual wavelength ultraviolet-visible spectrophotometer (190-900nm)
Modes of Operation	Double beam, single beam Absorbance, % transmittance, concentration, First through fourth derivative
Lower Detectable Limit	Depends on element, chemical method and pathlength
Range	Absorbance: 0-3A, 0-0.1A, 0.01A Transmittance: 0-100% Concentration: Up to 10x expansion
Interferences	Depends on element and chemical method used
Multiparameter Capability	Spectrophotometry, colorimetry, turbidimetry
Sampling	Method: Batch or semiautomatic (optional) Volume: Capacity: Temperature Control: Available Maximum Cell Length: 100mm Turbidity Position: Yes
Performance and Specifications	Electronics: Solid state integrated circuitry, microcomputer controlled Photometric Linearity: Photometric Stability: Scale Expansion: 0.001A or 0.1%T over entire range Detector: 2" photomultiplier Zero Suppression: Entire range Readout: Digital-3 1/2 digits in %T, A or C, dedicated recorder

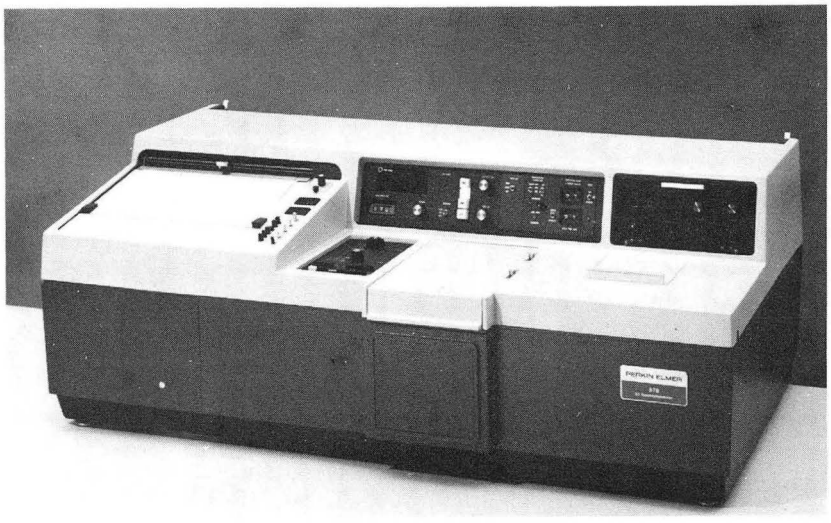
Performance and Specifications (continued)	Output: Digital or analog Warm Up: Response Time: Optical System: 2 diffraction grating monochromators with automatic filter insertion and lamp change Grating: Wavelength Range: 190-900nm Wavelength Accuracy: ± 0.4nm Wavelength Repeatability: ± 0.2nm Resolution: Continuously variable from 0.3 to 10mm bandwidth Slits: To achieve the above spectral bandwidths Scan Speeds: Forward - 30, 60, 120, 150, 240, 300, 600 1200nm/min Stray Light: Backwards - 240, 120nm/min Lamp: Tungsten bromide and deuterium
Operation	Calibration: Standard samples Training: Maintenance: Unattended Period:
Requirements	Power: 115 VAC, 60 Hz Weight: Dimensions: Temperature:
Features	Double beam, double monochromator, UV-VIS spectrometer Absorbance, % transmittance concentration, 1st derivative Measurements on turbid samples
Options	TLC scanner, gel scanner Stopped flow apparatus Digital baseline corrector
References	Manufacturer's Specifications
Cost	Model 557 $31,350
Address	Perkin Elmer Corp. Coleman Instrument Division 2000 York Road Oakbrook, IL 60521 (312) 887-0770

INSTRUMENTATION
FOR ENVIRONMENTAL
MONITORING

Ultraviolet/Visible Spectrophotometer

Perkin Elmer 57 Series

Models 571, 572, 575 and 576



Class	Laboratory
Description	High resolution recording double beam ultraviolet visible spectrophotometer series
Modes of Operation	Model 571: Absorbance, concentration Model 572, 575, 576: Absorbance, % transmission, concentration, first derivative
Lower Detectable Limit	Depends on element, chemical method and pathlength
Range	Absorbance: 0-3A % Transmittance (not on 571): 0-100% Concentration: 0.1 = 10x
Interferences	Depends on element and chemical method
Multiparameter Capability	Spectrophotometry, colorimetry Model 576: Turbidimetry
Sampling	Method: Batch Volume: Capacity: Temperature Control: Available Maximum Pathlength: 100 cm Turbidity Position: Standard on Model 576
Performance and Specifications	Electronics: Photometric Stability: Baseline stability - ± 0.0005A/hr after warm up; at 340nm and 3nm slit Photometric Accuracy: ± 0.003A or ± 0.3%T, measured with NBS SRM 93b filters (includes DVM uncertainty of ± 0.001A or ± 0.1%T Photometric Linearity: Noise: 0.005A @ 2A, 340nm, 3.0mm slit

Performance and Specifications (continued)

Scale Expansion: 0.01 over entire scale digital recorder
0.1A increments over full scale
Zero Suppression: 0.1A increments to 3A
Response: Model 571 - 1 second (98% full scale)
Models 572, 575, 576: 0.25, 1 and 4 secs
Detector: Models 571, 572, 575: end on photomultiplier
Model 576: 2" end on PMT with silica diffusion/collection plate
Readout: Built-in recorder
External Output: Model 571: analog
Models 572, 575, 576: analog, digital BCD encoded ordinate, TTL compatible

Optical System

Grating: 1440 lines/mm
Wavelength Range: Models 571, 572 - 190-750nm (900nm, opt.)
Models 575, 576 - 190-900nm
Wavelength Accuracy: ± 0.5nm
Wavelength Reproducibility: ± 0.2nm
Resolution: 0.2, 0.5, 1.0 and 3.0nm
Slits: To achieve the above bandpass
Stray Light: <0.1% @ 320, 370nm
Scan Speeds: 60 Hz - 12, 24, 60, and 120nm/min
50 Hz - 10, 20, 50, 1000 and 200nm/min
Chart Drive - 2, 12, 24, 60, 120, 240mm/min
Light Source: Tungsten halogen, deuterium, auto switchover
Power Supply: Dedicated

Operation

Calibration: With standard solutions
Training: Minimal
Maintenance: Minimal
Unattended:

Requirements

Power: 115/230 VAC, 50/60 Hz
Weight: 80 kg (175 lb)
Dimensions: 107 cm W × 60 cm D × 40 cm H (42" × 23 1/2" × 16")
Temperature:

Features

Model 571: Auto zero, x-10 ordinate expansion (0.01A full scale)
Model 572: %T, concentration modes, response times
Model 575: Rep Scan
Background correction
x-10 scale expansion
auto zero, %T, A, concentration
Model 576: 575 plus special photo multiplier, and sample chamber for turbid samples

Options

References

Manufacturer's Specifications

Cost

Model 571	$ 9,500
Model 572	11,980
Model 575	11,000
Model 576	12,500

Address

Perkin-Elmer Corp.
Coleman Instruments Division
2000 York Road
Oak Brook, IL 60521
(312) 887-0770

Visible Spectrophotometer

Perkin-Elmer Coleman Junior Series

Junior II (Models 6/20 and 6/35, IIA and III)

Class	Laboratory
Description	Single beam, visible spectrophotometers (335-825 nm)
Modes of Operation	Single beam Absorbance, transmittance concentration
Lower Detectable Limit	Depends on element chemical method and pathlength
Range	Absorbance 0-2A (II,III-log, IIA-linear) Transmittance 0-100%
Interferences	Depends on elements and chemical method
Multiparameter Capability	Spectrophotometry, colorimetry
Sampling	Method: batch Volume: 1 mℓ to 12.0 mℓ Capacity: Temperature control: Max pathlength: Turbidity positions: no
Performance and Specifications	Electronics: Solid state Photometric linearity: Photometric stability: Scale expansion: no Zero suppression: N/A Detector: Photomultiplier

Performance and Specifications (continued)

Readout: II, III: galvanometer (log A, linear %T)
IIA: galvanometer (linear in A, %T)
Output: analog
Warm up:
Response: maximum 2 sec. (approximately)

Optical System:

Grating: Echelette
Wavelength range: 335-825 nm
Wavelength accuracy: ±1nm at 610 nm (Junior II, IIA); Junior III
Wavelength reproducibility:
Resolution: II Model 6/20, IIA, 20 nm bandpass
II Model 6/35 - 35 nm bandpass

Scan speeds: not available
Stray light:
Junior III - < 0.1% at 340 nm
Light source: Junior II,IIA - tungsten lamp
Junior III - quartz-halogen
Power supply: built-in

Operation

Calibration: Standard samples
Procedure:
Training:
Unattended period:
Maintenance: Service centers in the U.S.

Requirements

Power: 115 V AC, 50/60 Hz
Weight: 15 kg (33 lbs)
Dimensions: 16" × 15" × 10" - 8" for Junior II
Temperature: Laboratory

Features

Single beam, visible spectrophotometers with galvanometer (II,IIA,III) or meter readout

Options

Vacuvette accessories

References

Manufacturer's Bulletin

Cost

Junior Model II	$ 1,050
Junior Model IIA	1,180
Junior Model III	1,210

Address

Perkin-Elmer Corporation
Coleman Instrument Division
2000 York Road
Oak Brook, IL 60521
(312) 887-0770/242-4050

INSTRUMENTATION
FOR ENVIRONMENTAL
MONITORING

Visible Spectrophotometer

Perkin Elmer, Coleman Model 35

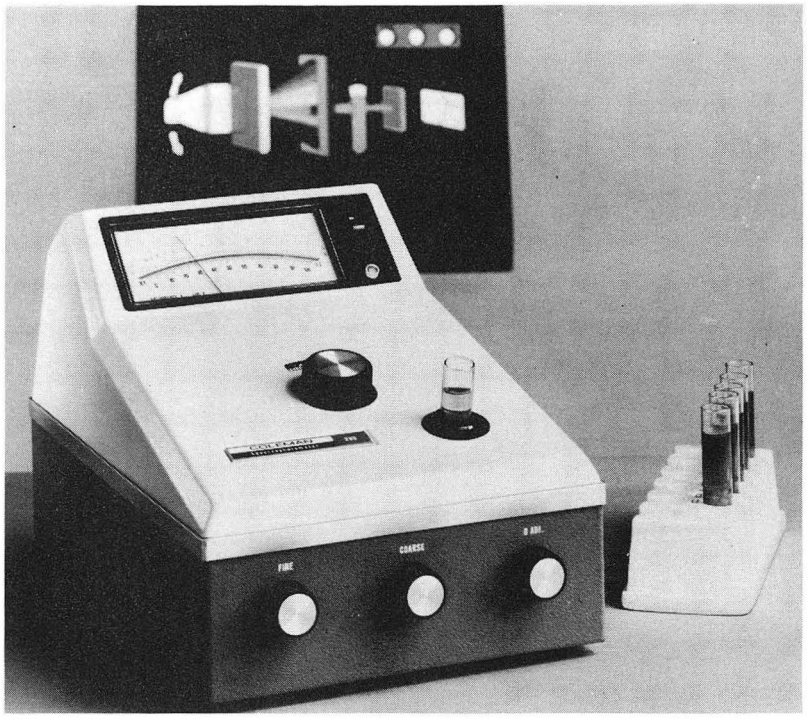
Class	Laboratory
Description	Single beam, digital visible spectrophotometer
Modes of Operation	Absorbance, % transmission, concentration
Lower Limit of Detection	Depends on element, chemical method and pathlength
Range	Absorbance: -0.3 to 1.999A % transmittance: 0 to 199.9%T Concentration: 0-1999
Interferences	Depends on element and chemical method
Multiparameter Capability	Colorimetry, spectrophotometry
Sampling	Method: batch Volume: 1.0 to 12 mℓ Capacity: Temperature control: Maximum pathlength: Turbidity position: no
Performance and Specifications	Electronics: Photometric linearity: Photometric accuracy: ±0.01A @0.5A, ±0.8%T (when measured with NBS SRM filters, includes DVM uncertainty of 0.001A , 0.1%T

Performance and Specifications (continued)	Photometric stability: 0.003A drift/hour Noise: ±0.001A @ 0A and 1A, ±0.002A @ 2A Scale expansion: 0.1 - 5x Zero suppression: no Response: 3 seconds Detector: phototube Readout: digital External output: 0-50 mV/absorbance unit
	Optical System
	Grating: Wavelength range: 335-825 nm Wavelength accuracy: ± 1 nm @ 365, 436, 546 and 630 nm Wavelength reproducibility: within 1 nm. Resolution: 8 nm ± 20% @ 436 nm Slits: to achieve above bandpass Stray light: > 0.1% @ 340 nm Scan speeds: N/A Light source: Quartz halogen lamp Power supply: integral
Operation	Calibration: with standard solutions Training: minimal Maintenance: minimal Unattended:
Requirements	Power: Weight: Dimensions: Temperature:
Features	
Options	Calibration scale Cells (matched pairs, "perfect" rounds)
References	Manufacturer's Bulletin
Cost	Model 35 $1,400
Address	Perkin-Elmer Corporation Coleman Instrument Division 2000 York Rd. Oak Brook, IL 60521 (312) 887-0770/242-4050

INSTRUMENTATION
FOR ENVIRONMENTAL
MONITORING

Visible Spectrophotometer

Perkin Elmer, Coleman Junior Model 295



Class	Laboratory
Description	Single beam visible spectrometer
Modes of Operation	Single beam, absorbance, % transmittance
Lower Detectable Limit	Depends on element, chemical method used, and pathlength
Range	Absorbance: 0-2.0 A Transmittance: 0-100% T, ±0.5% T
Interferences	Depends on element and method used
Multiparameter Capability	Colorimetry
Sampling	Method: batch Volume: 1.0 ml to 12.0 ml Capacity: Temperature control: none Pathlength: Turbidity position: no
Performance and Specifications	Electronics: Solid state Linearity: Stability: reproducibility ±0.5% T Photometric accuracy: Noise level: Scale expansion:

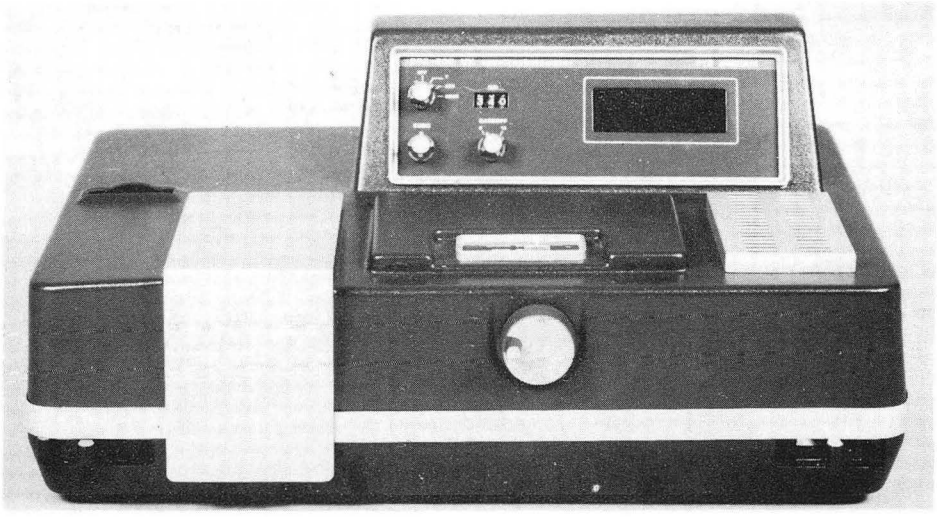
Performance and Specifications (continued)	Zero suppression Detector: photocell Readout: meter External output: None Warm up: Response: Optical System: Echelette Grating: Echelette Slit width: 20 nm bandpass Wavelength range: 400-700 nm Wavelength accuracy: ± 1 nm at 585 nm Wavelength reproducibility: ±0.5 nm or less Stray light: Light source: Tungsten lamp Power supply: built-in
Operation	Calibration: standard samples Procedure: Manual provided Training: teaching package, aids, and wall charts available Unattended period: none Maintenance: 33 service centers in the U.S.
Requirements	Power: Weight: 7.7 kg (17 lbs) Dimensions: 25.4 cm W × 42 cm D × 23.4 cm H (10" W × 16.5" × 9.25" H) Temperature: laboratory
Features	Single beam visible spectrophotometer Removable components, modular makeup for viewing
Options	Educational Aids Vacuvette - rapid sampling assembly
References	Manufacturer's Bulletin
Cost	Model 295 $ 605
Address	Perkin-Elmer Corporation Coleman Instrument Division 2000 York Rd. Oak Brook, IL 60521 (312) 887-0770/242-4050

INSTRUMENTATION
FOR ENVIRONMENTAL
MONITORING

Ultraviolet/Visible, Visible Spectrophotometers

Pye Unicam SP6 Series - SP6-200, SP6-300,

SP6-400, SP6-500



Model SP6-500

Class	Laboratory
Description	A series of UV-visible and visible spectrophotomers with color coded controls for ease in use. The major differences to the user are the ranges (325-1000nm - SP6-200, -300 and 220-1000nm in the SP6-400, and -500) and the display (meter in the SP6-200, 400 and digital in the SP6-300, 500)
Modes of Operation	Single beam Absorbance, % transmittance, concentration
Lower Detectable Limit	Depends upon element, chemical method and pathlength
Range	Absorbance: 0-1A, 0-2A Transmittance: 0-10%, 0-100% Concentration: 0.2 to 10xA
Interferences	Depends upon metal and chemical method
Multiparameter Capability	Spectrophotometry, colorimetry
Sampling	Method: Batch standard, can be automated Volume: Minimum 0.5 mℓ Temperature Control: Built-in tubes to accept option Maximum Cell Length: 400mm Turbidity Position: No
Performance and Specifications	Electronics: Solid State, plug in circuit boards Linearity: Photometric Stability: Baseline drift: - 0.003A/hr after warm-up Photometric Accuracy: <1% Noise Level: Scale Expansion: 0-1A,0-2A, 0-10%T, 0-100%T Detector: 2 vacuum phototubes Zero Suppression Readout: Meter in 200, 400, digital in 300, 500

Performance and Specifications (continued)

External Output: All versions 2V, 10mV analog
Warm Up: 30 mins to reach stability spec.
Response:

Optical System: Manual light change in SP6-400, 500

Grating: Planar, Littrow mount
Wavelength Range: SP6-200, -300, 325 - 1000nm
SP6-400, -500, 220 - 1000nm
Wavelength Accuracy: Within 1nm
Wavelength Reproducibility:
Resolution: 8nm bandwidth
Slits: To achieve the above bandwidth
Scan Speeds: Not available
Stray Light: <0.4% at 340nm
Light Source: For visible-tungsten-halide, SP6-400, 500 deuterium lamp.
Power Supply: Supplied with SP6-400, SP6-500. Not necessary with SP6-200, 300

Operation

Calibration: Standard samples
Training: Minimal
Maintenance:
Unattended Period:

Requirements

Power: 110240 VAC, 50/60 Hz
Weight:
Dimensions:
Temperature:

Features

Single beam UV-VIS or visible spectrophotometer

Options

Auto cell
Test tube holder
Teaching kit
Liquid chromatography kit
Thermostatted cell holder
Manual cell changer

References

Manufacturer's Specifications

Cost

SP6-200	$1995
SP6-300	2350
SP6-400	2350
SP6-500	2725

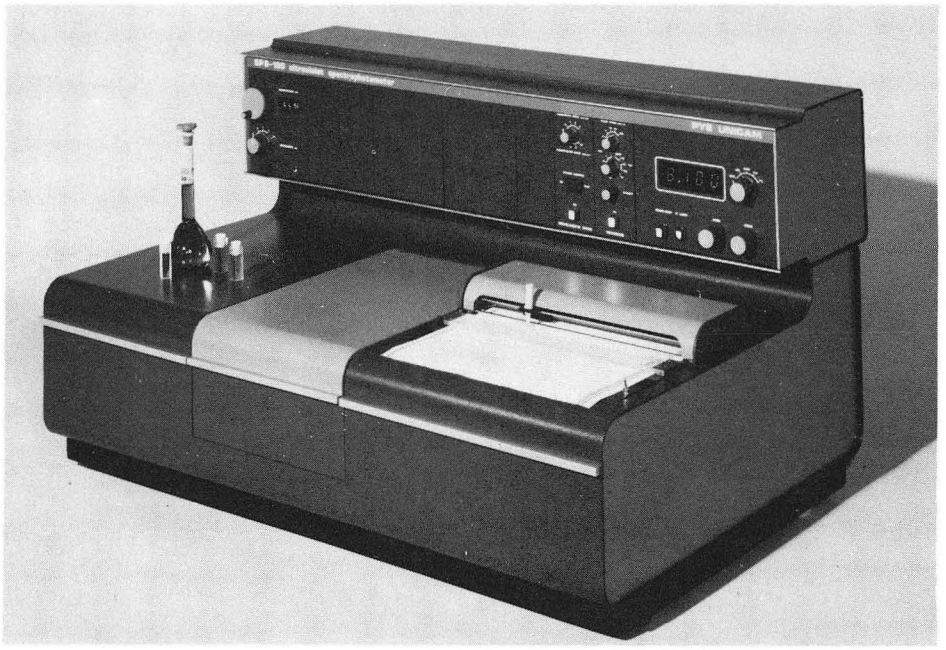
Address

Pye-Unicam Instruments
Phillips Electronics Instruments
85 McKee Drive
Mahwah, N.J. (07430)
(201) 529-3800

INSTRUMENTATION
FOR ENVIRONMENTAL
MONITORING

Ultraviolet/Visible Spectrophotometer

Pye Unicam SP8-100



Class	Laboratory
Description	Digital, double beam, scanning ultraviolet/visible (190-900nm) spectrophotometer
Modes of Operation	Double beam Absorbance, transmittance, concentration, kinetics (optional)
Lower Detectable Limit	Depends upon element, chemical method and pathlength
Range	Absorbance: 0-3.000A Transmittance: 0-100.0%T Concentration: 0-8000
Interferences	Depends upon metal and chemical method
Multiparameter Capability	Spectrophotometry, colorimetry
Sampling	Method: Batch, optional automation - scan/select system Volume: Minimum 300µℓ using microcells or 500µℓ using auto cell Capacity: 50 samples/batch Temperature Control: Optional Maximum Cell Length: 2-40mm standard, or 100mm with accessory cell holder. Turbidity Position: Yes (with accessory)
Performance and Specifications	Electronics: Linearity: Within the accuracy specification Photometric Stability: (Baseline) better than 0.0001A/hr after warm up Photometric Accuracy: ± 0.5% of absorbance value ± 1 digit from 0-2A, relative to filters traceable to National Physical Laboratory Standards Photometric Noise: < ± 0.001A near 0A, < ± 0.004A near 2A at 340nm, with 1nm bandwidth

Performance and Specifications (continued)

Scale Expansion: 0-0.05, 0-0.1, 0-0.2, 0-0.5, 0-1, 0-2A; 10, 100%T
Detector: End-on photomultiplier
Zero Suppression: Manual - to 3A
Readout: Recorder and digital
External Output: Analog, digital
Warm Up: 20 mins. max.
Response: 0.5 sec.

Optical System: Ebert monochromator, with automatic lamp and filter change

Grating: 1200 lines/mm
Wavelength Range: 190-900nm
Wavelength Accuracy: ± 0.5nm
Wavelength Reproducibility: ± 0.25nm
Resolution: Bandwidth - 0.2, 0.5, 1, 2nm and high energy (10nm)
Slits: To achieve the above bandwidths
Scan Speeds: 0.2, 0.5, 1, 2, 5nm/sec, recorder: - 2,5,10,20,100 sec/cm
Stray Light: < 0.1% at 220nm
Light Source: Deuterium lamp and quartz-halogen lamp
Power Supply: Built-in

Operation

Calibration: Standard samples
Training: Minimal
Maintenance: Minimal
Unattended Period: Depends on program selected

Requirements

Power: 110-120/220-240V ± 10%, 50/50 Hz, consumption - 400VA (max)
Weight: 70 kg
Dimensions: 88 cm × 56 cm × 48 cm
Temperature:

Features

Double beam digital operation,
Large sample compartment

Options

Auto sample changer	$1995
Manual cell changer	575
Wavelength programmer	750
Program controller	875
Cycle timer	550
Multirange accessory	610
Automatic cell changer	850
Thermostatted cell holder	310
Cell temperature controller	575
Printer serializer	525
Teletype serializer	525
Turbid sample holder	90
Diffuse reflectance accessory	1500
Densitometer	1975
Fluorescence accessory	1020
Liquid chromatography kit	675
Derivative and log A mode	850
Automatic superimpose	650

References

Manufacturer's Specifications

Cost

SP8-100 from $ 8950

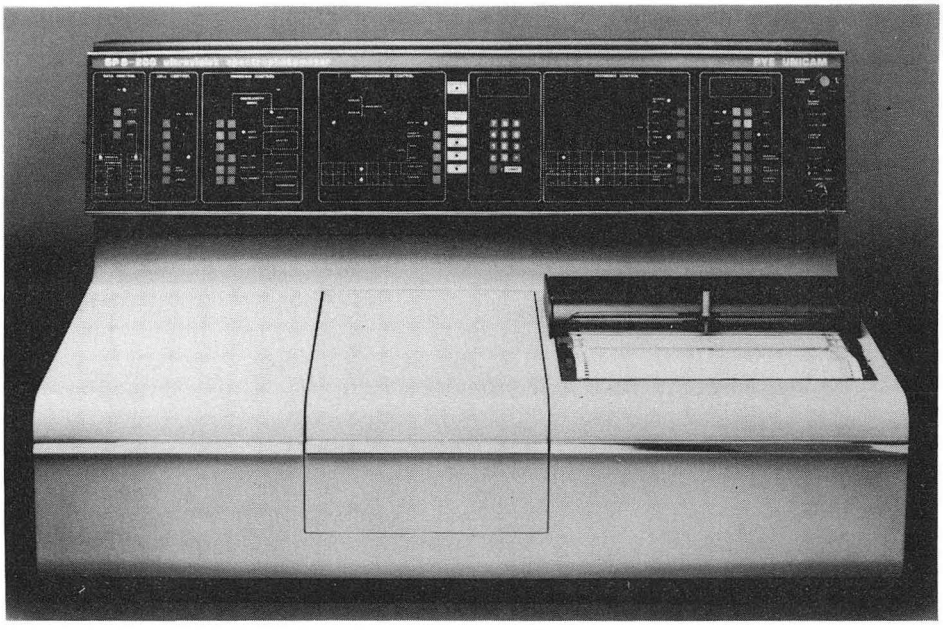
Address

Pye-Unicam Instruments
Philips Electronics Instruments
85 McKee Drive
Mahwah, N.J. 07430
Attn: Mr. Frank Hamm
(201) 529-3800

INSTRUMENTATION
FOR ENVIRONMENTAL
MONITORING

Ultraviolet/Visible Spectrophotometer

Pye Unicam Model SP8-200



Class	Laboratory
Description	Microprocessor-controlled digital, double beam, scanning ultraviolet/visible spectrophotometer
Modes of Operation	Double beam Absorbance, transmittance, concentration, kinetics (optional)
Range	Absorbance: -3 to 3.300A Transmission: 0-200.0%T Concentration: 0000-9999
Multiparameter Capability	Spectrophotometry, colorimetry, turbidimetry
Sampling	Method: Batch, optional automation Volume: 300µℓ using microcells or 500µℓ using autocell Capacity: 50 samples/batch in auto sampler Temperature control: Optional - 0-100.0°C Maximum Pathlength: 2-40mm standard, or 100mm with accessory holder Turbidity Position: Yes (with accessory)
Performance and Specifications	Electronics: Photometric Linearity: Within accuracy specification Photometric Accuracy: ±0.0015A @ 1A ±0.003A @ 2A ±0.020A@ 3A Photometric Stability: Better than 0.0001A per hour @ 0A, after warm-up Noise: 0.001A @ 0A, 0.004A near 2A (340nm, 2nm bandwidth) Scale Expansion: 0.01, 0.02, 0.1, 0.2, 0.5, 1, 2, 4A full scale on recorder Zero Suppression: Up to 2.999 in 0.001 steps Response: Better than 0.5 or 5.0 sec. for full scale deflection Detector: End-on PMT Readout: Recorder, dedicated and LED displays External Output: Bit serial-character serial, ASC11 RS232 and 20 or 60mA current loop

Performance and Specifications (continued)

Optical System: Ebert monochromator with auto lamp and filter change
Grating: Holographic silica coated, 1200 lines/mm blazed at 250nm
Wavelength Range: 185-950nm
Wavelength Accuracy: ± 0.3nm
Wavelength Reproducibility: Within 0.1nm
Resolution: 0.1, 0.2, 0.5, 1, 2nm and high energy (10nm)
Slits: To achieve the above bandwidths
Stray Light: < 0.01% @ 220 & < 0.001 @ 360
Scan Speeds: 0.1, 0.2, 0.5, 1, 2, 5 and 10 nm/sec
Light Source: Quartz halogen, deuterium lamp
Power Supply: Integral

Operation

Calibration: With standard solutions
Training: Minimal
Maintenance: Minimal
Unattended: Depends on program selected

Requirements

Power: 110-120/220-240V ± 10%, 50/60 Hz, 400VA max.
Weight: Model 200-68.5 kg
Dimensions: 88 cm × 56 cm × 50 cm
Temperature:

Features

Microprocessor controlled, computer interfacing capability

Options

Auto sample changer		$1995
Manual cell changer		575
Program control module:	wavelength programer program controller cycle timer	1258
Multirange accessory		610
Automatic cell changer		850
Thermostatted cell holder		310
Cell temperature controller		575
Printer serializer		525
Teletype serializer		525
Turbid sample holder		90
Diffuse reflectance accessory		1500
Densitometer		1975
Fluorescence accessory		1020
Liquid chromatography kit		676
Derivative and Log A mode		850
Automatic superimpose		650

References

Manufacturer's Bulletins

Cost

SP8-200

Address

Pye Unicam Instruments
Philips Electronics Instruments
85 McKee Drvie
Mahwah, N.J. 07430
Attn: Mr. Frank Hamm
(201) 529-3800

INSTRUMENTATION
FOR ENVIRONMENTAL
MONITORING

Ultraviolet/Visible Spectrophotometer

Shimadzu UV 100/110 Series

Class	Laboratory
Description	Single beam ultraviolet visible spectrophotometer (100 meter, 110 digital)
Modes of Operation	Single beam. absorbance, transmittance, concentration
Lower Detectable Limit	Depends on element, chemical method and pathlength
Range	Absorbance: Model 100 - 0-2A, 0-1A Model 110 - 0-3A, 0-2A % Transmittance: 0-100%T Concentration: Model 110 - 0.000 - 1.999 Model 100 - 0 - 100
Interferences	Depends on element and chemical method
Multiparameter Capability	Spectrophotometry, colorimetry
Sampling	Method: Batch holds 4 cuvettes, flow through optional Volume: Micro cells available (opt.) Capacity: Four samples and one reference Temperature Control: Optional Maximum Pathlength: Up to 10 cm Turbidity Position: No
Performance and Specifications	Electronics: Photometric Linearity: less than 0.03A Photometric Accuracy: ± 0.005A Photometric Stability: 0.001A/hr Noise: Less than ± 0.001 near 0A, less than ± 0.003A near 1A Scale Expansion: None Zero Suppression: Available Response: Fixed Detector: Models 100-01, 110-01-silicon photocell, Models 100-02, 110-02 Silicon photocell and phototube

Performance and Specifications (continued)

Readout: Model 100 - meter, Model 110-digital voltmeter
External Output: Analog 1 mV per A, Model 110 - BCD 1248

Optical System: Diffraction grating monochromator

Grating: 1200 lines/nm. blazed at 200nm.
Wavelength Range: Model UV-100-01,110-01 - 325-1000nm
Model UV-100-02,110-02 - 200-1000nm
Wavelength Accuracy: ± 2nm
Wavelength Reproducibility: ± 0.3nm
Resolution: 7nm bandwidth
Slits: To attain bandwidth above
Models 100-01,110-01 - less than 0.1% @ 340nm
Models 100-02,110-02 - less than 0.1% @ 340nm, less than 0.15% @ 220nm
Scan Speeds: N/A
Light Source: Models 100-01,110-01-tungsten lamp; Models 100-02, 110-02 tungsten and D_2 lamp
Power Supply: Built-in (included and integral)

Operation

Calibration: With standard solutions
Training: Minimal
Maintenance: Minimal; service contract available.
Unattended: Manual operation

Requirements

Power: 110/115, 220/240V, 50/60 Hz, Model 100 70VA, Model 110 160VA
Weight: 20 kg
Dimensions: 50 cm W × 36.1 cm D × 25.2 cm H
Temperature: Laboratory

Features

7nm, spectral bandwidth
New detector system requires no detector change-over.

Options

Flow through cell
Recorder
Digital Printer (Model 110)
Temperature control

References

Manufacturer's Bulletins

Cost

Model UV 100-01	$1660
Model UV 100-02	2200
Model UV 110-01	2360
Model UV 110-02	2900

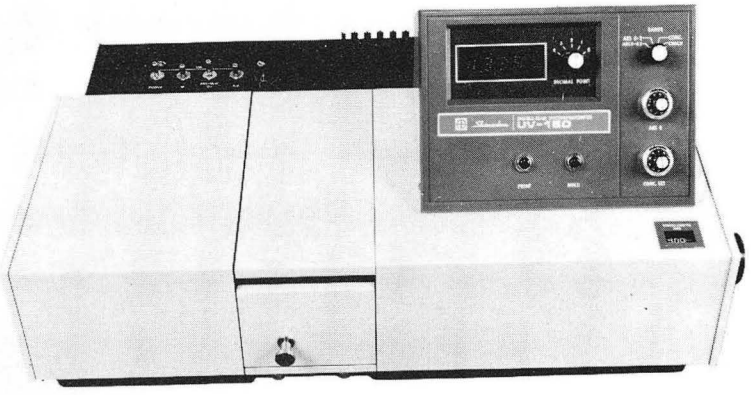
Address

Shimadzu Scientific Instruments, Inc.
9147-H Red Branch Road
Columbia, MD 21045
(301) 596-6978, or (301) 997-1227

INSTRUMENTATION
FOR ENVIRONMENTAL
MONITORING

Ultraviolet/Visible Spectrophotometer

Shimadzu 140/150 Series



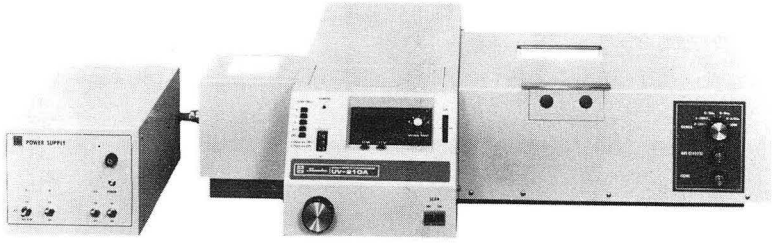
Class	Laboratory
Description	Double beam ultraviolet-visible spectrophotometer, with meter (140 series) or digital (150 series readout)
Modes of Operation	Double beam, single beam Absorbance, transmittance, concentration
Lower Detectable Limit	Depends on element, chemical method and pathlength
Range	Absorbance: 0-1A, 0-2A, (UV-140); 0-2A, (UV-150) %Transmittance: 0-100% (nonlinear on the UV-140) Concentration: Yes
Interferences	Depends on element and chemical method
Multiparameter Capability	Colorimetry, spectrophotometry, reflectance (opt.)
Sampling	Method: Batch holds 4 cuvettes standard, automation possible Volume: From 0.1 mℓ Capacity: Four samples and one reference Temperature control: Optional Maximum Pathlength: 10 cm Turbidity Position: No
Performance and Specifications	Electronics: Photometric Linearity: UV-150 - 0.005A UV-140 - 0.01A Photometric Accuracy: + 0.505A Photometric Stability: Baseline stability 0.004A/30 minutes Noise: Less than ± 0.00025A near 0 Abs. Scale Expansion: 10x Zero Suppression: Available Response: Fixed Detector: Model 140-01, 150-01 - silicon photocell Model 140-02, 150-02 - silicon photocell, phototube

Performance and Specifications (continued)	Readout: Model 140 - meter, Model 150-digital External Output: Analog 1V/A unit, digital (150) BCD 1248
	Optical System: Czerny-Turner, Diffraction grating monochrometer
	Grating: Wavelength Range: Model 140-01, 150-01 - 325 - 1000nm Model 140-02, 150-02 - 200 - 1000nm Wavelength Accuracy: ±0.1nm Wavelength Reproducibility: ±0.2nm Resolution: 5mm bandwidth Slits: To obtain the above bandwidth Stray Light: 1200 lines/mm, blazed at 200 nm Scan Speeds: N/A Light Source: Model 140-02, 150-02-tungsten and D_2 lamps Power Supply: built-in (included and integral)
Operation	Calibration: With standard solutions Training: Minimal Maintenance: Minimal. Service contract available
Requirements	Power: 100/115, 220/240V, 50/60 Hz, 150VA Weight: 30 kg Dimensions: 64 cm W × 37 cm D × 33 cm H Temperature: Laboratory
Features	Double beam spectrophotometer
Options	Recorder Flow through cell, micro cells Printer (150 only) Temperature control Auto sample changer
References	Manufacturer's Bulletins
Cost	Model 140-01 $2500 Model 140-02 2850 Model 150-01 3200 Model 150-02 3550
Address	Shimadzu Scientific Instruments 9147H Red Branch Road Columbia, MD 21045 (301) 596-6978, or (301) 997-1227

INSTRUMENTATION
FOR ENVIRONMENTAL
MONITORING

Ultraviolet/Visible Spectrophotometer

Shimadzu UV-200S and 210A Series



Class	Laboratory
Description	Scanning, double beam, ultraviolet visible Spectrophotometer with meter (200S) or digital (210A) readout
Modes of Operation	Double beam, single beam Absorbance, transmittance, concentration (opt. on 200S, standard on 210A)
Lower Detectable Limit	Depends on element, chemical method and pathlength
Range	Absorbance: Model 200S - 0-1A 0-2A Model 210A - 0-2A 0-3A %Transmittance: 0-100% Concentration: Optional on 200S, standard on 210A
Interferences	Depends on element and chemical method
Multiparameter Capability	Spectrophotometry, colorimetry, reflectance, turbidimetry
Sampling	Method: Batch or automated Volume: From 0.1 mℓ (cell volume, 5 mm path length) Capacity: Micro cell available Temperature Control: Optional Maximum Pathlength: 10 cm Turbidity Position: N/A

Performance and Specifications

Electronics: Solid state, integrated circuitry

Photometric Linearity: Less than 0.002A
Photometric Accuracy: ± 0.002 (@ 0.5A), ± 0.004 (@ at 1A) and ± 0.3%T (0-100%T)
Photometric Stability: @100%, ±1.0% Baseline stability 0.0004A/h. Baseline flatness ± 1.0%.
Noise: ± 0.0002 at 240 nm.
Scale Expansion: 10x over entire range
Zero Suppression: To 0.5, 1.0, 1.5 and 2.0A and continuously variable (not available on 200S)
Response: Model 210A - 3 steps changeable. Model 200S - 2 steps changeable
Detector: R-446 U
Readout: Model 200S - meter
Readout: Model 210A - digital
External Output: 1V/Abs., digital (210A)-BCD 1248 - TTL for printer

Optical System: Czerny-Turner grating monochromator

Grating: 1200 lines/mm, blazed at 200 nm
Wavelength Range: 190-900nm
Wavelength Accuracy: ± 0.3nm (full range)
Wavelength Reproducibility: ± 0.1nm
Resolution: Model 200S: 0.25, 0.5, 1.0, 2.0, and 5.0nm bandwidth
Model 210A: 0.1, 0.2, 0.5, 1.0, 2.0 and 5.0nm bandwidth
Slits: To obtain above bandwidth
Stray Light: Better than 0.1% @ 220nm
Scan Speeds: 60, 120, 240, 480nm/min
Light Source: Tungsten and D_2 lamps, manual change
Power Supply: Non-integral

Operation

Calibration: With standard solutions
Training: Minimal
Maintenance: Minimal
Unattended: Possible.

Requirements

Power: 100/115, VAC 50/50 Hz, 140VA
Weight: 55 kg
Dimensions: Spectrophotometer - 85 cm W × 60 cm D × 21 cm H
Power Supply - 20 cm W × 35 cm D × 17 cm H
Temperature: Laboratory

Features

Unique symmetrical double-beam optics

Options

Integrating sphere, Flow-through cell, micro cell, recorder - printer (210A only), derivative spectrophotometry attachment.
Cell positioner.

References

Manufacturer's Bulletins

Cost

Model UV-200S	$6000
Model UV-210A	7500

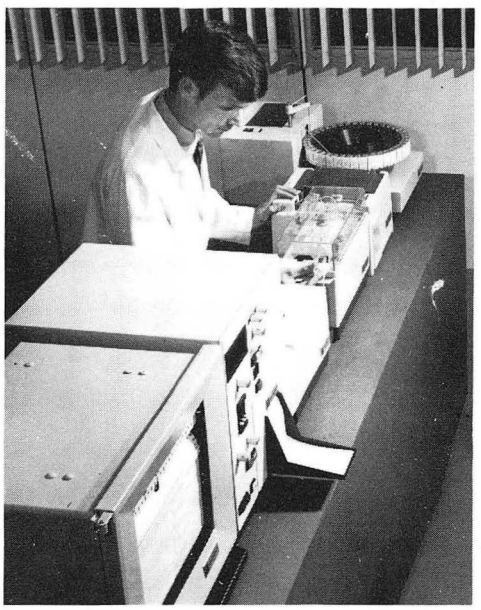
Address

Shimadzu Scientific Instruments
9147H Red Branch Road
Columbia, MD 21045
(301) 596-6978 or (301) 997-1227

INSTRUMENTATION
FOR ENVIRONMENTAL
MONITORING

Automatic Multiparameter Monitor

Technicon AutoAnalyzer II



Class	Laboratory batch
Categories of Water	Fresh, Saline, Waste, Process
Principle of Operation	Colorimetric Ion Selective Electrode, Thermometric, Flourimetric Flame Photometric; UV-VIS Spectrophotometric. Samples are aspirated into a sampling line, segmented by air bubbles, and mixed with a reagent stream by dialysis. The resulting product is measured by the appropriate detector.
Minimum Detectable Sensitivity	Equivalent to manual method
Interferences	
Multiparameter Capability	See comparable manual method.

PARAMETER	TYPICAL RANGE (mg/ℓ except where indicated)	AUTOANALYZER II RATES OF ANALYSIS
Ammonia	0-10	60/hr
Ammonia (seawater)	0-10 µg at /1	60/hr
Nitrate + Nitrite	0-2	40/hr
Nitrate + Nitrite (seawater)	0-45 µg at /1	40/hr
Nitrite	0-1	60/hr
Nitrite (seawater)	0-5 µg at /1	60/hr
Ortho-Phosphate	0-10	50/hr
Ortho-Phosphate (seawater)	0-4 µg at /1	30/hr
Total Inorg. Phos	0-10	40/hr
Silicate	0-10	60/hr
Silicate (seawater)	0-50 µg at /1	60/hr
Total Soluble Iron	0-10	20/hr
Sulfide (seawater)	0-10 µg at /1	50/hr
Hexavalent Chromium	0-5	40/hr
Copper	0-10	40/hr
Sucrose	0-100	40/hr
COD	0-500	20/hr
Cyanide	0-3	40/hr
Phenol	0-5	40/hr
Fluoride	0-2	20/hr
Hardness	0-300	30/hr

Multiparameter Capability (continued)

Table Continued

PARAMETER	TYPICAL RANGE (mg/ℓ except where indicated)	AUTOANALYZER II RATES OF ANALYSIS
Sulfate	0-300	30/hr
Alkalinity (pH 3 min)	0-500	60/hr
Alkalinity (pH 8 min)	0-100	50/hr
Chloride	0-10	60/hr
Total Kjeldahl Nitrogen	0-100	20/hr
	0-1000	20/hr
Total Phosphorus	0-50	20/hr
Uranium	2-100	60/hr
TOC	1-100 or .2-20	30/hr
pH	2-12 pH units	30/hr
Conductivity	2-2000 μ-ohms	30/hr
Boron	.02-1	30/hr
Carbonate	0.2-20	50/hr
Hydrazine	2-100	40/hr
Formaldehyde	40-2000	40/hr
Cumene	.005-25%	20/hr
Sulfuric Acid	.02-1.0%	50/hr
Silver	1-50 g/ℓ	40/hr

*Additional parameters and ranges available upon request

Sampling

Method: Semi-continuous
Maximum Temperature Input: 29°C

Performance

Accuracy: Method dependent
Reproducibility: Method dependent
Linearity: Method dependent
Noise: Method dependent
Response Time: 15 minutes dependent on chemistry selected
Zero Drift: Self-compensated
Span Drift: Self-compensated

Operation

Ambient Temperature Range: 13°C - 29°C
Temperature Compensation: Self-compensating
Relative Humidity Range: 10-80%
Calibration: Automatic, periodically, with blank and standard solutions
Procedure: Automatic
Unattended Period: Generally no more than 24 hours
Maintenance: Change reagents as needed

Requirements

Power: 117 VAC; 50 to 60 Hz, 11A
Weight: 70 kg (150 lbs) maximum
Dimensions: (cm)

Module	L	W	H
Sampler IV	38.1	45.7	22.8
Proportioning Pump III	30.5	27.9	22.8
Manifold	43.2	25.6	27.9
Colorimeter	43.2	27.9	33.0
Digital Printer	26.6	39.4	43.2
Recorder	45.7	44.5	45.7

(Inch)

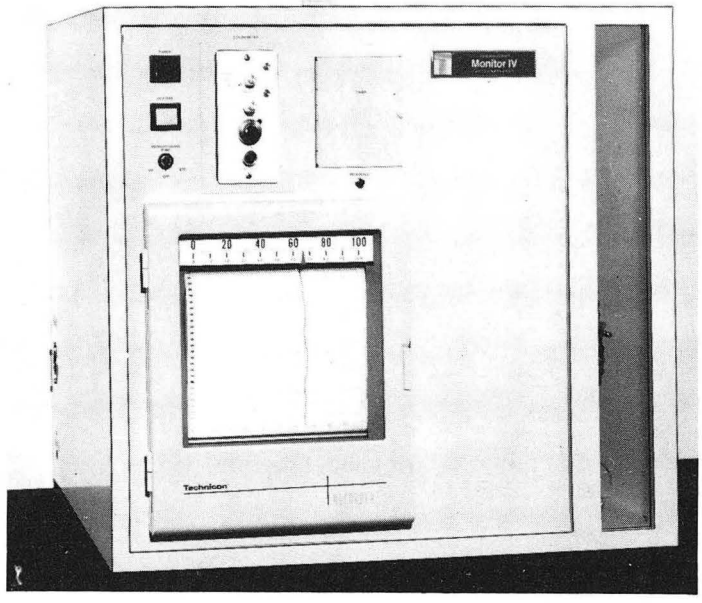
Module	L	W	H
Sampler IV	15	18	9
Proportioning Pump III	12	11	9
Manifold	17	10	11
Colorimeter	17	11	13
Digital Printer	8-1/2	15-1/2	17
Recorder	18	17-1/2	18

Features	Output: Recorder or digital printer		
	Training: Free at Tarrytown, N.Y.		
	Options: SOLIDprep Sampler II	$12,530	
	On Stream Filter-Sampler	5,200	
	Block Digestor	3,050	
	Continuous Filter	1850	
	Analytical Cartridge		
	Fluoronephelometer	5,895	
	Flame Photometer IV	7830	
	Block Digestor, BD-40	3050	
References	Manufacturer's Bulletin "AutoAnalyzer II"		
Cost	Autoanalyzer II (one channel)	$15,155	
		22,515	(two channels)
		30,380	(three channels)
	w/o digital display	12,045	
		17,485	
		23,530	
Remarks	Requires a 2' × 8' bench top; many sample ranges available		
Address	Technicon Instruments Corporation 511 Benedict Avenue Tarrytown, N.Y. 10591 Tel. (914) 631-8000		

INSTRUMENTATION
FOR ENVIRONMENTAL
MONITORING

Automatic Multiparameter Monitor

Technicon Monitor IV



Class	Continuous
Categories of Water	Waste, process streams, saline
Principle of Operation	Colorimetric or ION Selective Electrode. Sample stream and reagent stream are merged and mixed automatically. The sample stream is segmented by air bubbles. The segmented stream is pumped through a train of modules; each module performs a specific function (e.g., mixing, heating, distillation, color development).
Minimum Detectable Sensitivity	Dependent upon chemistry selected
Interferences	Dissolved color, turbidity, (Colorimetric reactions only)

Multiparameter Capability

PARAMETER	TYPICAL RANGE (ml/l except where indicated)
Ammonia	0-10
Ammonia (seawater)	0-10 µmol/l
Nitrate + Nitrite	0-2
Nitrate + Nitrite (seawater)	0-45 µmol/l
Nitrite	0-1
Nitrite (seawater)	0-5 µmol/l
Ortho-Phosphate	0-10
Ortho-Phosphate (seawater)	0-4 µmol/l
Total Inorganic Phosphate	0-10
Silicate	0-10
Silicate (seawater)	0-50 µmol/l
Total Soluble Iron	0-10
Sulfide (seawater)	0-10 µmol/l
Hexavalent Chromium	0-5

Multiparameter Capability

PARAMETER	TYPICAL RANGE (mℓ/ℓ except where indicated)
Copper	0-10
Sucrose	0-100
Phenol	0-200 µg/ℓ
pH	2-12 pH units
Conductivity	2-2000 µ-ohms
Boron	0.02-1.0
Carbonate	0.2-20
Cyanide	0-1.0
Hardness	0-250
COD	0-150
TOC	1-100
Hydrazine	2-100
Formaldehyde	40-2000
Sulfuric Acid	0.02-1%
Cumene	0.005-0.25%
Silver	1-50
Flouride	0-5

Additional parameters and ranges available upon request

Sampling

Method: Continuous
Maximum Temperature Input: 29°C
Filter: Optional
Maximum Number of Sample Sources: 2 (alternately)

Performance

Accuracy: Method dependent
Reproducibility: Method dependent
Linearity: Method dependent
Noise: Method dependent
Response Time: 7-15 minutes
Zero Drift: Self-compensated
Span Drift: Self-compensated

Operation

Ambient Temperature Range: 13°C to 29°C
Temperature Compensation: Self-compensated
Relative Humidity Range: 10% to 80%
Calibration: Automatic; at selected intervals between 2-24 hours, either a wash solution (zero reading) or a standard solution are run through the analyzer. Any adjustment is done automatically.
Procedure: Automatic
Unattended Period: Generally 7 days
Maintenance: (7 days or greater)

Requirements

Power: 110-120 VAC, 60 Hz; 5A maximum
Weight: 63.4 kg (140 lb)
Dimensions: 57.1 cm H × 62.9 cm W × 47 cm D
(22 1/2" × 24 3/4" × 18 1/2")

Features

Output: Recorder; 0-5 Vdc for telemetry or control
Training: Free to employee of purchaser at Tarrytown, N.Y.
Options: Continuous filter-sampler

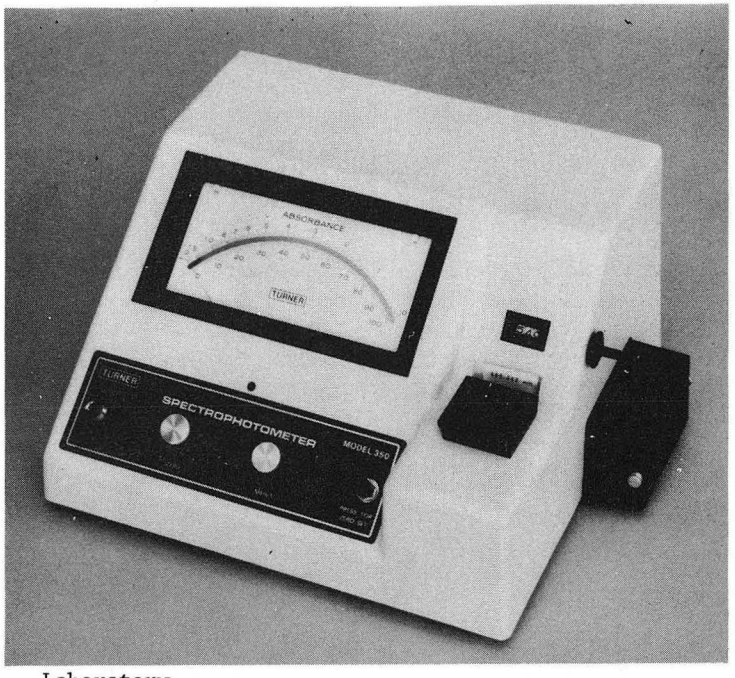
References

(1) Manufacturer's bulletin "Technicon Monitor IV" 1971
(2) "A Significant Advance in the Technology of Industrial Wastewater Monitoring", Frederick D. Buggie, 1971. Available from Technicon.

Cost	Monitor IV Basic Instrument
Remarks	Up to ten sources sampled with special accessories
Address	Technicon Instruments Corporation Tarrytown, N.Y. 10591 (914) 631-8000

Visible Spectrophotometer

Turner Models 330 and 350



Class	Laboratory
Description	Single beam - Visible Spectrophotometer (320-710 nm)
Modes of Operation	Absorbance, % transmission
Lower Detectable Limit	Mercury: 2 µg without concentration (Nabrzyskim, Anal. Chem. 45, 2438 (1973)) Cadmium: 0.006 to 0.008 µg/mℓ (Ackerman, et al., Anal. Chem. 250, 353 (1970)) Depends upon metal, chemical method and pathlength
Range	ppb to %, depends on the particular analysis 0 - 100% Transmission 0 - 2 Absorbance
Interferences	Dirty or scratched cells, depends on metal or chemical
Multiparameter Capability	Spectrophotometry, colorimetry
Sampling	Method: Discrete, discrete flow-through Volume: Depends on cuvette size or attachment used. With 100 mm × 13 mm cuvette, minimum volume is approximately 4 mℓ. With the INSTAFILL accessory sample size down to 0.6 mℓ with 0.075 mℓ in the cell. Temperature Control: Water jacket provided with INSTAFILL or some accessory cuvette holders requires an external temperature regulated water supply and pump. Maximum Pathlength: 25 mm Turbidity Position: No

Performance

Electronics: Solid State

Linearity: Up to an absorbance of 1.7 at 340 nm
Stability:
Photometric Accuracy:
Scale Expansion: Not available
Detector: Photodiode (210-710 nm range)
Zero Suppression:
Readout: Meter
External Output: Analog, 0-1V
Warm Up: 2 min
Response (damping): Fixed

Optical System: Monochromator with Ebert Mount, f7

Grating: 600 lines/mm
Dispersion:
Wavelength Range: 320-710 nm (standard - extendable to 210 nm with deuterium lamp accessory; extendable to 1000 nm with IR accessory
Wavelength Accuracy: ± 2 nm throughout range sometimes
Wavelength Reproducibility: 0.5 nm
Slits:
Resolution: 9-nm bandwidth
Scan Speeds: Not available
Stray Light: 0.5% throughout operating range
Light Source: Tungsten lamp
Power Supply: Built-in

Operation

Calibration: Standard solutions
Procedure: Calibration curve; standard additions
Training: Manual provided
Unattended Period:
Maintenance: Service available from distributors or Turner factory. Technician can repair from manual sometimes

Requirements

Power: 100-130 or 200-260 VAC; 50/60 Hz; 30 W average, 50 W maximum
Weight: 6.3 kg (14 lb) - Model 330, Model 350 39.6 kg (18 lb)
Dimensions: Model 330: 29 cm W × 30.5 cm D × 16 cm H (11 3/4" × 12" × 6 1/2")
38.7 cm W × 31.8 cm D × 20.3 cm H (15 1/4" × 12 1/2 × 8")

Temperature:

Features

UV-Visible Spectrophotometer
Experimental Flexibility

Options

Cuvette Holders; Round, jacketed, square, vacuum emptying	$ Varies
Ultraviolet Attachment, to 210 nm	1170
INSTAFILL Automatic Filling Device	746
IR Accessory	49.80

Wavelength Setting: By means of digital counter

References

a) Manufacturer's Bulletin, "Turner Laboratory Instruments" 1977

Cost

Model 330	$ 780
Model 350	940

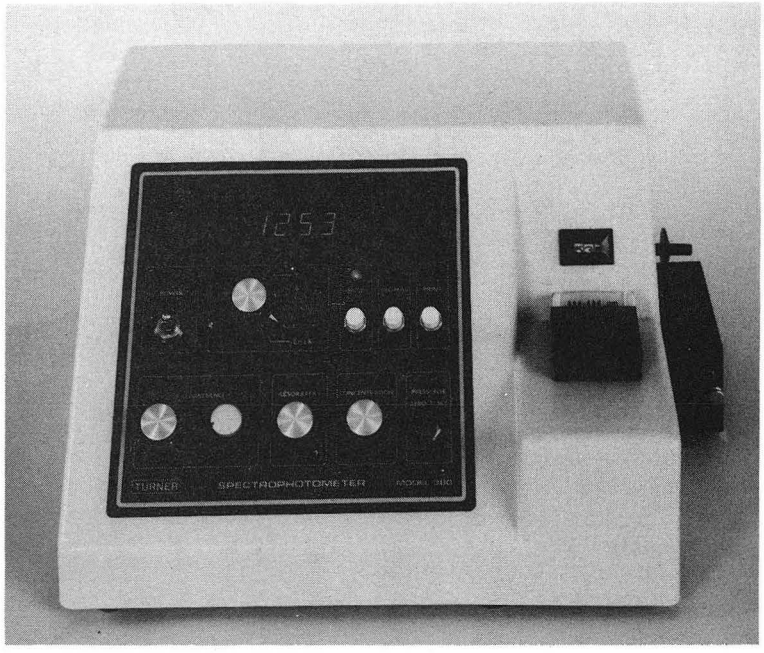
Address

Turner Associates, Division American Sterilizer Company
2524 Pulgas Avenue
Palo Alto, CA 94303
(415) 324-0077

INSTRUMENTATION
FOR ENVIRONMENTAL
MONITORING

Ultraviolet/Visible Spectrophotometer

Model 380



Class	Laboratory
Description	Digital readout, single beam, visible spectrophometer; UV optional
Modes of Operation	Absorbance, concentration, transmittance
Lower Detectable Limit	Depends on element, chemical method and pathlength
Range	Absorbance: 0.000 to 1.999 % Transmittance: 0.0 to 100% Concentration: 0 to 1999
Interferences	Depends on element and chemical method
Multiparameter Capability	Spectrophotometry; colorimetry
Sampling	Method: Batch, automated, optional Volume: Depends on cuvette size: RE: 330, 350 information Capacity: Temperature Control: Water jacket with INSTAFILL; RE: 330-350 information Maximum Pathlength: 25 mm standard or some accessory cuvette holder requires external temp. regulated water supply and pump. Turbidity Position: No
Performance and Specifications	Electronics: Solid State Photometric Linearity: Up to 1.7A @ 340nm Photometric Accuracy: Photometric and Stability: Noise: Scale Expansion: No Zero Suppression: No Response: Fixed Detector: Wide range photoiodide (210-710nm)

Performance and Specifications (continued)	Readout: Digital External Output: Multiplexed BCD, TTL compatible Analog: 0-1V ± 0.2V DC, negative grounded Optical System: f7 Ebert Mount Grating: 600 lines/mm Wavelength Range: 320-710 (to 210 with accessory) Wavelength Accuracy: ± 2nm, full range Wavelength Reproducibility: Within 0.5nm Resolution: 9nm bandwidth Slits: To achieve the above bandwidth Stray Light: < 0.5% Scan Speeds: N/A Light Source: Tungsten (320 to 1000) Power Supply
Operation	Calibration: With standard solutions Training: Minimal Maintenance: Minimal Unattended:
Requirements	Power: 115V/230V, 50/60 Hz, 75W Weight: 10.9 kg (shipping wt), 24 lbs Dimensions: 32.5 cm W × 19.4 cm H × 30 cm D (13" × 7 3/4" × 12") Temperature: Laboratory
Features	
Options	Micro flow through cells Printer Far UV NIR Enzyme, calculator/printer
References	Manufacturer's Bulletins
Cost	Model 380 $1725
Address	Turner Associates 2524 Pulgas Avenue Palo Alto, CA 94303 (415) 324-0077

INSTRUMENTATION
FOR ENVIRONMENTAL
MONITORING

Visible and Ultraviolet/Visible Spectrophotometers

Varian 634 Series, 634 UV and 634 S

Class	Laboratory
Description	A Series of digital double beam, ultraviolet/visible and visible spectrophotometers Model 634 UV - ultraviolet/visible, manual scan (190-900nm) Model 634S - ultraviolet/visible, automatic scanning (190-900 nm)
Modes of Operation	Double beam, single beam Absorbance, % transmittance, concentration
Lower Detectable Limit	Depends upon element, chemical method and pathlength
Range	Absorbance: -0.5 to + 2.0A Transmittance: 0-100% Concentration: Any range to 1999 units
Interferences	Depends upon metal and chemical method used
Multiparameter Capability	Spectrophotometry, colorimetry, fluorescence - total and spectral, kinetics, gel scanning
Sampling	Method: Batch or automatic, auto 50 sampling system Volume: 1.5 - 3 mℓ. Capacity: 3 samples/1 min Temperature Control: Optional Maximum Cell Length: 10 mm Turbidity Position: No
Performance and Specifications	Electronics: Solid state modules Linearity: Photometric Stability: Zero drift 0.002A/hour, span drift 0.0004A/hr Photometric Accuracy: < ± 0.002A at 1.0A Noise Level: < 0.001 Abs. at 500 nm, 2 nm SBW. Scale Expansion: Any 0.1 segment of absorbance range between 0 and 1.5A can be expanded to full scale

Performance and Specifications (continued)	Detector: Photomultiplier Zero Suppression: Readout: Digital, 4 digit Output: Analog 0-100mV, digital BCD Warm Up: Response: 1 second
	Optical System: Czerny Turner mounting
	Grating: 32×27 mm, 1276 grooves/mm blazed at 275 nm Dispersion: 3.3 nm/mm Wavelength Range: 190-900 Wavelength Accuracy: < ± 0.5nm Wavelength Reproducibility: < ± 0.25 nm Slit Width: Step adjustable 0.2, 0.5, 1.0 and 2.0 nm Resolution: 0.2nm Scan Speeds: 634S only 10, 25, 50, 100 nm/min. Stray Light: < 0.1% at 220nm Light Source: 50W tungsten ; deuterium arc. Power Supply: Built-in to instrument.
Operation	Calibration: Manual -- one control Procedure: External standards; wavelength by internal standards Training: One hour required Unattended Period: Two hours Maintenance: 27 service centers in U.S. Temperature Compensation: Both wavelength and electronics
Requirements	Power: 110, 115, 220 or 240 VAC; 50/60 Hz; 200W maximum Weight: 34 kg (75 lb) Dimensions: 72 cm W × 40 cm D × 33 cm H (28-1/2" × 15-3/4" × 13") Temperature: 0 to 45° C
Features	

Options		
	Automatic Sampler, Model Auto-50	$2430
	Digital Printer, DP 37	1800
	Fluorescence total	260
	Reflectance, diffuse	2015
	Recorder, 9176-04	1290
	Auto-5 Programmer	2800
	Gel Scanner	1810

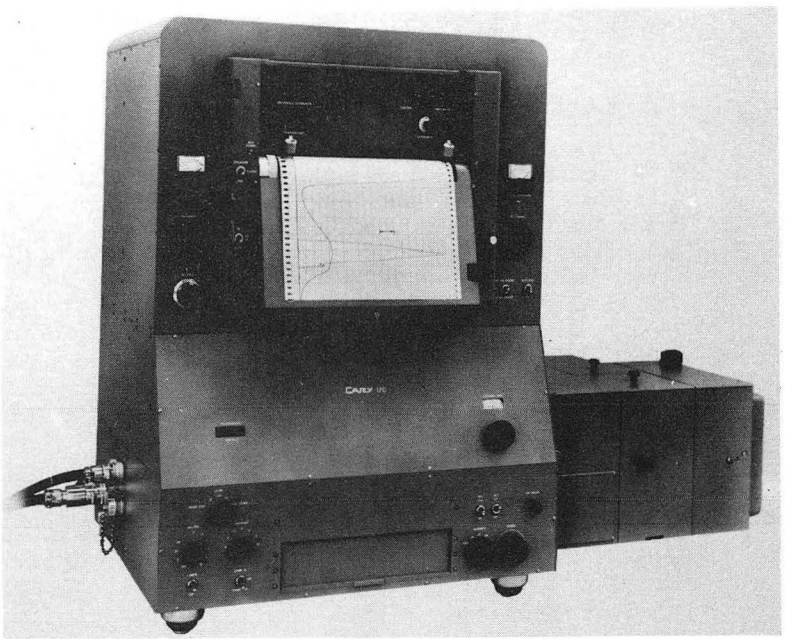
References	Manufacturer's Specifications

Cost		
	Model 634 UV	$5450
	Model 634 S	5950

Address	
	Varian Instrument Division 611 Hansen Way Palo Alto, CA 94303 (415) 493-8100

Ultraviolet/Visible/Near Infrared Spectrophotometer

Varian, Cary Model 17D



Class	Laboratory
Description	Double beam, double monochromator, digital ultraviolet-visible-near infrared spectrophotometer (186-2650nm, 186-3000nm opt.)
Modes of Operation	Double beam, single beam Absorbance, transmittance, concentration, reflectance, fluorescence or derivative
Lower Detectable Limit	Depends upon metal, chemical method and pathlength
Range	Absorbance: 0-1, 1-2, 0-0.5, 0.5-1, 0-0.2, 0.2-0.4, 0-0.1 and 0.1-0.2 Transmittance: 0-100%, optional 5, 10, 20, 50% T
Interferences	Depends upon element and method
Multiparameter Capability	Spectrophotometer, colorimetry, fluorescence, scattered transmission, reflectance, derivative spectra
Sampling	Method: Batch or automated Volume: Minimum 20μℓ Temperature Control: Optional, available Maximum Cell Length: Turbidity Position: No
Performance and Specifications	Electronics: Solid State Linearity: 0.004 at 0A 0.0015 at 1.0A 0.005 at 2.0A 0.03 at 3.0A Photometric Stability: < 0.005A/hr baseline drift Noise Level: 0.001 Abs Scale Expansion: 1x to 10xA, 1x to 5x in %T Detector: Lead sulfide, phototube

Performance and Specifications (continued)	Zero Suppression: 0-2.4 abs in steps of 0-.1 abs, 0-100%T continuously useable Readout: Recorder built-in, digital - 4 digit display External Output: Digital Response (Period): 1, 5, 25 sec Optical System: Prism and grating monochromators Grating: 600 lines/mm Prism: 30 degree fused silica Wavelength Range: 186-2650 nm, 186-3000nm opt. Wavelength Accuracy: better than +0.4nm Wavelength Reproducibility: Less than 0.05nm in UV-VIS, 0.25nm in near IR Resolution: 0.07nm in UV-VIS, 0.3nm in near IR Slit Width: 0 to 3mm, servomotor control Stray Light: < 0.0001% - 240-500nm Scan Speeds: 0.005, 0.01, 0.02, 0.05, 0.1, 0.2, 0.5, 1, 2, 5, 10nm/sec Light Source: Tungsten-halogen, deuterium Power Supply: Included
Operation	Calibration: Standard samples Procedure: Manual provided Training: Requires about 1 hour Unattended Period: With optional accessories Maintenance: 27 service centers in U.S.
Requirements	Power: 115 or 230 volts, 50/60 Hz, 11 amps Weight: 317 kg (700 lbs) Dimensions: 144 cm W, 93 cm H, 84 cm D (57" W, 36.5" H, 33" D)
Features	

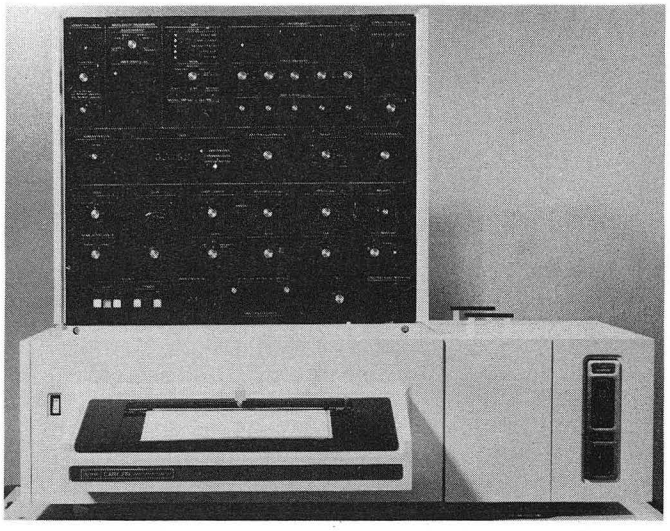
Options		
	Automatic Sample Changer, Model 1729000	$ 3740
	Digital Repetitive Scan Accessory, Model 1718000	2580
	Fluorescence Accessory, Model 1712000	4100
	Fluorescence Excitation Accessory, Model 1412800	1430
	Diffuse Reflectance Accessory (monochromate source) Model 1711000	6625
	Diffuse Reflectance Accessory, Model 1711150	5850
	Specular Reflectance Accessory, Model 1413000	4695
	Cell Space Diffuse Reflectance Accessory, Model 1411750	1670
	Scattered Transmission Accessory, Model 1762000	5840
	Derivative Accessory, Model 1790900 (Standard with 17D)	n/c

References	a) Manufacturer's Bulletin b) Price List, Aug. 14, 1978	
Cost	Model 17D	31,995
Address	Varian, Instrument Division 611 Hansen Way Palo Alto, CA 94303 (415) 493-8100 Box D-070	

INSTRUMENTATION
FOR ENVIRONMENTAL
MONITORING

Ultraviolet/Visible Spectrophotometer

Varian Cary Model 219



Class	Laboratory
Description	Direct ratio-recording, scanning UV-VIS double beam spectrophotometer with double pass monochromator
Modes of Operation	Absorbance, % transmittance, concentration Derivative and Log A (optional)
Lower Detectable Limit	Depends on element, chemical method and pathlength
Range	Absorbance: -0.1000 - 4.000A, -0.6000 - 3.5000 Transmission: 000.00 - 100.00 Concentration: 00000 - 40000 with six decimal positions
Interferences	Depends on element and chemical method
Multiparameter Capability	Spectrophotometry, colorimetry, turbidimetry, reflectance (opt.), kinetics
Sampling	Method: Batch, 5 cell turret Volume: From microcell to 10 cm pathlength Capacity: Standard 5 cell turret Temperature Control: A variety of methods available Maximum Pathlength: 10 cm, long path gas cells (opt.) Turbidity Position: No
Performance and Specifications	Electronics: Photometric Linearity: 0.0016A @ 1.0A 0.003A @ 2.0A 0.03A @ 3.0A Photometric Accuracy: Photometric and Stability: At 0.0A - 0.0004A/hr Noise: Scale Expansion: A: 0.01, 0.02, 0.05, 0.1, 0.2, 0.5, 1, 2A full scale T: 0-100%, 0-10% C: 0.3-30x

Performance and Specifications (continued)

Zero Suppression: A: 20 calibrated steps of 0.1000A from 0-2A
also -0.5A available
T: 0-50%T
Response: 0.5, 1, 2.5, 10 sec.
Detector: Photomultiplier
Readout: Digital-5 digit LED, 00000-40000
External Output: Digital and analog

Optical System: Double pass monochromator, Ebert
Grating:
Wavelength Range: 187-875
Wavelength Accuracy: ± 0.2nm
Wavelength Reproducibility: ± 0.1nm
Resolution: 0.07nm (limiting)
Slits:
Stray Light: < 0.002%T @ 220nm
Scan Speeds: Stepper motor, 0.01 nm/step, 0.01, 0.02, 0.05, 0.1, 0.2, 0.5, 1, 2, 5, 10, nm/sec
Light Source: D_2 and tungsten
Power Supply: Built-in

Operation

Calibration: With standard solutions
Training: Minimal
Maintenance: Minimal
Unattended: With optional accessories

Requirements

Power: 115/250V, 50/60 Hz, Max. 10 amps.
Weight: 100 kg (222 lbs), shipping wt. 159 kg (350 lbs)
Dimensions: 109 cm L × 71 cm W × 89 cm H (43" L × 28" W × 35"H)
Temperature:

Features

Options

Neutral Density Filter	$ 70
Glass Filter	85
Wavelength Calibration Accessory	295
Rear Beam Attenuator	295
Stirrer	675
Wavelength Programmer	795
Cell Programmer	1380
Timer	695
Derivative, Log A	995
Digital Printer	1950
Thermosttated cell holders	355
Routine sampler (thermosttated)	1595
Routine sampler	995

References

Manufacturer's Bulletins
Price List - June, 1978

Cost

Model 219 — 12,995

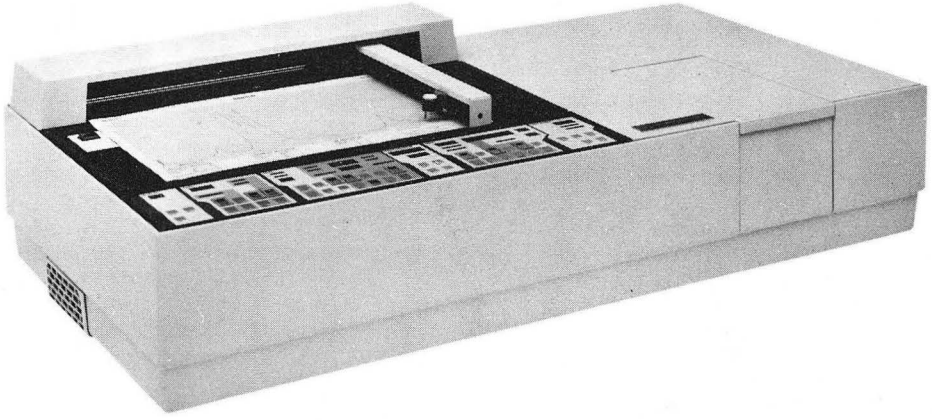
Address

Varian
Instrument Division
611 Hansen Way
Palo Alto, CA 94303
(415) 493-8100

INSTRUMENTATION
FOR ENVIRONMENTAL
MONITORING

Ultraviolet/Visible Spectrophotometers

SuperScan™ Series, SuperScan 1BE, 2 and 3



Class	Laboratory
Description	A series of digital, double beam ultraviolet-visible spectrophotometers SuperScan 3-recorder and digital readout, 200-900nm SuperScan 2-recorder and digital readout, 200-900nm SuperScan 1BE-digital readout, 200-900nm
Modes of Operation	Single beam, double beam Absorbance, transmittance, concentration, kinetics, first derivative (SuperScan 3, 2 only)
Lower Detectable Limit	Depends upon element, chemical method and pathlength
Range	Absorbance: 0-0.05, 0-0.1, 0-0.5, 1.0, 2.0 or 4.0A Transmittance: 0-5%, 0-10%, 0-50%, 0-100%, 0-200%, 0-400%T Concentration: variable
Interferences	Depends upon metal and chemical method
Multiparameter Capability	Spectrophotometry, colorimetry, kinetics
Sampling	Method: Batch or optional automatic Volume: 1.5 - 3.0 mℓ Temperature Control: Optional Maximum Cell Length: 10 mm Turbidity Position: No
Performance and Specifications	Electronics: Solid State, replaceable printed circuit forces Linearity: Photometric Stability: Better than 0.0004A/hr Photometric Accuracy: within 0.001A at 0.1A within 0.003A at 1.0A within 0.006A at 2.0A within 0.01A at 3.0A Noise Level: Better than ± 0.001 Abs at 1Abs. Measured at 480 nm, 2 nm SBW.

Performance and Specifications (continued)

Scale Expansion: 20x, 10x, 2x, 1x, 0.5x, 0.25x
Detector: Photomultiplier
Zero Suppression:
Readout: 1:4 digit, digital
2 & 3: Recorder and 4 digit, digital tal
External Output: 100mV for 1.0A, analog, digital-BCD
Response: 1.0 sec.

Optical System:

Grating: 31 × 27 nm, 1276 grooves/nm, blazed at 250 nm.
Dispersion: 3.3 nm/nm.
Wavelength Range: 200-900nm
Wavelength Accuracy: Better than ± 0.2nm
Wavelength Reproducibility: Better than 0.1nm
Resolution: Continuously variable from 0.2nm to 4nm
Slits: 0.2nm
Scan Speeds: 10, 20, 50, 100, 200nm/min
Cycle times: 0, 1, 2, 5, 10 or 20 minutes
Stray Light: < 1% at 200nm (< 0.1% at 220 nm).
Light Source: UV-deuterium arc, visible tungsten halide
Power Supply: Supplied, built-in to instrument.

Operation

Calibration: Standard samples
Training: 2 hours
Maintenance: 27 service centres in USA
Unattended Period: 2 hours

Requirements

Power: 220/240 VAC, 100/115 VAC, 50/50 Hz, 220W max.
Weight: 55 kg unpackaged
Dimensions: SuperScan 3,2 - 112.5 cm L × 58.5 cm W × 29 cm H
SuperScan 1BE - 112.5 cm L × 58.5 cm W × 23 cm H

Features

Double beam UV-VIS spectrophotometer, with remote digital control capability
Digital
Electronic baseline correction (3, 1BE)

Options

Auto 50 Sampling System	2430
Auto 5 Cell Programmer	2800
Gel Scanner	1810
Digital Printer, DP 37	1500
Total Fluorescence	280
Thermostated Cell Holders	various
4-Position Sample Changer	300
Programmable Calculator	4500

References

Manufacturer's Bulletin

Cost

Model SuperScan 3	9975
Model SuperScan 2	9250
Model SuperScan 1BE	7620

Address

Varian Instrument Division
611 Hansen Way
Palo Alto, CA 94303
(415) 493-8100

INSTRUMENTATION
FOR ENVIRONMENTAL
MONITORING

Ultraviolet-Visible Spectrophotometer
Carl Zeiss DM 4

Class	Laboratory
Description	Double-beam ratio-recording ultraviolet-visible spectrophotometer with digital readout, and optional wavelength drive
Modes of Operation	Single beam, double beam, absorbance, concentration
Lower Detectable Limit	Depends upon element, chemical method and pathlength
Range	Absorbance: -0.3 to +2.5A Concentration: -9999 to +9999
Interference	Depends upon element and chemical method
Multiparameter Capability	Spectrophotometry, colorimetry
Sampling	Method: Batch, up to 6 positions, automatic available as an option Volume: From 0.3 mℓ to 10 mℓ Temperature: Available Maximum Pathlength: Up to 50 mm Turbidity Position: Turbity can be measured at 180°
Performance and Specifications	Electronics: Solid state Photometric Linearity: Stardard deviation - <0.0006 @ 0A <0.001 @ 1A <0.006 @ 2A at 2 nm bandwith, 0.4 sec. response, 200-800 nm Photometric Accuracy: 0.001 + 0.5% of value up to 2A Photometric Stability: 0.005A for 24 hours after warm up Noise Level: Scale Expansion: 10x, concentration factor continuously variable from 0010 to 1100

Performance and Specifications (continued)

Detector: Photomultiplier
Readout: LED display; recorder printer optional
External Output: Digital - 4 digital BCD parallel, positive logic, moving decimal point; analog - 1V/1A, 10 mV/1A
Zero Suppression: Up to 2.0A
Response: Digital - 0.4 or 3.2 sec., analog - 1 or 5 sec
Warm Up: 10 min.

Optical System:

Grating:
Wavelength Range: 195-850nm
Wavelength Accuracy: ±0.5nm
Wavelength Reproducibility: ±0.1nm
Resolution: 0.5 and 2nm bandwidth
Stray Light: < 0.1% @ 220nm
Scan Speeds: (optional) 30nm/min, 120nm/min.
Light Source: Deuterium and halogen lamps with automatic switchover
Power Supply: Integral

Operation

Calibration: With standard solutions and built-in equivalent signal for 1.0 and 2.0A
Training: Minimal
Maintenance: Minimal
Unattended Periods: 24 hrs.

Requirements

Power: 100/110/115/127/220/240V, 50/60 Hz, 150VA
Weight: 40 kg
Dimensions: 56 cm W × 59 cm D × 35 cm H
Temperature: Ambient laboratory

Features

Options

Strip Chart Recorder	$ 650
Printer	1348
Variety of Cells	
Absorbance Standard	49.50

References

Manufacturer's Bulletin

Cost

DM 4	$7173
DM 4 with wavelength drive (factory installed)	8405
DM 4 with automatic sample changer (factory installed)	9272.50
DM 4 with wavelength drive, auto sample changer (factory installed)	10504.50

Address

Carl Zeiss Inc.
444 Fifth Avenue
New York, N.Y. 10018
(212) 730-4400

INSTRUMENTATION
FOR ENVIRONMENTAL
MONITORING

Ultraviolet/Visible Spectrophotometer

Carl Zeiss, Model PM 2 DL

Class	Laboratory
Description	Single beam ultraviolet/visible spectrophotometer, 200-850 with digital readout
Modes of Operation	Single beam Absorbance, transmittance, concentration
Lower Detectable Limit	Depends upon element, chemical method and pathlength
Range	Absorbance: -0.300 - 2.0A % Transmittance: 0-120% Concentration: 0-1999
Interference	Depends upon metal and chemical method
Multiparameter Capability	Spectrophotometry, colorimetry
Sampling	Method: Batch

Volume: Pathlength and temperature:

	Pathlength	Volume	Temperature
Suction funnel cell	10mm	0.5mℓ	Thermostatable and non-thermostatable
Standard trough	10mm	1.5mℓ	Thermostatable
Trough	10mm	1.5mℓ	
Semimicrocell	10mm	0.5mℓ	
Flow-through microcell	10mm	flow through	from 1 mℓ to 8µℓ hold-up volume, thermostatable, and non-thermostatable

Capacity: Approximately 30 samples/min.
Turbidity Position: May be measured at 180°

Performance and Specifications

Electronics: Solid State, plug-in integrated circuit boards

Linearity: Better than 0.3% of full scale
Photometric Stability: Better than 0.005A/m at OA
Photometric Accuracy: < 0.5% @ 1.0A
Noise Level:
Scale Expansion: 5x, 1x, concentration factor, 0-1000
Detector: Broad range HTV R521 Photocell
Readout: Digital
External Output: Printer output in BCD, parallel
TTL pos. logic; analog - 1V for 100%T, 2V for A = 2 or C = 1999
Zero Suppression: Auto zero range, -0.3 - + 2.0A; continuously adjustable zero suppression over entire chart width
Response: 0.6 sec
Warm Up: 10 min.

Optical System:

Grating: 600 lines/mm
Wavelength Range: 200-850nm
Wavelength Accuracy: ±1nm
Wavelength Reproducibility: Better than 1nm
Resolution: Spectral bandwidth - 10nm
Stray Light: < 0.5% over full spectral range, < 0.1% @ 340nm
Scan Speeds: Servogar R Recorder; 30, 120, 300, 600mm/hr;
30, 60, 120, 60mm/min (optional)
Light Source: High intensity halogen, deuterium (accessory)
Power Supply: Requires 110/220 VAC, 50/60 Hz, 100VA
12.5 × 39 × 21.5 cm, 8 kg

Operation

Calibration: Standard samples
Training: Minimal
Maintenance: Minimal
Unattended Periods: 24 hrs.

Requirements

Power: 100/110/115/127/220/240V, 50/60 Hz, 60VA
Weight: 15 kg
Dimensions: 47 W × 47 D × 22 H cm
Temperature: Ambient Laboratory

Features

Single beam ultraviolet spectrophotometer with autom. blank reference

Options

Servogar R Recorder	$ 675
XP 2 Printer	1225
UV Accessory	670

References

Manufacturer's Bulletin

Cost

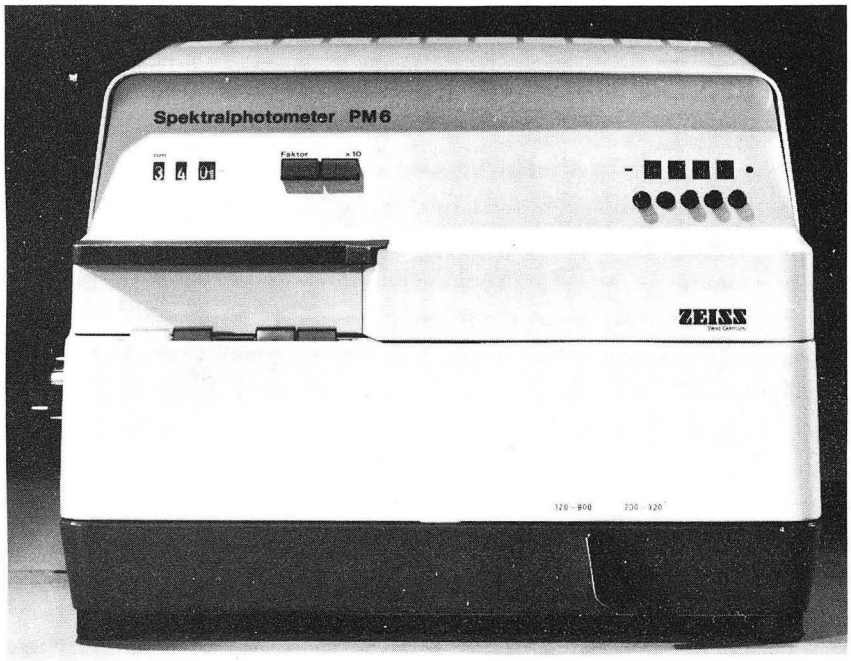
PM 2-D	1606
PM 2-DL (complete) includes automatic "blank reference" and foot switch	1730

Address

Carl Zeiss Inc.
444 Fifth Avenue
New York, N.Y. 10018
(212) 730-4400

INSTRUMENTATION
FOR ENVIRONMENTAL
MONITORING

Ultraviolet/Visible Spectrophotometer
Carl Zeiss, Model PM 6 P, PM 6 T, PM 6 K, PM 6 KS



Class	Laboratory
Description	A series of digital single beam, ultraviolet/visible spectrometers differing in sampling options, 200-850 nm
Modes of Operation	Single beam, absorbance, concentration
Lower Detectable Limit	Depends upon metal, chemical method and pathlength
Range	Absorbance: -0.300 to +3.000 Concentration: -2000 to +9999 continuously variable
Interferences	Depends upon method, metal
Multiparameter Capability	Spectrophotometry, colorimetry, kinetics (K,KS) Densitometry (Gels)
Sampling	Method: PM 6 P - automatic sample changer - 12 positions PM 6 T - with funnel cuvette, pour in solutions PM 6 K - motorized sample changer for 4 positions PM 6 KS - programmable motorized sample changer for 4 positions Volume, pathlength and temperature control:

Model	Pathlength (cm)	Volume (mℓ/cm)	Temperature
Standard cell	0.1, 0.2, 0.5 1, 2, 5	1.5	Thermostatable and non-thermostatable depending upon model
Semimicrocell (normal)	1	0.5	
Semimicrocell (long)	0.5, 1,2	0.5	
Suction semimicro	0.5, 12	0.6	
Microcell	1	0.2	
Suction microcell	1	0.27	
Flow-through cell	1	flow through	Non-thermostatable and thermostatable
Semimicro funnel cell	1	>1 mℓ	

Capacity: 12 samples/3 minutes for "P", 150/hr for "T"
Turbidity Position: Can be measured @ 180°

Performance and Specifications

Electronics: Solid state, integrated plug-in circuit boards

Linearity: < 0.2% over entire range
Photometric Stability: Better than 0.005A/hr without auto reference
Better than 0.001A/hr with auto reference
Photometric Accuracy: Better than 0.002A at 0.3A
Noise Level: ± 1 digit up to 1.000A, ± 4 digits @ 2.0A
Scale Expansion: Calibrated 10x multiplier
Detector: Photomultiplier 200-800nm range
Readout: Digital (4 digit-LED)
External Output: Analog - + 1V for display of 1000
Source impedance 10K ohm
digital: BCD (1-2-4-8) parallel, TTL levels, positive logic
Zero Suppression: Not applicable
Response: 0.35/FS
Warm Up: 10 min.

Optical System: Double grating, automatic filter insertion

Grating: 600 lines/mm, blazed at 300nm
Dispersion: 4nm/1mm of slit width
Wavelength Range: 200-1000nm
Wavelength Accuracy: ± 0.5nm
Wavelength Reproducibility: ± 0.2nm
Resolution: 2nm bandwidth
Slits: 5nm height
Stray Light: Less than 0.05% over entire range
Scan Speeds: Servogor R and S-30, 120, 300, 600nm/hr;
30, 60, 120, 600mm/min.
Light Source: High intensity halogen and deuterium
Power Supply: Integral

Operation

Calibration: Standard samples, factor display
Training: Minimal
Maintenance: Minimal
Unattended Periods: 24 hrs.

Requirements

Power: 100/110/115/127/220/240V (+10% to -15%), 50/60 Hz, 150VA
Weight: 25 kg (55 lbs)
Dimensions: 36 cm W × 53 cm D × 28 cm H
Temperature: Ambient Laboratory

Features

Single beam ultraviolet/visible spectrophotometer with autom. blank reference
Digital
Variety of sampling options

Options

22-speed recorder	$ 675
Digital Printer	1348
Gel Scanner	1375
Thermo-electric temp. control	1500

References

Manufacturer's Bulletin

Cost

Model PM 6 P	$7967
Model PM 6 T	4934.50
Model PM 6 K	5129
Model PM 6 KS	7270

Address

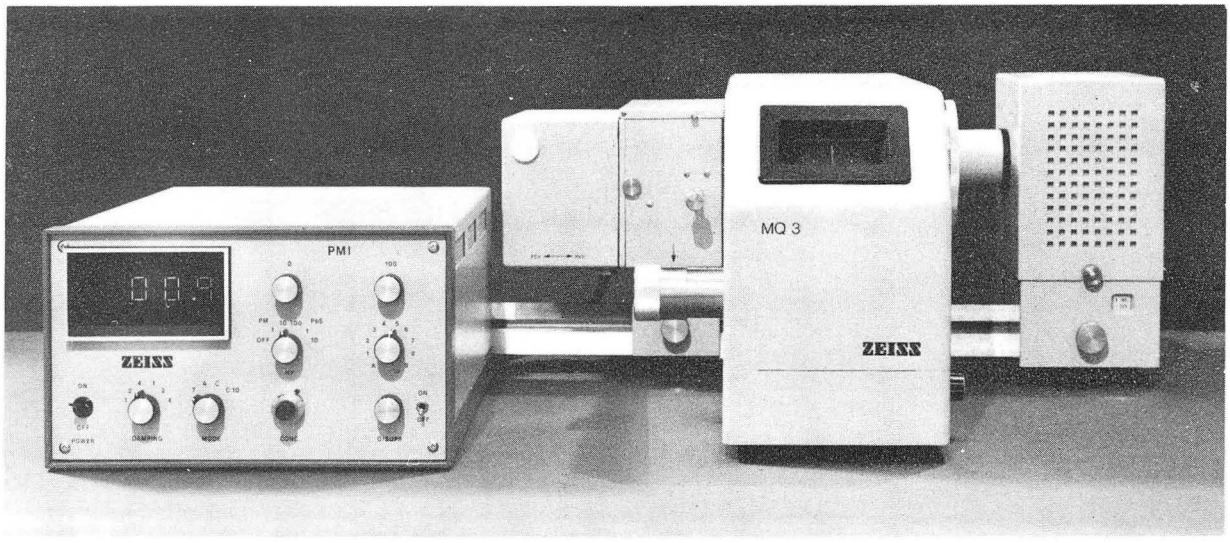
Carl Zeiss, Inc.
444 Fifth Avenue
New York, N.Y. 10018
(212) 730-4400

INSTRUMENTATION
FOR ENVIRONMENTAL
MONITORING

H20-MET
NOTES, UV-VIS
Zeiss 4
August 1978

Ultraviolet/Visible Spectrophotometer

Zeiss, Model PMQ 3



Class	Laboratory
Description	Single-beam ultraviolet-visible spectrophotometer with prism monochromator
Modes of Operation	Single beam, absorbance, %transmittance, concentration
Lower Detectable Limit	Nanogram range (depending on compound)
Range	ppb to %: ppb - 100% (depending on compound) Absorbance: Direct to 3.7A with range manipulation to 5.0A %Transmittance: 0-200%, Concentration: 9999
Interferences	Depends upon element and chemical method
Multiparameter Capability	Reflectance, flame, fluorescence, TLC, gel, absorbance, transmission, concentration
Sampling	Method: Batch, solutions and solids Volume: 0.06 mℓ minimum Capacity: 60 samples/minute with automatic changer; flow-cell equipment available Maximum Pathlength: 0.01 to 5 cm
Performance	Electronics: Photometric Linearity: 0.1% Photometric Stability: ±0.1%/hr Scale Expansion: 0-10x Detector: Photomultiplier R 446 (185-850 nm), PbS cell (620-2500 nm) Zero Drift: ±0.1%/hr Span Drift: ±0.1%/hr Photometric Accuracy: Better than .005A @ 1.0A

Performance (continued)

Readout: Digital
External Output: Analog - 100.0%T: 1V, 1.000 O.D. = 1V
Digital - 4 digit, 1-2-4-8 BCD, decimal position, positive true logic, standard TTL levels
Zero Suppression: For entire signal

Monochromator:

Prism: M4QIII 30° quartz, Littrow mounting
Wavelength Range: 185-2500nm
Resolution: 0.03nm in U.V., 1nm @ 600nm
Accuracy of wavelength setting: < 0.05nm @ 200nm
Dispersion: @ 200nm = 1.5nm/mm
Slit width: Continuous between 0-2mm
Stray Light: < 0.1% between 200 and 1000nm

Operation

Calibration: Internal calibration standards and automatic blank control
Training: Minimal
Unattended Period: 24 hrs.
Maintenance: Preventive Maint. 1/yr.
Temperature Compensation: Temperature control available

Requirements

Power: 110V; 60 Hz; 370 VA
Weight: 54.5 kg (120 lb)
Dimensions: 70 × 50 × 25 cm (27.5 in., 19.7 in., 9.8 in.)

Features

Output: Analog 0 - 1V. Linear for %T, A, C. Digital BCD.
Display: 4 digits

Options

Xenon Lamp Assembly	$2005
Gel Scanner Accessory	842
Recorder	675
Printer	1348
Wavelength Drive	1313
Integrating Sphere	1449
Reflectance Attachments	2064 - 2738
Fluorescence Attachment	3256 - 4786

References

a) Manufacturer's bulletin "Zeiss PM Q3 Spectrophotometer"
b) Price List, January 1978

Cost

Model PMQ 3 — 9042.60

Address

Carl Zeiss, Inc.
444 Fifth Avenue
New York, N.Y. 10018
(212) 730-4400

U.S.GPO:1979-690-894/189

NITROGEN, PHOSPHORUS AND SULFUR WATER MONITORING INSTRUMENTATION

A. INTRODUCTION

This section discusses nitrogen, phosphorus, and sulfur (designated here as NPS) in fresh, waste, and saline waters, and particularly the effects of environmental factors on NPS monitoring. Topics covered include the sources, forms, and harmful effects of NPS in water, and a discussion on the natural cycling of NPS within the biosphere. These topics are discussed in detail in various publications (Ref. 1-5, 8,9).

The EPA has been promulgating new rules and regulations which set high standards for pollution including decreased effluent discharges from point sources. See Table A-1 for a listing of criteria for NPS for typical point source categories constructed from The Federal Register. A discussion is included in this section on methods for controlling NPS discharge which may be used to fulfill these regulations. A recent example of decreased pollutant discharges is that of ammonium nitrate (Ref. 13).

The brief discussion is also included on standards relevant to human health and welfare, and to national standards on the NPS content in drinking and other waters. Standards have been found necessary for both health and environmental reasons. Nitrate has been limited in drinking water due to the methemoglobinemia it can cause in infants. Nitrite is equally dangerous but occurs much less frequently at high concentrations. Discharges into waterways are limited in permissible nitrogen and phosphorous because of eutrophication of the receiving waters. Sulfur in the form of sulfide is of concern for health, environmental, and aesthetic reasons.

Apart from the effect of nitrate and nitrite on infants, and the laxative effect of high concentrations of sulfate, NPS limits in drinking water are of minor concern in most cases, phosphates even being added to water to control corrosion. NPS are of much more frequent concern in discharges into waterways, where the nutrient balance can be unfavorably affected by relatively small amounts of NPS in the discharges. Associated problems include harmful effects to aquatic animals, injurious effects related to the dyeing of wool and silk fabrics, harmful effects in fermentation processes, and increased corrosion. Some of these problems can be translated into an annual cost; for example, the cost for the restoration of eutrophic lakes, or the need to use excessive chlorine for purification of raw water containing a high NH_3-N content. Many problems are not as easily assessed, such as the cost for the loss of a recreational stream or lake. Some advances have been made in the reduction of NPS in man-related discharges, but much remains to be done.

Detailed reports and summaries of NPS in water are contained in various reports including in Water and Wastewater Engineering by Fair, Geyer, and Okun (Ref. 1), Water Quality Criteria by McKee and Wolf (Ref. 2), the EPA technology transfer document Process Design Manual for Phosphorus Removal by Black and Veatch (Ref. 3), the series of articles on the biosphere in Scientific American (Ref. 4), and the "Sources of Nitrogen and Phosphorous in Water Supplies: report by the American Water Works Association (AWWA) (Ref. 5).

1. Characteristics

Nitrogen, phosphorus and sulfur are common constituents of water which arise from both natural and man-released sources. Nitrogen and phosphorus are classified as nutrients because they are included among the elements essential to the growth of algae and other aquatic plants. The growth of algae in water requires a number of elements, but nitrogen and especially phosphorus are the ones most likely to be in limited supply in fresh waters. Many forms of NPS are found in fresh, saline, and waste waters, but only nitrate (NO_3-N) and sulfate (SO_4-S) are listed in the 1962 U.S. Public Health Drinking Water Standards. The 1975 Interim Drinking Water Standards list NO_3-N. This section will briefly summarize the characteristics of NPS.

Compounds of nitrogen and phosphorus are the primary nutrients that stimulate growths of algae and other plants and cause eutrophication of lakes and ponds. See Figure A-1. The following discussion is taken from Reference 1:

> *Eutrophication of the biosphere is the intensive cycling of phosphorus, nitrogen and sulfur. Curved arrow at bottom represents beginning of the process: the human use of phosphorus as fertilizer, which returns phosphorus to the lithosphere, thereby reversing the phosphorus cycle. Stright arrows at left and right indicate that phosphrous added to the lithosphere (and to phosphorus already present) is then taken up by phytoplankton and other organisms as well as by crops. Other straight arrows at right and left show that phosphorus and other elements return to the lithosphere and hydrosphere by decay. Once phosphorus is plentiful, scarcity of nitrogen and sulfur may limit eutrophication. Arrows at top represent carbon dioxide, nitrate and sulfate from industrial activity rising into atmosphere and falling in rain. They may promote eutrophication of dry land since vegetation may reabsorb them from air and*

TABLE A-1.
Typical Rules and Regulations on Point Source Discharges of NPS Pollutants.

Point Source Category	Pollutant	[a] Maximum	[b] Average	Reference
Steam Electric Power Cooling tower blowdown	Phosphorus	5.0 mg/ℓ	5.0 mg/ℓ	15
Electroplating (existing source)	Phosphorus	320 mg per m^2 per operation	160 mg/m^2 per operation	16
Electroplating (new source)	Phosphorous	160 mg/m^2 per operation	80 mg/m^2 per operation	17
Poultry Processing Products	Ammonia	8.0 mg/ℓ	4.0 mg/ℓ	18
Poultry Processing Products (new sources)	Ammonia	0.40 mg/k kg of LWK	0.20 mg/k kg of LWK	18
Inorganic Chemical Manufacturing	Ammonia	No discharge of process water to navigable waters		19
	Ammonia	8.8 kg/khg of product	4.4 kg/khg of product	19
Meat Products (Meat Cutter subcategory)	Ammonia (as N)	8.0 mg/ℓ	4.0 mg/ℓ	20
Fertilizer (Ammonium Sulfate subcategory)	Ammonia (as N)	[c] 30 mg/ℓ		21
Meat Products and Rendering Processing	Ammonia	0.04 kg/hkg of raw material	0.02 kh/hkg of raw material	
Phosphate Manufacturing	Total Phosphorous	70 mg/ℓ	35 mg/ℓ	23
Glass Container Manufacturing (new sources)	Ammonia	104.0 g/hkg of product frosted	52.0 g/hkg of product frosted	24
Ferroalloys Manufacturing electrolytic manganese	Ammonia	40.667 hg/hkg of product	20.334 kg/hkg of product	25
electrolytic manganese dioxide	Ammonia	10.574 hg/hkg of product	5.287 hg/hkg of product	

[a] Maximum for any one day.

[b] Average of daily values for 30 consecutive days shall not exceed this number.

[c] Pretreatment Standard.

soil. Curved arrows indicate routes followed by elements that are both soluble and volatile.

The major drinking water quality problems that result from heavy algal growths are undesirable taste, odors, and filter clogging. In 1966, these problems were indicated to have affected as much as 56% of the total municipal surface water supplies in the United States. The important forms of nitrogen in water are ammonium-ammonia (NH_3-N), nitrite (NO_2-N), and nitrate (NO_3-N). These forms are water soluble and can be readily used for plant growth.

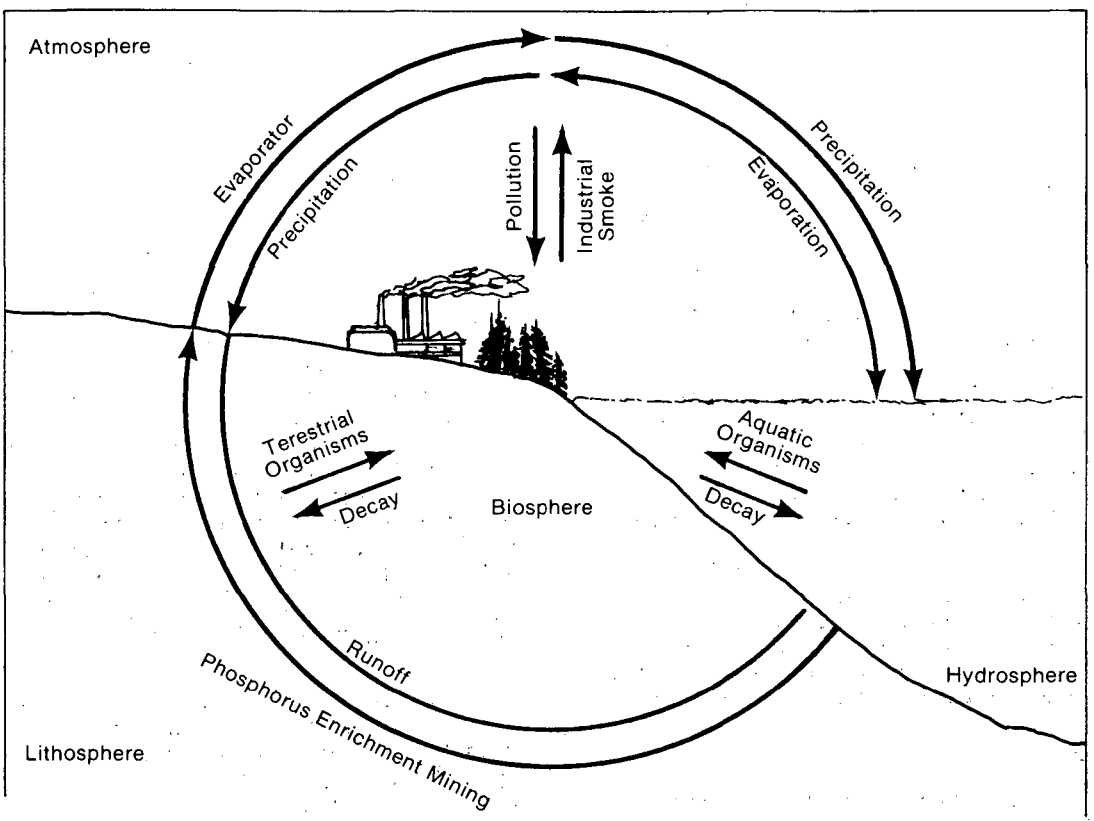
The elemental forms of NPS do not occur as such in water, and are of little or no importance in water quality monitoring. They are only briefly included in this discussion. A detailed treatment on the chemistry of nitrogen and phosphorus is contained in the Final Report of the Water Quality Division on Nutrients in Water, entitled "Chemistry of Nitrogen and Phosphorus in Water" (Ref.8).

Besides the natural cycling shown in Fig. A-1, NPS undergo a variety of chemical reactions, including complexation by metal ions, oxidation by dissolved oxygen, precipitation by cations such as iron and calcium. Gaseous forms of NPS (e.g. H_2S, NH_3) are removed to some extent in nature by volatilization, but environmental considerations make this an impractical treatment process in most cases.

The background concentrations of some forms of NPS in fresh waters is usually below 30 µg/ℓ, except for sulfur, see Table A-2. Polluted waters, effluent discharges, estuarine water, and bottom sediments and sludges may have elevated levels of these pollutants.

2. Forms

The forms of NPS in water include both anions and cations, proteinaceous substances, dissolved gases, polymeric substances, in particles of detritus, in bottom sediments and in biological sludges. The NPS do not necessarily remain in their original form, but often are converted from one form to another depending on the conditions. For example, nitrogen originally discharged as ammonia is converted by oxidation into nitrite and eventually nitrate; a change in pH can convert sulfide



(XBL 771-129)

Figure A-1. Eutrophication of the biosphere showing the cycling of phosphorus, nitrogen, and sulfur. (Ref. 4).

TABLE A-2.

Background Concentrations of Selected Forms of NPS in Fresh Waters

Element	Form	Amount	Reference
Nitrogen	NH_3-N	< 0.1 (as N)	12
	NO_3-N	< 10	11
	NO_2-N	< 0.1	11
Phosphorus		10-30 µg/ℓ	12
Sulfur	SO_4-S	median of 26 mg/ℓ	12

(HS^- or $S^=$) into gaseous hydrogen sulfide (H_2S); soluble phosphate can be converted into an insoluble phosphate by some metal cations. Water parameters which affect the form of NPS include pH, presence of oxidizing constituents such as dissolved chlorine and dissolved oxygen, and the presence of precipitating cations. Except for the refractory forms, virtually all forms of NPS are converted by bacterial action to other forms and are incorporated into algae and plants. The principal refractory form of phosphorus is that contained in soil, most of which is not immediately biologically available. Turbid runoff water from unoccupied watersheds may have total phosphorus values in excess of 1 mg/1. If impounded and allowed to settle, the overlying water may have filtrable phosphate values less than 0.01 mg/1. The amount of phosphate biologically available for eutrophication can not be judged from total phosphate values, although slow transformations and chemical equilibria can cause a release of phosphate from such refractory sources. Many data on phosphorus are impossible to interpret due to lack of knowledge of the form that was measured. Filtrable phosphate in raw water reservoirs is rarely of much significance since most of the phosphate is tied up in algae but is readily recycled.

From a monitoring standpoint, NPS pollutants are commonly analyzed, and results reported on the form which exists in the sampled water. For example, ammonia, nitrite, and nitrate are analyzed and measured as such.

3. Sources

Water supplies receive NPS in various forms from a large number of both natural and man-released sources including naturally occurring minerals, domestic waste waters, industrial effluent discharges, and water runoff from streets and agricultural land. Fresh and saline waters contain traces of phosphorus and sulfur which are leached or dissolved from naturally occurring minerals; waste waters contain nitrogen which primarily originates from feces, urine, and waste food (Ref. 5). Some forms of NPS may be greater than expected under certain conditions, for example sulfide may be found in distribution systems as a result of bacterial action on organic matter under anaerobic conditions (Ref. 11).

There has been an increase in the domestic supply of NPS. For example, over the five year time span 1970-1974, the domestic supply of phosphorus increased from 3,171,000 tons to 5,359,000 tons, nitrogen increased from 3,982,000 tons to 9,969,000 tons (Ref. 6). In 1973, the U.S. consumed 10,250,000 long tons of sulfur (all forms), and an estimated 10,955,000 long tons in 1974 (Ref. 7).

In a study of street surface contaminations, the EPA estimated streets contained weighted means of 1.1 lb/curb mile phosphates and 0.094 lb/curb mile nitrates (Ref. 26). These street contaminants (as well as other pollutants) have been found to contribute substantially to urban pollution when washed into receiving waters by storm runoff.

The reader is referred also to Table A-1 which lists typical manufacturing point sources for ammonia and phosphorus pollutants. Besides the references to The Federal Register given in this table, Standard Methods, 14th edition, contains information on natural man-released sources of NPS pollutants.

4. Control

Methods of controlling the NPS content of water discharges include natural purification, removal by chemical or physical means, and by biological treatment. An example of natural purification is the oxidation of sulfite to sulfate by dissolved oxygen. The rate of natural purification by a stream depends on many factors, for example pH, temperature, concentrations of other water constituents, and the extent to which the receiving stream previously has become acclimated to such pollutants. For sulfite, the reaction velocity coefficient ranges from 0.236 per day to 0.412 per day, where the rate of oxidation follows a first-order law (Ref. 2).

Man-operated controls for NPS commonly use biochemical processes to remove NPS. For example, municipal sewage treatment depends upon the establishment of a complicated mixed culture of microorganisms that is acclimatized to the particular type of waste. This culture then uses the dissolved and suspended organics in the waste as an energy and carbon source. The biological solids are then separated from

liquid wastes which are subsequently discharged either to the environment or to additional treatment. Nitrates and phosphates are added if the waters being treated are deficient in either of these essential minerals.

Some wastewater effluents, even though they have been biologically treated, may still contain substantial amounts of phosphates. Under these conditions phosphates are removed from the effluents by chemical precipitation using multivalent metal ions, such as ferric alum or calcium (Ref. 1, p. 29-32 and p.34-5). Hydrogen sulfide is removed from water by aeration techniques.

Oxygen is needed both for the microorganisms in the aerobic decomposition of organic matter and for the plants and animals that resynthesize organic matter. Gaseous oxygen supplies the normal dissolved oxygen requirements in water: about 0.8% by volume at normal temperatures (50°F) as compared to 21% by volume in the atmosphere. In the absence of dissolved oxygen, anaerobic bacteria utilize the oxygen contained in NO_3-N, PO_4-P, SO_4-S. The cyclic anaerobic transformations of nitrogen, sulfur, and phosphorus are shown schematically in Fig. A-2. Carbon dioxide and methane are the most common gases released; they escape to the atmosphere after the waters become saturated (Ref. 1).

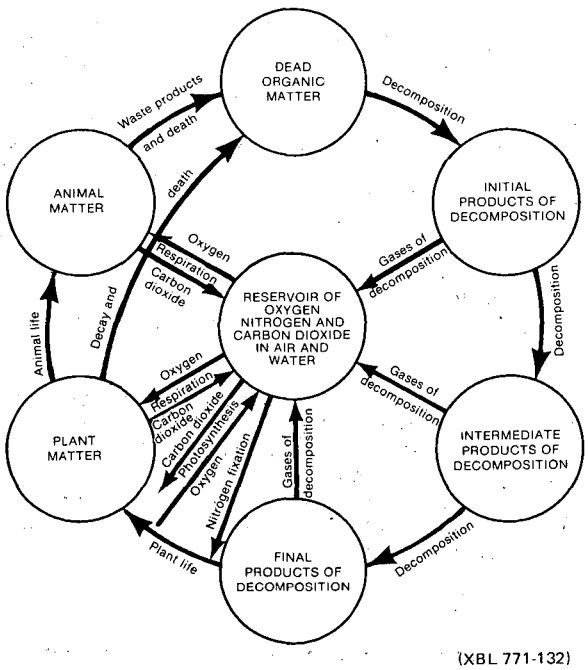


Figure A-2. Cycles of carbon, nitrogen, and sulfur in anaerobic decomposition. (Ref. 1).

Some of these control processes simply replace one form of an NPS pollutant by another; so that the overall approach must be examined to evaluate fully the various options. For example biochemical oxidation of the nutrient ammonia yields nitrate, which is also an algae and plant nutrient.

In the case of ammonium nitrate, ion exchange techniques were used in a recent application. The wastewater was contacted with a strong acid cation exchange resin that removed the ammonium contaminant and reduced its level to less than 3 mg/1. The decationated water was then contacted with a weak base resin in the hydroxide form that reduced the nitrate content to 7-100 mg/1 NO_3-N (Ref. 13).

5. Effects

The harmful effects of NPS to man and aquatic biota depend on such factors as the form, concentration, and water pH. For example, the toxicity of ammonia and ammonium salts to fish is directly related to the concentration of undissociated ammonium hydroxide in the water. This, in turn, is a function of the pH of the water. See McKee and Wolf (Ref.2).

Specific effects on man and fish differ for the various forms of NPS, and are discussed in the individual sections for nitrogen, phosphorus, and sulfur.

6. National Water Quality Standards for NPS

The U. S. Public Health Service has published guidelines for drinking water which include recommended limits for nitrate, sulfate, and a threshhold odor number. These guidelines have been periodically reissued over the past fifty years to reflect changes in recommended limits. The drinking water standards have been revised four times; a summary of the last revision (1962) is given in Introduction to this volume. The EPA issued interim drinking water standards in March 1975 which are expected to form the basis for the National Standards. See Appendix III.

Similar guidelines also are available for water used for recreation; fish and wildlife, agricultural uses; and various industries. Information may be obtained from the Introduction to this volume, McKee and Wolf (Ref. 2), and Water Quality Criteria, 1972 (Ref. 12).

7. National Discharge Standards for NPS

Point source effluent discharge standards related to the discharge of nitrogen, phosphorus, or sulfur into waters are currently being promulgated. There are many such standards, and the reader should consult The Federal Register for the appropriate point source classification. See Table A-1.

B. MONITORING SYSTEMS

The number of steps or modules required for measuring NPS contents in water depends to a large extent on both the interferences and concentration of NPS. For example, turbidimetric analysis can be applied directly to fresh water samples for SO_4-S, and the gas permeable electrode can be applied to measure NH_3-N in fresh, waste, and saline waters. Other methods may require pre-measurement steps to separate NPS from interferences, or to enhance the concentration of NPS. Ion-exchange, distillation, filtration and precipitation methods are among these pre-measurement steps.

The different forms of NPS usually are converted by chemical reactions into a single form, which is subsequently measured. Thus, evaluation of methods for monitoring to determine their reliability must include the entire system and not just the instrumental measurement.

Although the actual instrumental measurement is central to the analytical procedure, it is only one portion of an overall water monitoring system. The integrity of the analysis performed by a complete monitoring system depends on a number of factors including sampling site selection, pollutant sampling and preservation procedures, pollutant chemical or physical separation methods, completeness of any required chemical reactions, sensor operation and signal quantification, data processing, and calibration. Each of these steps is of importance, so that the entire monitoring system must be fully understood to assess the reliability of the data. Erroneous data are frequently worse than no data at all.

Water quality measuring systems can be classified for use in either fresh, waste, or saline waters. Freshwater systems are those designed for natural (unpolluted) and treated waters. They are used for a reconnaissance of the Nation's resources, and to establish background levels for water constituents. Wastewater monitoring systems are those suitable for analyzing the discharges from point sources such as industrial or municipal effluents. They may require filtration of the sample to remove floating particles and other debris that would interfere with subsequent steps of analysis. Saline water systems are used to measure pollutants in estuarine waters or brines. They may require special features as means of compensation for the high mineral content of the sample.

The complete system for monitoring water quality must be evaluated for reliability, durability, ruggedness, and cost. The integrity of the processed data requires accuracy when compared with known standards, specificity in the presence of interfering constituents, sensitivity for the pollutant being determined, and repeatability in terms of repetitive measurements by one laboratory as well as reproducibility among many testing laboratories. To allow intercomparison of data, one needs also to record the temperature, depth, flow rate, and direction of the water stream being sampled. These data permit assessment of mass concentration, mass flow, and water composition.

1. Systems Concept

Systems for monitoring NPS in water can be classified as either manual or automated analyzers. In addition, they may be of the laboratory or field type.

Laboratory manual NPS monitoring systems involve sampling on-site grab samples followed by analysis in the laboratory. Manual implies human involvement in all stages of analysis except the actual instrumental measurement. Samples for NPS analysis usually are collected in a bottle fabricated from polyethylene or a similar material to minimize adsorption or leaching contaminants from the sides of the container. A preservative technique (e.g., addition of zinc solution, storage at 4°C) is often used for the sample.

Laboratory automated NPS systems involve sampling on-site, followed by anlysis in the laboratory. One or more of the following steps are then performed automatically, sample uptake, reagent mixing, color development, and sometimes instrumental readout. As in laboratory manual systems, samples are contained usually in plastic bottles to which a preservative is added. Field manual analyzers are portable, and contain any needed chemical reagents in kits. Any necessary measuring instruments are usually battery powered. Analyses are performed on grab samples at the site; preservatives are not required to minimize losses of NPS.

Field automated monitoring systems are of the type in which a sample stream is separated from the water and analyzed on-site with an automatic analyzer. Data may be continuous or periodic.

When data taking is not interrupted it is defined as being continuous. If data are recorded only periodically, a sampling process takes place, and the information is called sampled data. For example, an uninterrupted chart record of NH_3-N is continuous, a reading every hour is sampled.

2. Sampling

Sample collection and preparation are complicated for NPS in water because of such factors as the low concentrations, frequent necessity of sampling from a moving stream, interferences, diversity of soluble forms and the presence of NPS in the particulate state and in sediments. Samples taken for laboratory

analysis are collected in a polyethylene or glass bottle to which preservatives have been added. See Table B-1 (Ref. 27). The added preservatives guard against losses of NPS. For example, added H_2SO_4 converts gaseous NH_3 to the nonvolatile NH_4^+; added Zn acetate converts gaseous H_2S to insoluble ZnS (zinc sulfide). The pollutants are regenerated by adding NaOH, thus converting NH_4^+ back to NH_3; and H_2SO_4 to convert ZnS to H_2S.

TABLE B-1.

EPA Recommended Grab Sample Containers, Preservatives, and Holding Periods for NPS Pollutants (from Ref. 27)

Pollutant	Preservative	Holding Period (Days)
NO_3-N	pH < 2 with H_2SO_4; 4° C	1
NO_2-N	4° C	1
NH_3-N	pH < 2 with H_2SO_4; 4° C	1
Kjeldahl-N	pH < 2 with H_2SO_4; 4° C	1
PO_4-P	Filter at site; 4 C	1
Total Dissolved-P	Filter at site; 4° C	1
H_2S-S	2 ml Zn acetate	1
SO_3-S	4° C	1
SO_4-S	4° C	7

Either plastic or glass containers are satisfactory sample containers.

The necessity for sample preservation is indicated by the study on the kinetics of oxidation of sulfide in water by dissolved oxygen as a function of pH (Ref. 32). As shown in Fig. B-1, the specific rates of sulfide disappearance go through maxima at pH 8 and pH 11, and a minimum at pH 9. The solubility of H_2S and NH_3 in water decreases with increasing temperature; low temperatures for storing samples are required to prevent significant losses due to temperature fluctuations.

Sample concentration methods include precipitation of H_2S-S as ZnS and increasing the sample size from 500 to 1000 ml for NH_3-N.

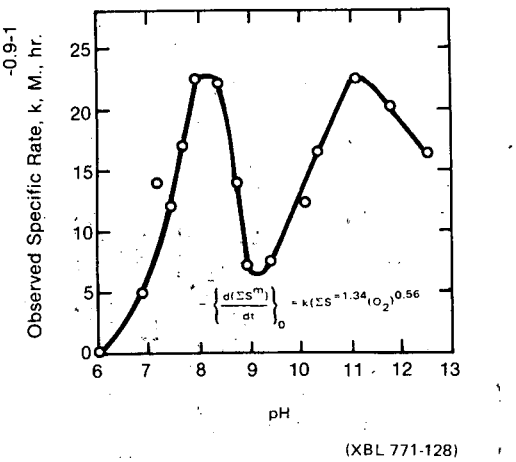


Figure B-1. pH dependence of observed specific rate of sulfide oxidation (see Table II for details). (Ref. 32).

Interferences are minimized by using a number of methods including the following: distillation (e.g. NH3-N), stripping with an inert gas, (e.g., H_2S-S); and background correction (e.g., PO_4-P).

When a NPS pollutant exists in samples in several different forms, sequential analyses of the same form may be used. For example, if NO_2-N is determined, NO_3-N may then be reduced to NO_2-N, another nitrite determination made, and the NO_3-N calculated by difference. Similarly, after the determination of PO_4-P (filtrable), organic phosphorus may be oxidized to PO_4-P which is determined, and the organic phosphorus calculated by difference. Polyphosphates may be hydrolyzed to PO_4-P and calculated in the same manner, in the absence of organic phosphates. Such techniques must be used with care to avoid compounding errors, since the treatment necessary to release one form may also affect another form.

Tradeoff considerations related to different sampling procedures for laboratory and field monitoring systems include: (1) the laboratory sample usually is at a low temperature and may contain acid added as a preservative; the field sample may not, (2) the time lapse between sampling and analysis is longer for laboratory monitoring. A significant time lapse may be undesirable. For example, real-time information is necessary for water quality surveillance within a time frame which encompasses the instant of undesirable occurrence through an ensuing period of time when successful correction is practical (Ref. 33).

Sampling may also be automatic. Once set up, the automatic sampler does not require human assistance other than periodic checking. See Figure B-2 for a schematic of a typical commercially available automatic sampler (Ref. 29). In this example, water being sampled

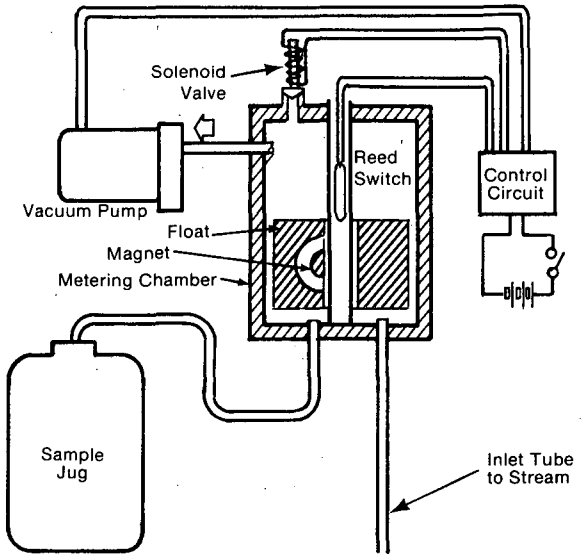


Figure B-2. Typical automatic sampler (from Ref. 29).

is pumped into the metering chamber and causes the float to rise. When a pre-determined volume of water has entered the chamber, the magnet closes the reed switch to activate the solenoid valve. Activation of the solenoid stops pumping and permits the sampled water to flow both into the sample jug and, in a rinsing action, back through the inlet tube.

Additional information on NPS sampling is contained in Standard Methods, 14th ed. (Ref. 28). The U.S. Geological Survey Book 5 entitled Methods for Collection and Analysis of Water Samples for Dissolved Minerals and Gases contains a detailed description of both sampling and manual samplers (Ref. 30). About 40 commercially available automatic sewer flow samplers are described in the EPA report on An Assessment of Automatic Sewer Flow Samplers (Ref. 31).

3. Calibration

Calibration can be one of two kinds: instrument and systems. Instrument calibration methods include impression of a known electrical signal at the inputs of the instrument, use of an optical filter, or introduction of a known concentration of NPS through a portion of the monitoring system. The true concentration of NPS in water samples cannot be calculated if only the instrument is calibrated because NPS may be gained or lost in untested portions of the monitoring system. Calibration of the entire monitoring system is best accomplished by introducing known concentrations of NPS directly at the sampling stage.

Calibration methods generally include the categories: (1) calibration curves and (2) standard additions.

A calibration curve is obtained by analyzing known concentrations of the NPS in exactly the same way that the samples will be analyzed. Use of the identical, or a similar sample, to minimize matrix effects is important. The instrumental readout is corrected for the blank and plotted versus known NPS concentration to obtain the calibration curve. Changes in room temperature, instrumental blank, or reagent purity affect this curve.

In the method of standard addition, small volumes (often several microliters) of a solution containing a known concentration of NPS are added to the sample prior to analysis. Any necessary volume correction is made to take into account dilution caused by addition of the standard, and the instrument readout is calculated for both the known and unknown NPS concentrations. The fraction of the signal output related to the known concentration of the added NPS is determined and the concentration of the NPS in the sample is calculated. The method depends on a linear relationship between concentration and signal output; a blank correction for background must be made. Two or more standard additions should be carried out to obtain reliable results.

TABLE B-2
Ortho- and Total Phosphate in River Water Before and After Addition of Orthophosphate

	Mg/ℓ.ortho P			Mg/ℓ.total P		
Sample	Before	Added	After	Before	Added	After
1	0.05	0.25	0.29	0.07	0.25	0.32
2	0.05	0.25	0.25	0.06	0.25	0.28
3	0.32	0.25	0.56	0.42	0.25	0.68
4	0.15	0.20	0.32	0.20	0.20	0.40
5	0.29	0.20	0.45	0.33	0.20	0.45

Average % recovery of added orthophosphate: ortho P = 95.0, total P = 97.0.

Table B-2 shows calibration data for PO_4-P in river water samples using the method of standard additions. The monitoring system used was a Technicon Auto Analyzer with automated sample-reagent mixing, and colorimetric intensity readout on a strip-chart recorder. A solution of disodium hydrogen phosphate (Na_2HPO_4) was used as the calibration standard. The solution was prepared by drying 4.759 g of solid Na_2HPO_4 for 1 hour at 105° C; this was dissolved in 1000 ml. of distilled water containing 10 ml. of 37% formaldehyde solution. The final solution had a concentration of 1000 mg/1 PO_4-P (Ref. 34).

Table B-3 shows calibration data for NH_3-N for both standard additions and a calibration curve (direct measurement). (Reference 35). As shown, both methods gave comparable results. The method of standard additions is preferred because matrix effects (e.g., temperature changes, differences in ionic strength, etc.) are better compensated. The NH_3-N standard was prepared from solid NH_4Cl. This NH_4Cl was first dried at 100°C for 3 hours; then 3.819 g. were dissolved in 1000 ml of Super Q water to give a final concentration of 1000 mg/1 NH_3-N. This standard solution was stable for at least one month.

TABLE B-3
Direct Measurement and Known Addition Comparison (Ref. 35).

Sample	Direct measurement, mg NH_3-N/ℓ	Known addition, mg NH_3-N/ℓ	Difference mg NH_3-N/ℓ	Difference %
A	0.367	0.376	+0.009	+2.5
B	0.146	0.145	-0.001	-0.7
C	0.198	0.201	+0.003	+1.5
D	0.168	0.167	-0.001	-0.6
E	0.137	0.134	-0.003	-2.2
F	0.122	0.118	-0.004	-3.3
G	0.112	0.114	+0.002	+1.6
H	0.026	0.032	+0.006	+23.0
I	0.191	0.198	+0.007	+3.7

Calibration standards for NPS monitoring systems are available from a very large number of laboratory supply houses. Analytical Chemistry published a laboratory guide in August 1974 which listed a number of these supply houses.

Caution is required in the use of standard methods because of the multiplicity of forms which may be present and not all of which may respond to the analytical method. Properly chosen pre-treatment is essential in such cases.

Additional information on NPS calibration is obtained from Standard Methods, 14th Ed. (Ref. 28), and the EPA Methods Manual (Ref. 27).

4. Units

NPS are commonly reported as mg/1 (milligrams per liter) or µg/1 (micrograms per liter).

C. NPS IN WATER INSTRUMENTATION

Prior to about 1940, NPS pollutants were analyzed by using volumetric and gravimetric procedures. These methods still form the basis for many standard methods used today. Since then, however, instrumental methods have achieved greater prominence because of increased sensitivity, selectivity, amenability of automation, and eventual lower cost per sample due to a decrease in turnaround time.

Instrumentation for monitoring NPS in water can be classified in a number of ways. It is convenient to separate it as follows: manually operated laboratory analyzers, automated laboratory instrumentation, manual field monitors, and automatic field monitors. Table C-1 lists the four classes of instrumental techniques commonly used for measuring NPS in fresh, waste, or saline water.

Well-designed automated laboratory instrumentation can perform mechanical operations more rapidly and with more precision than can an operator with the equivalent manual means; also, the results obtained have a higher repeatability than manual laboratory methods. For example, the EPA has found that automated instruments such as the Technicon AutoAnalyzer permit 20 to 60 NH_3-N determinations per hour without requiring operator attention. However, these automated analyzers have the disadvantage that a given manifold arrangement can cover only a limited concentration range, making the instrument incapable of compensating for an unusual sample condition (for example, unexpectedly high concentration). The setup time required to perform a given analysis is fairly long so that automation is worthwhile only when a large number of samples are to be examined.

1. Manual Laboratory Analyzers

Manual operation implies human involvement to progress along the various steps in an analytical procedure. Despite significant advances in instrument automation, most NPS water monitoring information is still obtained with manually operated laboratory analyzers. This is due in part to cost considerations in comparing manual and automated equipment, as well as the lengthy time involved in accepting new procedures as standard methods.

1.1. Colorimetry

Colorimetric methods (ultraviolet-visible absorption spectrophotometry) generally involve forming a colored species by means of chemical reactions between a reagent and the NPS pollutant under analysis. Polychromatic light from a source such as a tungsten lamp is passed through a monochromator, which directs a narrow bandwidth of the incident light through a cell containing the absorbing species. The attenuation in light intensity owing to absorption is corrected for background ef-

TABLE C-1
Commonly Used Instrumental Methods for NPS in Water Measurements

Instrumental Method	Pollutant Measured
Manual laboratory analyzers	
Colorimetric	NH_3-N, NO_2-N, NO_3-N; SO_4-S, H_2S-S, PO_4-P
Turbidimetric	SO_4-S
Gas Membrane Electrode	NH_3-N; NO_2-N
Ultraviolet Spectrophotometry	NO_3-N
Charged Particle Activation Analysis	NO_3-N
Ion Selective Electrode	NO_3-N
Automated laboratory analyzers	
Colorimetric	NH_3N, NO_2-N, NO_3-N
Manual field monitors	
Colorimetric	NH_3-N, NO_3-N; PO_4-P, H_2S-S
Volumetric Titration	SO_4-S; SO_3-S
Automated field monitors	
Colorimetric	PO_4-P; NH_3-N
Gas Membrane Electrode	NH_3-N

fects and related to concentration of NPS in the water sample through calibration data. Optimum results may depend on several factors, including the following: adjustment of oxidation state, maintenance of the correct pH, removal of interferences, and solvent extraction. Samples should be measured within a specified time period after the color-forming reaction to minimize problems of color fading.

Colorimetric methods lack specificity and sensitivity, and are time consuming. To obtain suitable specificity distillation or precipitation techniques are commonly used.

Attractive features of colorimetric techniques for water analysis include the relatively low costs (less than $1000 for some instruments), portability, and the known reliability of the analytical methods.

The schematic of the essential parts of a typical colorimeter is shown in Fig. C-1. See the specific sections on NPS monitoring analyzers for typical analytical procedures, and the H2O-MET Section for a discussion of colorimeters. Additional discussions are found in Standard Methods, 14th Ed., the ASTM Book, Part 31 (Ref. 36), and the EPA methods manual, and Instrumental Methods of Analysis, 5th Ed. (Ref. 37).

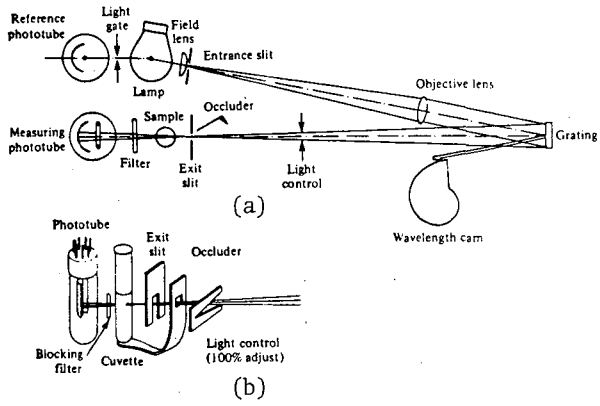


Figure C-1. Bausch & Lomb Spectronic 20 colorimeter. (a) Schematic optical diagram. (b) Detail of photocell.

Turbidimetric methods are principally used to monitor SO_4-S using either light scattering or light transmission measurements. See H2O-PHY, Turbidity. A potential source of error here is the effect of dissolved (or true) color. This effect is compensated for by measuring the sample before the addition of $BaCl_2$ reagent to establish a background level.

1.2. Gas Permeable Membrane Electrode

In gas permeable membrane electrode analyzers, the gaseous pollutant dissolved in water diffuses through a semi-permeable membrane (e.g., Teflon) into an electrochemical cell compartment. The electro-chemical cell compartment contains a sensing electrode, a reference electrode, and a supporting electrolyte such as ammonium chloride or potassium hydroxide. The semi-permeable membrane serves a dual function: it separates the electrochemical cell from the water sample, and it permits primarily only the dissolved gas being monitored to diffuse from the water sample through the membrane into the supporting electrolyte. The dissolved gas may subsequently react at the sensing electrode, and thus cause an electrical current. The dissolved oxygen electrode (DO probe) is an example of this kind of electrode. Alternatively, the gas may change the acidity of the supporting electrolyte, and thus cause a change in the measured pH. The ammonia electrode functions in this manner. See Figure C-2 (Ref. 37).

The ammonia electrode is not affected by other dissolved gases in the water sample unless these gases both diffuse through the membrane, and have an acidic or basic nature (for example, CO_2, H_2S) when dissolved in ammonium chloride. When measuring total ammonia at high pH, CO_2 and H_2S do not interfere because they are present as $CO_3^=$ or $S^=$ ions and are no longer in the gaseous form.

In water solutions containing ammonia, the following chemical equilibrium holds:

$$NH_4^+ + OH^- \rightleftharpoons NH_{3(gas)} + H_2O. \qquad (1)$$

At high pH values (e.g., pH 11), the equilbrium shifts to the right, and gaseous ammonia is freed from the ammonium ion (NH_4^+); it may subsequently diffuse through the membrane. The water sample is normally adjusted to pH 11 by addition of small amounts (e.g., 1 ml) of 10 N NaOH; equation (1) is thus shifted far to the right. The NH_3 which permeates the membrane then dissolves in the ammonium chloride filling solution where the reverse of equation (1) takes place:

$$NH_{3(gas)} + H_2O \rightleftharpoons NH_4^+ + OH^-. \qquad (2)$$

The increase in OH^- causes a rise in pH which is detected by a mirror flat glass electrode. The glass electrode responds to changes in the NH_3 concentration in the filling solution according to the Nernst equation:

$$E = E_x - S \log[NH_3]. \qquad (3)$$

Here, E is the potential of the NH_3 electrode, E_x is a constant, and S is the electrode slope which is approximately 50 mV per decade at 29°C. The reference electrode is a chloride ion-selective electrode; its potential remains fixed because the chloride concentration in the supporting electrolyte is fixed. Changes in the output voltage of the ammonia sensor are thus

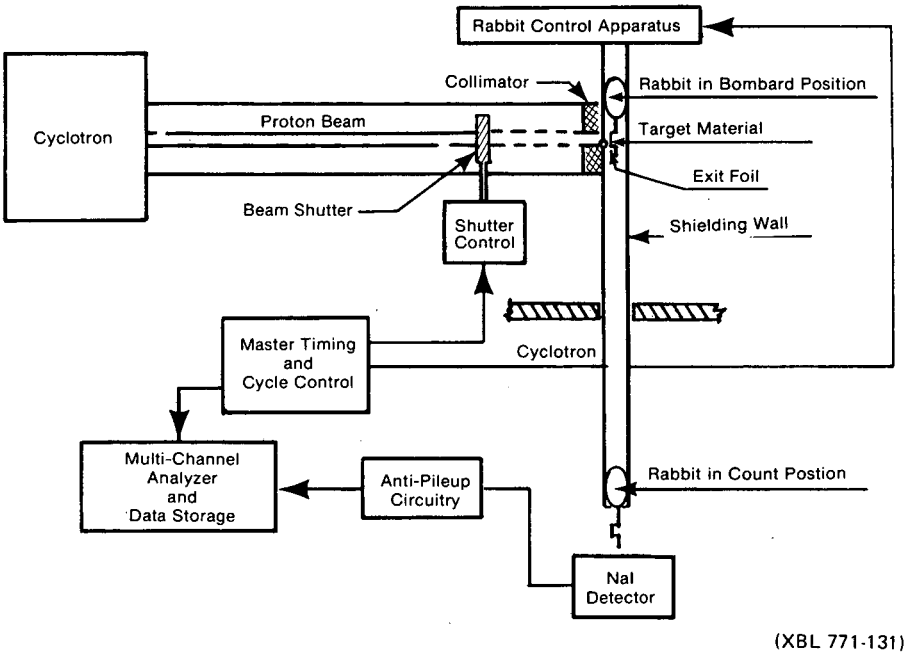


Figure C-2. Activation analysis techniques (Ref. 37).

due to changes in the pH-sensitive glass electrode and are related to NH_3 concentration in the water sample by calibration data.

The EPA has studied the application of the NH_3 gas membrane electrode (Ref. 2) to water monitoring. As a calibration standard, analytical reagent grade NH_4Cl is dried at 100°C for 3 hours; 3.819 gm (1000 mg/1 NH_3-N) are then dissolved in 1.0 liter of Super Q water which has been passed through a Millipore Super Q water purification system containing a prefilter, a carbon filter, a mixed-bed ion exchange column, and an 0.2 μ filter. The calibration standards prepared from the NH_4Cl and the Super Q treated water are stable for at least one month.

To test this standard, an Orion Model 95-10 NH_3 electrode was used as the sensor; readings were obtained on an Orion Model 801 digital pH meter, coupled to a Model 851 digital printer. To obtain readings, a 70-ml volume of the calibration standard was made basic by adding one ml of 10 N NaOH, and stirring with a magnetic stirrer. The electrode sensor was inserted immediately, and a reading taken after 5 min equilibration time. Calibration data covering the range 0.03 to 2.0 mg NH_3-N/1 are shown in Table C-1. The direct measurement calibration curve gave results comparable to the standard additions method. See Table C-2.

Interferences in the operation of the Orion 95-10 NH_3 electrode include volatile amines such as methyl amine or ethyl amine which diffuse through the membrane and cause a change in the pH of the electrolyte. Organic solvents and wetting agents may shorten the membrane electrode life. The temperature of measurements should be closely controlled, because there is a 1% change in apparent NH_3 concentration per °C.

TABLE C-2
Ammonia Concentration vs.
Electrode Potential at 25°C (from Ref. 35).

Concn. of Standard, mg NH_3-N/1	Absolute Potential, mV	Concn. Measured, mg NH_3-N/1
2.0	-21.0	2.06
1.0	- 3.3	1.00
0.5	14.3	0.49
0.2	38.3	0.19
0.1	53.8	0.099
0.05	69.1	0.053
0.03	83.4	0.029

The standard additions method has the advantage that changes in both temperature or ionic strength are more readily compensated for than with the direct method. However, any volume changes must be calculated for the known volume of added standard solution: the final NH_3 concentration must be on the linear portion of the calibration curve so that the concentration of NH_3-N in the water sample can be calculated by interpolation.

The selective ion method using gas permeable electrodes is listed in the EPA Methods Manual of December 1974 (Ref. 27). Both the Orion Model 95-10 and the EIL Model 8002-2 electrodes are listed in the apparatus section. Caution should be taken to ensure that the pH is 11 or above; otherwise freeing NH_3 from NH_4^+ ion will be incomplete.

1.3 Ion-Selective Electrode

Ion selective electrodes respond to the change in activity of the ionic species being measured in a water sample, but are not specific for that ion. The first highly selective electrode was the glass electrode which is used for pH measurement. Changes in the composition of the glass membrane in the construction of these electrodes permits enhanced response to ions such as NH_4^+.

The response of an ion selective electrode to several ionic species may be represented by the Nernst equation written in the following form:

$$E = E^\circ - \frac{RT}{NF} \ln(A + K_b B + K_c C)$$

where the K's represent the various selectivity ratios, plus the electrode response of any interfering ion relative to the response of the ion being measured. A,B, and C represent the activities of the NH_4^+ and interfering ions. Manufacturer's brochures often list the values of K for a given electrode, and these may be used to estimate the range of usefulness of an electrode in a given analytical situation. For example, the Beckman ion-selective electrode 39137 responds to K, NH_4, Na, and Li ions (in descending order of sensitivity).

The NH_4^+ electrode was used to develop a rapid method for determining NH_4^+ in water when concentrations are greater than 0.5 mg/1. Neither dilution nor pretreatment of the water sample is required. The accuracy of the NH_4^+ electrode for application to boiler feed water from power stations was investigated. The electrode response time varied from two minutes for concentrations at the 1000 mg/1 level, to 8 minutes for the 10 mg/1 concentration (Ref. 38).

1.4. Ultra Violet Absorption

The ultraviolet method is a spectrophotometric technique used for NO_3-N which depends on the attenuation of light at 220 nm and 275 nm. The method differs from colorimetric methods in that chemical reactions to form a colored solution are not required because NO_3-N absorbs near-UV radiation.

1.5. Charged Particle Activation Analysis

Charged particle (nuclear) activation analysis is an activation method in which neutrons are replaced by other nuclear particles. See H2O-MET for a discussion of neutron activation analysis. The schematic for laboratory instrumentation is shown in Figure C-3. The method was applied to nitrogen (NO_3-N) in fresh water, samples at the µg/1 level (Ref. 39).

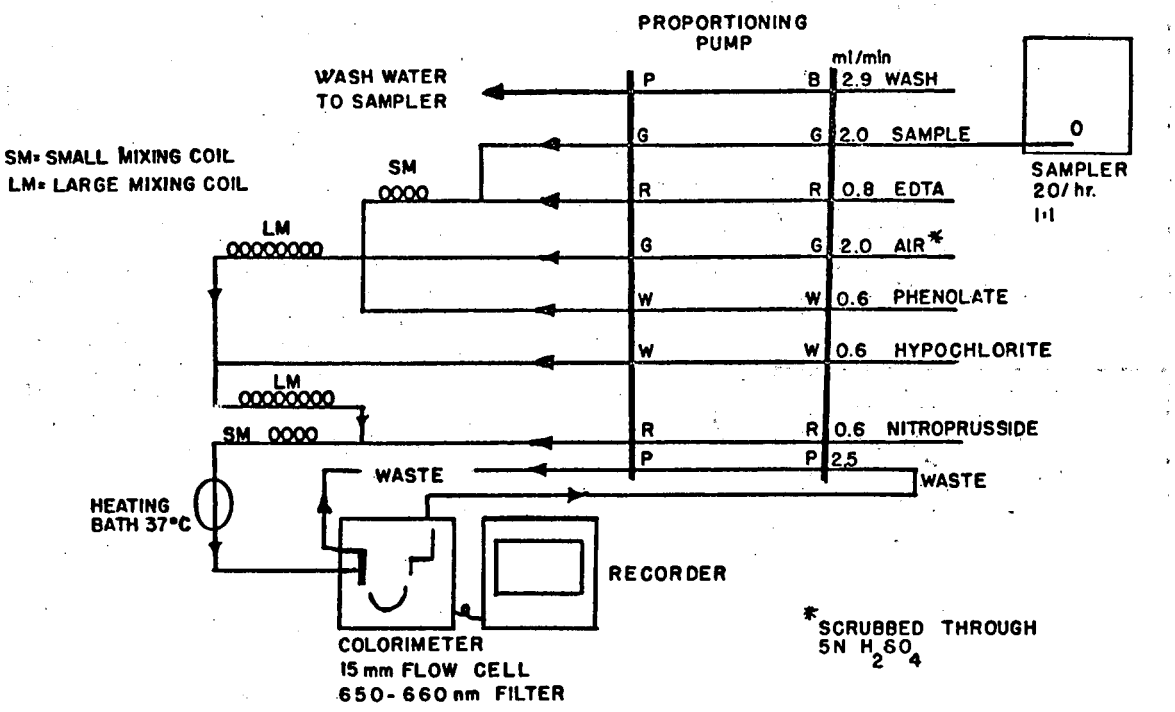


Figure C-3. Ammonia manifold AA1 (Ref. 39).

2. Automated Laboratory Analyzers

Automated laboratory instrumentation includes NPS systems in which one of the following functions do not require human intervention: (1) insertion of the sample into the colorimeter sample changer. An example is the Gilford 2443-A rapid sampler in which the cuvette remains in the measuring beam for both filling and purging. About 0.7 ml of the sample is drawn into the cuvette by means of a vacuum, and returned to the sample container by application of pressure. The sampler can process about 300 samples per hour; (2) Recording of concentration readings. The Varian Techtron Model 36 digital printer is an example of automated data recording: recordings are at a maximum rate of one line every two seconds, and results falling outside a pre-selected concentration range are tagged by asterisks. (3) Central measuring analyzers with attached modules in which required chemical reactions are automatically performed in chambers to which samples and reagents are pumped and mixed. The Technicon AutoAnalyzer is an example of this category of automated laboratory instrumentation. This system automatically performs the following functions: sampling, filtering, diluting, reagent addition, mixing, heating, digesting, color development, and measurement of the color produced. See Fig. C-4 (Ref. 27).

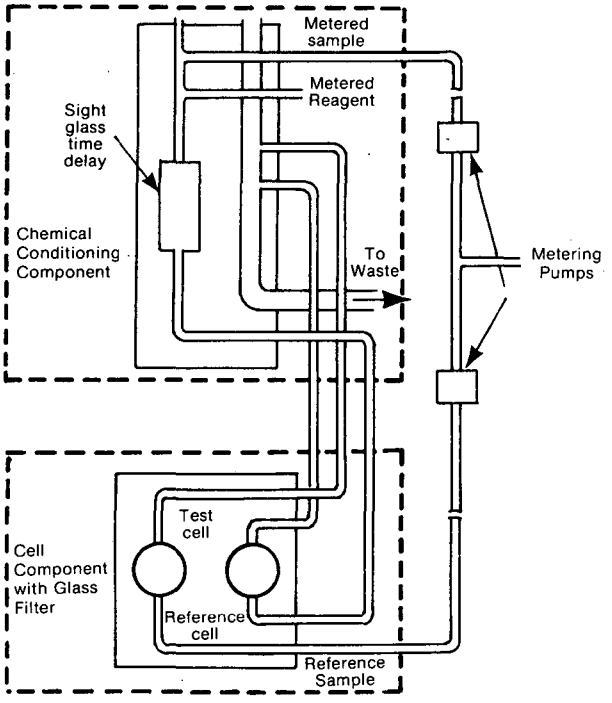


Figure C-4. Delta 8000 automated field monitor. (Ref. 27).

For example, the EPA includes a method of determining ammonia colorimetrically by using the AutoAnalyzer. The instrument train includes the following: sampler; manifold proportioning pump; heating bath with double delay coil; a colorimeter equipped with 15-mm tubular flow cell and 630- or 650-nm filters; and a recorder. The basic chemical reaction between ammonia nitrogen and sodium phenolate solution in the presence of sodium hypochlorite forms a blue-colored reaction product. The concentration of ammonia is related to the intensity of the blue color by calibration data.

See the specific NPS section for application of laboratory automated instrumentation.

3. Manual Field Monitors

These monitors are portable kits and instruments that measure pollutants by a variety of methods including volumetric titration and colorimetric reactions. In the latter case, the intensity of the color is determined by comparison with liquid-in-glass color standards, or a reagent-impregnated paper. For titration, a color change signals the end-point in the titration. The LaMotte Octet Comparator outfits are examples of the liquid-in-glass comparator measurements. Another approach to colorimetric intensity determination is that used by the Bausch and Lomb MiniSpec 20 battery-powered spectrophotometer. This instrument measures the attenuation in light intensity from a sample, and relates the reading to the pollutant concentration by calibration data.

The Delta Scientific Series 260 is a portable (weighs about 5 kg) colorimeter powered by two 6 volt batteries for field use. Readout is by means of an analog meter scale. It has a listed sensitivity of 0.05 mg/1 NH_3-N; 1.0 mg/1 H_2S-S; 0.15 mg/1 NO_3-N; 0.0006 mg/1 NO_2-N; 0.01 mg/1 PO_4-P; 1.0 mg/1 SO_4-S; and 0.6 mg/1 SO_3-S.

Manual field monitors contain reagents and necessary glassware for use in on-site measurements using standard procedures. They have the advantage that sample losses (e.g., H_2S_1 NH_3) are minimized, and preservatives may not be required. Caution is necessary to be certain the instrument is properly calibrated, that reagents have not deteriorated, and that glassware is free from contaminants.

4. Automated Field Monitors

Automated field monitors can be classified as either continuous or semicontinuous samplers. Continuous sampler instruments measure a constituent on an uninterrupted basis, and include both probe-type continuous samplers (such as NH_3 electrode) and wet chemical analyzers (such as Delta Model 8000 analyzer). The Enviro Control Series 2000 wet chemical analyzer is an example of a semicontinuous sampler. A

metered sample from the water stream is filtered and mixed with a fixed quantity of reagent. Depending on the rapidity of the chemical reaction between reagent and water constituent, the sample of water and reagent is passed either through a delay coil to allow time for color development, or directly into a colorimeter. The colorimeter contains a single lamp source and two matched cells. The colored sample stream passes through one cell, while the unreacted water stream passes through the other. The difference in light intensity is detected and recorded as a measure of the pollutant concentration.

Additional information on automated field monitors is obtained from Ballinger (Ref. 41), Stack (Ref. 42), and Ciaccio (Ref. 43).

5. Summary and Recommendations

Research needs for monitoring NPS in water are generally in the areas of: (1) increased selectivity, (2) development of methods for routine characterization and monitoring of individual forms of NPS, (3) development of reliable calibration techniques, especially for the field monitors, (4) simplified laboratory procedures, (5) development of point-source discharge monitors.

Monitoring NPS is hampered by the dependence on colorimetric measurements. These require the addition of color-forming reagents, and time for the color to develop. Turbidity, dissolved color, and other water constituents may interfere and must be compensated for, e.g., by filtration or distillation. Automated laboratory and field analyzers such as the Technicon and Orion monitors assist in removing some of the tedium of analyzing a large number of samples. The reliability of data gathered using automated field monitors depends on frequent calibration of the entire monitoring system.

The reader is referred to the sections on Nitrogen, Phosphorus, and Sulfur which follow this general introduction for a further discussion on recommendations for NPS monitoring system.

TABLE C-3
Direction Measurement and Known Addition Comparison (from Ref. 35).

Sample	Direct Measurement, mg NH_3-N/1	Known Addition, mg NH_3-N/1	Difference	
			mg NH_3-N/1	%
A	0.367	0.376	+0.009	+ 2.5
B	0.146	0.145	-0.001	- 0.7
C	0.198	0.201	+0.003	+ 1.5
D	0.168	0.167	-0.001	- 0.6
E	0.137	0.134	-0.003	- 2.2
F	0.122	0.118	-0.004	- 3.3
G	0.112	0.114	+0.002	+ 1.6
H	0.026	0.032	+0.006	+23.0
I	0.191	0.198	+0.007	+ 3.7

D. SELECTIVE NPS METHODS AND INSTRUMENTATION

This section surveys the literature on instrumental methods which are or might be applied to monitoring NPS in water. The literature coverage is selective; the intent is to give examples of both current and developing methods.

1. Nitrogen in Water

This section is limited to the NH_3-N, NO_2-N and NO_3-N forms of nitrogen.

Ammonia

a. Colorimetric

The primary limitations of colorimetry for analyzing nitrogen in water are interferences due to water constituents (e.g., turbidity) and the length of time required for analysis. For example, measuring the NH_3-N content in fresh waters by the Nessler method requires preliminary distillation of ammonia from sample buffered at pH 7.4. The distillation reduces interferences due to turbidity, dissolved color, alkalinity or acidity. Close control of pH is required to minimize conversion of organic compounds to NH_3-N, and to optimize the recovery of NH_3-N. The USGS method for distilling ammonia is similar to that in Standard Methods, 14 Ed., except that it follows the EPA procedure in adjusting to pH 9.5 with borate buffer. The water sample is adjusted to pH 9.5 using a borate buffer to decrease hydrolysis of any cyanate in organic nitrogen compounds. The released NH_3 is then distilled into a solution of boric acid (Ref. 3).

Following distillation, a portion of the distillate is Nesslerized. Essentially, Nesslerization is the reaction between potassium mercuric iodide ($HgI_2 \cdot 2KI$) and ammonia to form a red-brown complex of mercuric ammonobasic iodide, according to the following equation:

$$HgI_2 \cdot 2KI + NH_3 \rightarrow Hg(NH_2)I + 2KI + HI.$$

The concentrations of ammonia are then determined by standard UV-VIS spectrophotometric measurements. Alternatively, NH_3 in the distillate may be titrated with a standard sulfuric acid solution (Ref. 8).

Interferences include a number of aromatic and aliphatic amines, and any compounds which cause turbidity upon the addition of Nessler reagent. Direct Nesslerization of the water sample (i.e., without distillation) cannot be used because of the many interferences. For example, cyanate (CNO^-), will hydrolyze to some extent even at pH 9.5; volatile alkaline compounds such as hydrazine will interfere with the titrametric results. Residual chlorine must be removed by pretreatment of the sample with sodium thiosulfate before distillation, and if the sample has been preserved with a mercury salt (e.g., $HgCl_2$), the mercury ion must be complexed with sodium thiosulfate prior to distillation. The Nessler method is sensitive to 20 µg/1 NH_3-N under optimum conditions. Optimum results are obtained over the range 0.05 to 1.0 mg/1 for the colorimetric procedures, and from 1.0 to 25 mg/1 for the titrimetric procedure.

The precision and accuracy of the method given in the EPA manual was tested by 24 analysts in 16 laboratories using water samples containing concentrations of ammonia covering the range 0.21 to 1.92 mg/1. See Table D-1 (Ref. 14). Additional information on the precision and accuracy of this method for determining ammonia nitrogen is found in Standard Methods (Ref. 11).

Besides Nesslerization, Standard Methods lists a tentative phenate method for the colorimetric determination of ammonia. The method

TABLE D-1
Twenty-four Analysts in Sixteen Laboratories Analyzed Natural Water Samples Containing Exact Increments of an Ammonium Salt, With the Following Results (from Ref. 14).

Increment as Nitrogen, Ammonia (mg N/liter)	Precision as Standard Deviation (mg N/liter)	Accuracy as	
		Bias, %	Bias, ng N/liter
0.21	0.122	- 5.54	- 0.01
0.26	0.070	-18.12	- 0.05
1.71	0.244	+ 0.46	+ 0.01
1.92	0.279	- 2.01	- 0.04

utilizes the reaction of ammonia, hydrochlorite and phenol, catalyzed by manganous salt to form the intensely blue indophenol. Interferences in the method include: > 500 mg/1 alkalinity, > 100 mg/1 acidity, or any dissolved color or turbidity. These interferences may be removed by preliminary distillation. For information on the precision and accuracy of this method, see Ref. 5.

Automated laboratory colorimetric methods of analysis for NH_3-N in water usually employ the Technicon instrument system. The EPA is very active in developing automated methods for water monitoring, and lists an automated method for monitoring ammonia based on the indophenol blue color formed by the reaction of ammonia with alkaline phenol hypochlorite. The method is applicable to the determination of NH_3-N present in either surface or saline waters. Concentrations in the range 0.01 to 2.0 mg/1 NH_3-N may be determined, depending upon the selection of the size of the flow cell and the extent of dilution of the sample. See Figure D-1 (Ref. 44).

Calcium and magnesium ions cause precipitation during the analysis; adding a 5% solution of EDTA eliminates the source of error. Other sources of error include variations in the acidity or alkalinity of the water sample, due to the pH dependence in the intensity of the color which is measured. The pH of washwater and the standard ammonium solution should approximate that of the sample to avoid causing a pH change. Added $HgCl_2$ causes a negative interference because mercury complexes with ammonia. This complex may be compensated for by adding an equivalent amount of $HgCl_2$ to the ammonia standards which are used for the preparation of the standardization curve. As an additional precaution, when saline water samples are analyzed, substitute ocean water (SOW) should be used for preparing the ammonia standards used for the calibration curve.

The precision and accuracy of the method were tested by EPA's Analytical Quality Control Laboratory using surface water samples containing 1.41, 0.77, 0.59 and 0.43 mg/1 NH_3-N. The standard deviation was ± 0.005.

The Technicon AutoAnalyzer was also applied to the measurement of NH_3-N in sanitary and storm sewer waters in the Minneapolis--St. Paul sanitary district (Ref. 45). Besides ammonia, other measured parameters were COD, methylene blue-active substances, chlorides, Fe, PO_4-P, urea, and total (Kjeldahl nitrogen). The alkaline phenol method was used for NH_3-N; calibration solutions were prepared by dissolving 1.146 g/ℓ of NH_4Cl, (300 mg/1 NH_3-N) in a stock solution which also contained 20,000 mg/1 COD, 5000 mg/1 cl. 500 mg/1 PO_4-P, and 1000 mg/1 urea. The stock solution was diluted for calibration purposes.

The method of standard additions was applied for recovery studies. See Table D-2. The developed automated method was compared with the manual method for NH_3-N. See Table D-3.

Brinkmann Instruments has recently introduced a probe colorimeter that can be used to monitor NH_3-N. The probe is inserted directly into the test solution, which may be in a beaker or a test tube. The probe is

TABLE D-2
Recovery of Standards Mixed with Primary Effluent

Analysis	Prim.Eff. mg/liter	Prim.Eff. + Standard Actual mg/liter	Prim.Eff. + Standard Theor. mg/liter	% Recovery Min.	% Recovery Max.	% Recovery Avg.
NH_3-N	6.8		9.4	101.0	105.4	102.1
COD	293	543	546	95.8	105.1	99.4
Cl	80	142	140	100.7	103.0	101.5
PO_4	11.2	15.3	15.6	94.6	102.6	98.1
Urea	6.7	27.0	23.4	103.0	134.9	115.3
Fe	0.41	0.37	1.20	16.7	40.0	30.8
*Kjeldahl N	18.9	19.2	19.5	91.0	106.0	98.1

*4 days only.

TABLE D-3
Automated vs. Manual Ammonia Determinations

	Average NH_3-N-mg/liter				
			% of Manual		
	Manual	Auto.	Min.	Max.	Avg.
Raw	11.0	10.7	94.1	100.0	97.1
P.E.	11.2	11.3	98.4	103.9	101.2
S.E.	9.7	9.3	95.5	96.2	95.9

based on transmitting phase-shifted light through a fiber optic light guide to the probe tip. The probe tip is made of stainless steel and has both a glass window and an aluminized glass plate or convex lens held in place. Light passes through the sample to the mirror, and back through the sample again to the fiber optics. After passing through the sample, the light is passed through a filter and then to a photometric cell which converts the light intensity to an electrical signal read on a scale.

The probe colorimeter light is AC amplified and phase-shifted to minimize effects of the ambient light, thus permitting colorimetric measurements when the sample is in an open container. For the indophenol method, the range is 0.01 to 2.0 mg/1 of NH_3-N measured at 650 nm (Ref. 46).

Colorimetric methods are used in manual field analyzers. For example, the Hach DR/2 colorimeter is battery-powered for field use, and weighs about 6.5 kg. It covers the wavelength range of 400 to 700 nm, and has the following listed ranges for nitrogen in water analysis using standardized methods: o to mg/1 NH_3-N, 0 to 30 mg/1 NO_2-N, 0 to 0.2 mg/1 or o to 150 mg/1 NO_2=N. The optical light path is shown in Fig. D-1.

The Ecologic Instrument Corp. Series 500 instruments are examples of automated field analyzers. The monitors utilize wet chemical methods for color development, and utilize modified standard procedures. For example, NH_3-N is monitored by the phenol-hypochlorite method in which the blue color intensity is measured at 650 nm. The reagents required for color development are contained within the instrument, and are metered to a mixing coil using a peristaltic pump. The sample flow rate is 200 ml/hr.; the time required for a 90% response is about 15 minutes.

In summary, colorimetric methods are those most widely used for monitoring NH_3-N in the field and in the laboratory. Laboratory methods have the disadvantages of requiring sample

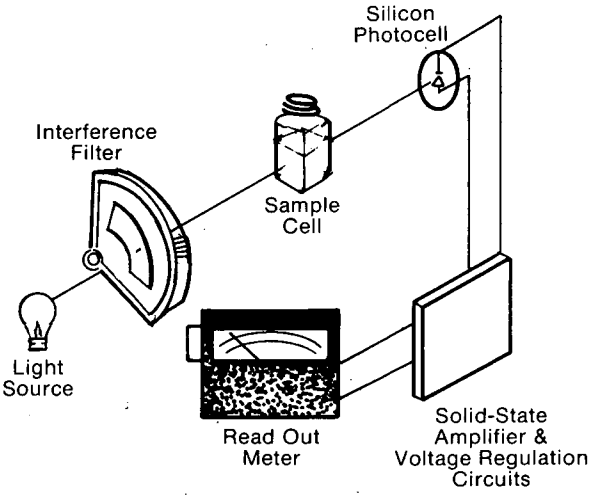


Figure D-1. Light path diagram.

preservation to minimize NH_3-N loss, and of having a time delay between sampling and analysis. Field analyzers can provide real-time data and may not require sample preservatives. However, unless NH_3-N is separated from the sample by distillation, the analyses are subject to interferences which require compensation. Automated methods provide the capability of analyzing a large number of samples relatively inexpensively and appear desirable.

b. Gas Membrane Electrodes

The laboratory analysis of NH_3-N using gas membrane electrodes is listed in the EPA Methods manual for fresh, saline, and waste water samples (Ref. 44). The method covers the range 0.03 to 1400 mg/1 NH_3-N; Color and turbidity do not interfere, and prior distillation is unnecessary. The samples are preserved for 24 hours by refrigeration at 4°C, or, for longer periods, by addition of H_2SO_4 to pH <2 (2 ml conc H_2SO_4 per liter of sample) for longer holding periods. Mercuric chloride forms strong complexes with NH_3-N; this complexed NH_3-N is not measured by the electrode so that Hg Cl_2 cannot be used as a preservative.

The distilled water used to prepare reagents must be free of NH_3-N; this is accomplished by passing the water through a strongly acidic cation exchange resin mixed with a strongly basic anion exchange resin. In analysis, 100-ml of the water sample are placed in a 150-ml beaker, an electrode such as the Orion Model 95-10 or EIL Model 8002-2 is inserted, 1-ml of 10 N NaOH is added, and the solution stirred while reading the meter. The final pH must be above 11. The meter reading is related to NH_3-N concentration by calibration data. The EPA found the following precision: using surface water samples of 1.00,

0.77, 0.19 and 0.13 mg/1 NH_3-N, standard deviations were ±0.038, ±0.017, ±0.007, and ±0.003, respectively.

The method has been applied to various waste waters. See Tables D-4, D-5, and D-6 (Ref. 47).

TABLE D-4
(Ref. 47) Comparison of Ammonia-Specific Ion Electrode With Standard Procedure for Petroleum Refinery Effluents

Laboratory reference number	Sample description	Ammonia N µg/ml, ammonia-specific ion electrode	Ammonia N µg/ml, distillation and acid titration	Ammonia N µg/ml, distillation and nesslerization
T-1111	Petroleum refinery A, effluent A (treated)	12.7		13.2
T-1112	Same as above	11.3		12.6
T-1113	Same as above	11.0		11.2
T-1114	Same as above	10.8		10.5
T-1115	Same as above	12.6		11.5
T-1118	Same as above	19.5		19.0
T-1219	Same as above	20.5	24.2	
T-1220	Same as above	11.8	9.9	
T-1222	Same as above	33.0	30.3	
T-1228	Same as above	10.0	10.5	
T-1296	Petroleum refinery B, effluent B (treated)	12.0	11.2	
T-1297	Same as above	13.0	13.3	
T-1298	Same as above	17.3	17.0	
T-1299	Same as above	19.3	20.4	
T-1300	Same as above	16.2	17.6	
T-1301	Same as above	15.8	15.4	
T-1302	Same as above	15.0	16.5	

TABLE D-5
(Ref. 47) Comparison of Ammonia-Specific Ion Electrode with Standard Procedure for Various Waste Waters

Laboratory reference number	Sample description	Ammonia N µg/ml, ammonia-specific ion electrode	Ammonia N µg/ml, distillation and acid titration	Ammonia N µg/ml, distillation and nesslerization
T-1156	Food processing plant effluent (untreated	108	101	99
T-1159	Food processing plant effluent (treated)	15.1	13.3	
TWB-1	Municipal sewage effluent (untreated)	5.4	5.6	5.6
TWB-2	Municipal sewage effluent (treated)	4.2	5.2	4.8
T-1231	Acid and explosive plant effluent (untreated)	99	92	
T-1232	Same as above	104	96	
T-1233	Same as above	2.4	3.0	
T-1234	Same as above	5.3	5.1	
TWB-10	Pulp and paper, sulfite mill effluent (untreated)	1300	1340	
TWB-11	Pulp and paper, kraft mill effluent (untreated)	3.2	34.6	39.0
TWB-12	Pulp and paper, kraft mill effluent (treated)	2.2	4.1	3.4
T-456	Chemical plant (detergent) effluent B (treated)	11.0	10.4	12.4
T-458	Chemical plant (detergent) effluent A (treated)	3.2	3.1	3.6
T-460	Chemical plant (detergent) effluent (untreated)	0.3	< 0.5	0.4

TABLE D-6
(Ref. 47) Comparison of Ammonia-Specific Ion Electrode with Distilled and Nondistilled Waste Waters

Laboratory reference number	Sample description	Ammonia N µg/ml, ammonia-specific ion electrode		Ammonia N µg/ml, distillation	
		Direct reading	Distillate	Nesslerization	Acid titration
TWB-1	Municipal sewage effluent (untreated)	5.4	6.1	5.6	5.6
TWB-2	Municipal sewage effluent (treated)	4.2	4.5	4.8	4.2
TWB-11	Pulp and paper, kraft mill effluent (untreated)	3.2	34.0	39.0	34.6
TWB-12	Pulp and paper, kraft mill effluent (treated)	2.2	3.6	3.4	4.1
T-1156	Food processing plant effluent (treated)	108	102	99	101
T-1220	Petroleum refinery A effluent (treated)	9.9	12.3		11.8
T-1222	Same as above	28.5	30.0		30.3
T-1228	Same as above	10.0	11.3		10.5
T-456	Chemical plant (detergent) effluent B (treated)	11.0	11.9	12.4	10.4
T-458	Chemical plant (detergent) effluent A (untreated)	3.2	3.5	3.6	3.1
T-460	Chemical plant (detergent) effluent (untreated)	0.3	0.4	0.4	< 0.5

Orion Research has recently introduced its Model 1110 automated field NH_3-N monitor. The standard range is 1.0 to 100 mg/1, with a lower limit of detection of 0.17 mg/1. See Fig. D-2. It requires 8 minutes for a 99% response to a change in NH_3-N concentration at the inlet. The sampled water stream is filtered prior to reagent mixing and measurement. (Ref. 48).

Enviro Control Inc. has available its Model 1057 NH_3-N gas membrane automated field monitor which is applicable to wastewaters. It covers the range 0.017 to 17,000 mg/1. The Model 1057 is combined with the Model 2052 or 2050 filtration unit which removes particles to 0.45 µ or 5µ, and the Model 1035 pH adjusting system. Total NH_3-N is measured by raising the pH, thereby converting NH_4^+ ions to dissolved NH_3 gas.

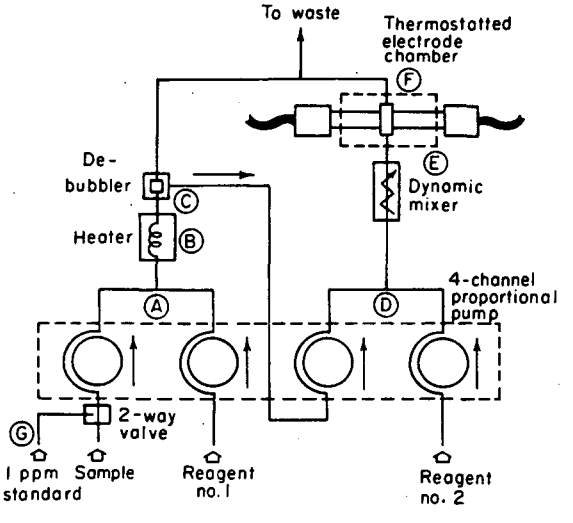


Figure D-2. Schematic of the Orion Research Model 1110 NH_3-N monitor (from Ref. 48).

In summary, the gas membrane method is utilized for measuring NH_3-N in waters; prior distillation is not required, and color and turbidity do not interfere. The method is promising for monitoring NH_3-N using laboratory or field methods. Caution must be exercised in choice of preservative, maintaining the required high pH and following the analytical procedure closely. The field automated monitors should be evaluated for application to specific joint source discharges.

Nitrate

Standard Methods, 14th Ed. and the EPA manual list colorimetric methods for NO_3-N; Standard Methods also includes a tentative UV absorption method.

a. Colorimetric

Colorimetric methods are most commonly used for analyzing NO_3-N in fresh, waste and saline waters. In fresh waters the phenol disulfonic acid method is listed in Standard Methods, while the brucine, cadmium and zinc reduction methods, as well as the chromotropic

acid method, are equally satisfactory. In waste waters, it is more difficult to determine NO_3-N than in fresh waters because of high concentrations of numerous interfering substances (e.g., chlorides, organic matter). Consequently, several tentative methods are given in Standard Methods. The EPA methods manual and the USGS manual both list the brucine method: NO_3-N and brucine react in acid medium to produce a yellow color whose intensity is a function of NO_3-N concentration. Close attention must be given to procedural techniques if accuracy and precision are to be obtained.

b. UV Absorption

Standard Methods also lists a tentative ultraviolet (UV) spectrophotometric method for measuring nitrate. Measurement of the nitrate concentration using the ultraviolet method is made at a wavelength of 220 nm. The nitrate calibration curve follows Beers Law up to 11 mg/1 nitrogen. To correct for any absorption effects caused by dissolved organic matter which also absorbs at 220 nm, a second measurement is made at 275 nm, where nitrate does not absorb. The correction for dissolved organic matter absorption is then made by subtracting the absorption at 275 nm from that at 220 nm. Besides dissolved organic matter, nitrite, hexavalent chromium and surfactants also interfere with the UV method. Sulfate, NH_4^+ . HCO_3^-, PO_4-P, and F^- have negligible interference at the concentrations normally present in drinking water. The minimum detectable concentration for NO_3-N using UV absorption is 40 µg/1.

In the brucine method for NO_3-N, organic color, NO_2-N, and strongly oxidizing or reducing agents interfere. The interferences are removed; for example, residual chlorine up to 5 mg/1 is eliminated by addition of sodium arsenite; interferences of NO_2-N to 1 mg/1 are eliminated by addition of sulfanilic acid. Brucine is reacted with NO_3-N in 13 N H_2SO_4 solution at a temperature of 100°C to form a yellow color which is measured at 410 nm. Temperature control of the color reaction is extremely critical. The absorbance of the nitrate-brucine solutions was investigated as a function of color development time over a nitrate range of 0 to 100 mg/1 and over a time interval of 5 to 35 min (Ref. 8). It was found that the absorption curve did not flatten out at the point of 1:1 stoichiometry between brucine and nitrate, but instead dropped to absorption levels within the rnage of the 0.1 - 2 mg/1 of NO_3-N standard curve before increasing again. See Fig. D-3. Results of the experiment showed that without a stoichiometric equivalent or excess of brucine over nitrate, the brucine method can lead to erroneous results. (Ref. 49).

The EPA methods manual lists the automated determination of nitrogen in either the NO_3-N or the NO_2-N form; the initial step involves

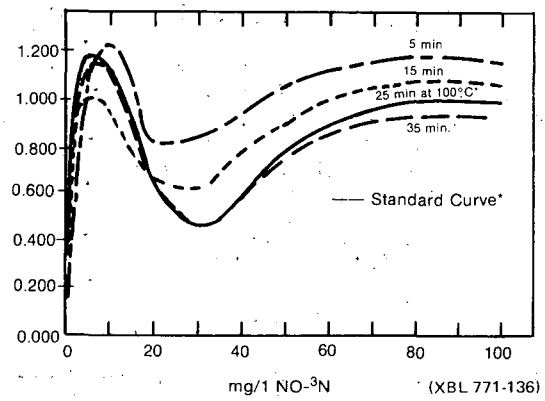


Figure D-3. Absorbance vs. NO_3-N concentration as a function of color development time (from Ref. 49).

reducing nitrate to nitrite using a cadmium-copper catalyst. The nitrites, those originally present, as well as any nitrate that has been reduced to nitrite, are then reacted with sulfanilamide to form a diazo compound. This is coupled in an acid solution at pH 2.0 - 2.5 with N-1-naphthylethylenediamine hydrochloride to form the azo dye. The azo dye color intensity is proportional to the nitrite concentration and is measured using a UV-VIS spectrophotometer.

Interferences are caused by the presence of ammonia and primary amines which are frequently present in natural waters and react to some extent with nitrites to form nitrogen. In the surface waters normally analyzed, the concentration of oxidizing or reducing agents and potentially interfering metal ions are well below the limits causing interferences with this method. When present in sufficient concentration, metal ions may produce a positive error; for example, Hg and Cu ions form complex ions having absorption bands at 543 nm where the colorimetric measurements are made. (Ref. 44).

The precision and accuracy of the automated method for nitrate-nitrite determination using cadmium reduction was assessed by three laboratories which analyzed four natural water samples containing exact increments of NO_3-N. See Table D-7.

TABLE D-7
Comparison of Precision Accuracy of Automated Methods for Nitrate-Nitrite (Ref. 14)

Increment as Nitrate Nitrogen (mg N/liter)	Precision as Standard Deviation (mg N/liter)	Accuracy as Bias, %	Accuracy as Bias, mg N/liter
0.29	0.012	+ 5.75	+0.017
0.35	0.092	+18.10	+0.063
2.31	0.318	+ 4.47	+0.103
2.48	0.176	- 2.69	-0.067

c. Charged Particle Activation Analysis

Charged particle activation analysis differs from neutron activation in that particles other than neutrons (e.g., protons, deuterons) are used in nuclear reactions. For example, the following reactions were used for analysis of nitrogen in water:

$$^{14}N + p \rightarrow {}^{14}O + n$$

$$^{14}O \rightarrow {}^{14}N + r + e^{+} + v.$$

These reactions were used to analyze NO_3-N in fresh water detritus (Ref. 50). A 4-ml. water sample was evaporated in a 5mm diameter, 1 mm deep indentation in a 1.59 cm diameter tantalum foil of 0.006 mm thickness. The Ta foils were irradiated with an 8 MeV beam of protons generated from a 76 cm cyclotron for 60 sec. After a 30 sec. wait, the gamma emission was counted using a NaI (Tl) crystal mounted on a photomultiplier tube. The limit of detection was about 20 µg/1. Silver nitrate was used for calibration.

Water samples from a number of sources were measured. The results shown in Table D-8 correlated well with chemical analysis for NO_3-N, indicating nitrogen was principally present as nitrate in these waters.

TABLE D-8
Results of Application of Nitrogen-activation Method to Various Water Sources. (Ref.21).

	Sample Origin	Date	ppb
1.	Lake Tahoe, California; supplied Dept. of Zoology, Univ. of Calif., Davis	March, 1972	21 ± 16
2.	Tapwater, Environmental Eng. Lab., Univ. of Calif., Davis	6/14/71	45 ± 31
3.	Drinking water, Walker Hall, Univ. of Calif., Davis	6/14/71 7/ 4/72	80 ± 32 340 ± 110
4.	City of Davis, California Well Number 10 Well Number 17 Well Number 18	6/ 7/72 6/ 7/72 6/ 7/72	755 ± 35 180 ± 45 2835 ± 266
5.	Sacramento River, Three-Mile Slough	April, 1972	83 ± 43
6.	Colorado River, below Lake Havasu	3/23/71	400 ± 80

Nitrite

a. Gas Permeable Membrane Electrode

Orion Research model 95-46 electrode measures NO_2-N dissolved in water. (Ref. 51). Nitrite is measured by acidifying the water sample to convert nitrite to nitrous acid according to the reaction

$$NO_2^- + H^+ \quad HNO_2 \rightleftharpoons NO_2 + NO.$$

The dissolved HNO_2 then is in equilibrium with NO_2 and NO. The NO_2 diffuses through a highly gas-permeable membrane to a filling solution until equilibrium is reached between the HNO_2 level in the sample and the internal filling solution (electrolyte) of the electrode. Hydrogen ions are formed in the internal filling solution by the dissociation of HNO_2 according to the reaction

$$HNO_2 \rightarrow H^+ + NO_2^- .$$

The hydrogen ion level of the internal filling solution is measured by the internal sensing element and is directly proportional to the level of HNO_2 in the water sample. The electrode potential is essentially Nernstian:

$$E = E_x + n\log[HNO_2] .$$

See Fig. D-4. Nitrite in sewage effluents and industrial waste waters can be measured to 0.02 mg/1, with the upper limit 460 mg/1 NO_2-N. Sample must be adjusted to pH 1.7 prior to analysis. The time response of the electrode

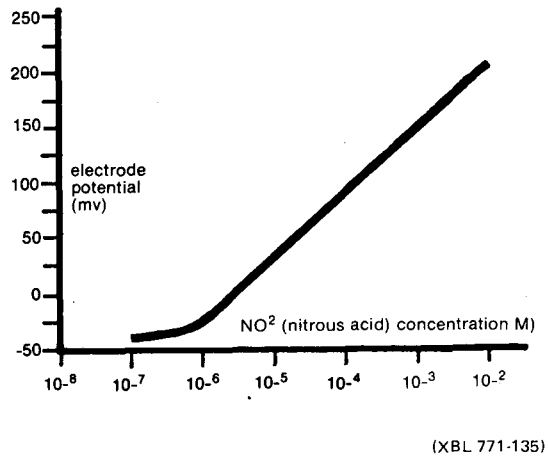


Figure D-4. Typical response of the model 95-46 nitrogen oxide electrode (from Ref. 51).

in going from dilution solutions to more concentrated solutions is 3 - 4 minutes. The maximum allowable concentration of interfering gases in 10^{-4} M HNO_2 solution is acetic acid, 3×10^{-3}; formic acid, 2×10^{-4}; HCl, > 1 molar.

b. Colorimetric

Standard Methods, the EPA methods manual, and USGS all list the diazotization method for analyzing nitrite in water. Nitrite is diazotized with sulfanilamide and the resulting diazo compound is coupled with N-(1-Naphthyl)-ethylenediamine dihydrochloride to form an intensely colored red dye. The intensity of the color measured at 540 nm is proportional to the nitrite concentration. The method is applicable in the range 0.05 - 1.0 mg/1 NO_2-N. There are very few known interferences at concentrations less than 1000 times that of nitrite. However, addition of strong oxidants or reductants to the samples will readily affect the nitrite concentrations. High alkalinity, greater than 600 mg/1, will give low results due to a shift in pH of the color reaction which should occur between 1.5 - 2.0. A synthetic unknown sample contining 250 µg/1 NO_2-N, 108 mg/1 Ca, 82 mg/1 Mg, 3.1 mg/1 K, 19.9 mg/ Na, 241 mg/1 Cl, 1.1 mg/1 NO_3-N, 259 mg/1 SO_4-S, and 42.5 mg/1 total alkalinity was determined by the diazotization method. The relative standard deviation was 21.4% and the relative error was 12.0% in 49 laboratories.

The automated method for NO_3-N listed in the EPA methods manual can be applied to the determination of NO_2-N. (Ref. 44).

2. Phosphorus in Water

This section is limited to orthophosphate (PO_4-P) because it is the most prevalent form of phosphorus in water, and because other forms are usually converted to PO_4-P prior to analysis. Two methods commonly used are discussed: manual UV-VIS (colorimetry), and automated methods.

Orthophosphate

a. Manual UV-VIS Absorption Spectrophotometry

Standard Methods, 14th Edition, lists three methods for PO_4-P: (1) vanadomolybdophosphoric, (2) stannous chloride reductant method, (3) ascorbic acid reductant method (Ref. 52). See Table D-9. The method determines PO_4-P, so that other forms of phosphorus must be converted to phosphate by chemical means (e.g., oxidation) prior to analysis.

In the vanadomolybdophosphoric method, a water sample containing 50 - 1000 µg PO_4-P

TABLE D-9
Manual UV-Visible Absorption Spectrophotometric Methods. (Ref. 52)

Method	Ortho-phosphorus Phosphate µg/1	No. of Laboratories	Relative Standard Deviation %	Relative Error %	Minimum Detectable Concentration
Vanadomolybdate	100	45	75.2	21.6	200 µg/1
	600	43	19.6	10.8	
	7,000	44	8.6	5.4	
Stannous chloride	100	45	25.5	28.7	3 µg/1
	600	44	14.2	8.0	
	7,000	45	7.6	4.3	
Ascorbic acid	100	3	9.1	10.0	30 µg/1
	600	3	4.0	4.4	
	7,000	3	5.2	4.9	

is mixed with a vanadate-molybdate reagent at pH 4 - 10. A yellow color develops with an intensity proportional to the PO_4-P concentration. There are a number of interferences: silica and arsenic increase the color intensity if the sample is heated; while a decrease in color intensity is caused by F^-, arsenate, Th, Bi, $S^=$ $S_2O_3^=$, SCN^-, or excess molydate. The method thus requires removal of these interferences by various means, for example, $S^=$ is eliminated by the addition of bromine water addition.

The colorimetric method is improved by mixing a molybdate reagent with PO_4-P, and then reducing the resulting molybdophosphate with stannous chloride to form an intensely blue colored complex. The molybdophosphate can be extracted into a benzene-isobutyl alcohol mxiture, thereby increasing the sensitivity and decreasing interferences.

A third method is the ascorbic acid method, also designated as the single reagent method in the EPA manual (Ref. 44). It may be applied to fresh, waste, and saline waters, and is used over the range 0.01 to 0.5 mg/1 phosphorus. Color development takes place in two steps: (1) solutions of ammonium molybdate and potassium antimonyl tartrate are mixed with the PO_4-P sample, and (2) this is reduced by ascorbic acid to form an intensely blue color at pH 7 $\pm$ 0.2. The minimum detectable concentration is somewhat higher than that of stannous chloride method, but solvent extraction is not required. Only arsenates, hexavalent chromium, and nitrite interfere; $S^=$ does not interfere at 1.0 mg/1, silicate does not interfere at 10.0 mg/1. The method is the only manual technique listed in the EPA manual. The ASTM book, Part 31, lists three methods, two of which are suited for fresh, saline and waste waters: ascorbic acid and amino-naphthol-sulfonic acid reduction (Ref. 53).

b. Automated

The EPA methods manual lists an automated procedure using a Technicon AutoAnalyzer to measure PO_4-P. The water sample is mixed with ammonium molybdate and antimony potassium tartrate reagent to form a complex which is reduced with ascorbic acid to form a blue-colored solution. The method applies over the range 0.001 to 1.0 mg/1 PO_4-P. Approximately 20-30 samples can be analyzed per hour.

The Technicon instrument system was applied by Osburn, Lemmel and Donvey to the automated analysis of PO_4-P, hydrolyzable, and total phosphate in surface and wastewater (Ref. 54). The method was developed so that it could be applied to water samples containing suspended solids (turbidity), unnatural color, and silicate. Turbidity was compensated by determining the attenuation in light intensity for samples containing all reagents; then making the same measurements for samples containing all reagents except ascorbic acid. The molybdenum blue color does not develop in the absence of ascorbic acid so that any attenuation in light intensity is related to sample turbidity. See Table D-10 for the effects of turbidity on water samples. The method was evaluated by standard addition of PO_4-P to river water samples. See Table D-11.

TABLE D-10
Effect of Turbidity on
Automated Orthophosphate Results (from Ref. 3)

Sample	Mg/1 Phosphate		
	Automated		Manual
	Uncorrected	Corrected	
1	0.12	0.05	0.02
2	0.38	0.11	0.12
3	0.24	0.22	0.28
4	0.47	0.11	0.11

TABLE D-11
Ortho- and Total Phosphate in River Water
Before and After Addition of Orthophosphate (from Ref. 3)

Sample	Mg/1 ortho P			Mg/1 total P		
	Before	Added	After	Before	Added	After
1	0.05	0.25	0.29	0.07	0.25	0.32
2	0.05	0.25	0.25	0.06	0.25	0.28
3	0.32	0.25	0.56	0.42	0.25	0.68
4	0.15	0.20	0.32	0.20	0.20	0.40
5	0.29	0.20	0.45	0.33	0.20	0.45

Average % recovery of added orthophosphate: ortho P = 95.0, total P = 97.0.

3. Sulfur In Water

This section surveys primarily the literature on instrumental methods which are, or might be, applied to monitoring sulfate (SO_4-S), sulfite (SO_3-S), and sulfide (H_2S-S) in water. Basically, methods discussed fall into one of the following categories: (1) the standard methods currently in use; and (2) new techniques which might be more selective, more sensitive, or take less time than current standard methods. The literature covered will be selective; no attempt will be made to include all the publications on sulfur analytical methodology.

Standard Methods, 14th edition, includes gravimetric, titrimetric, turbidimetric, and colorimetric methods for determining SO_4-S, SO_3-S, and H_2S-S in water and wastewater (Ref. 11). The U. S. Geological Survey Methods, Book 5, lists titrimetric methods for SO_4-S and H_2S-S; the EPA Methods Manual lists turbidimetric, automated colorimetric and gravimetric for SO_4-S: and titrimetric for H_2S-S and SO_3-S (Ref.27); and ASTM, Part 31, Water, lists gravimetric, volumetric, turbidimetric for SO_4-S, and titrimetric for SO_3-S (Ref.36).

Sulfate

a. Gravimetric

The gravimetric method for SO_4-S is based on precipitation by Ba, as $BaSO_4$, from an acidified solution of the water sample. It is applicable to SO_4-S contents above 10 mg/1. However, the method is subject to a number of errors depending on the other constituents in the water sample. High results are caused by some constituents (e.g., silica, suspended matter, sulfite); low results by other constituents such as alkali metal sulfates. The interferences must be removed from the water sample prior to analysis (e.g., cation exchange). Standard Methods contains a detailed discussion of interfering constituents and their removal (Ref. 11).

b. Turbidimetric

In the turbidimetric method, SO_4-S is mixed with $BaCl_2$ in HCl solution to form a suspension. The resulting suspension is placed in a cell, and the scattering for light attenuation is measured using either a nephelometer or a spectrophotometer. The method is subject to interferences by dissolved color, suspended matter, > 500 mg/1 silica, and organic matter. The color and suspended solids can be corrected for by measuring a water sample to which $BaCl_2$ reagent has not been added as a blank. The method has a minimum detectable limit of 1 mg/1 SO_4-S.

The EPA has developed an automated colorimetric method for SO_4-S using a Technicon AutoAnalyzer (Ref. 3). The method is based on the following color-forming reaction of SO_4-S with barium chloranilate:

$$\underset{\text{(colorless)}}{\text{Ba Chloranilate}} + SO_4^{=} \rightarrow BaSO_4\downarrow + \underset{\text{(purple)}}{\text{chloranilate}}$$

The released chloranilate has a purple color for which the intensity is proportional to the concentration of SO_4-S. Interferences are removed by ion-exchange. The method may be applied for the range of 10 to 400 mg/1 SO_4-S.

Some developing methods for SO_4-S analyzers are described in the review article by Fishman and Erdmann (Ref. 5). The articles reviewed show a continued interest in automated colorimetric methods. For example, a method has been developed centering around the reaction between SO_4-S and thorium-SPADNS reagent to yield a colored solution.

Sulfite

The Standard Method for SO_3-S is titrimetric, and is based on titration with an iodide-iodate solution of known concentration to a starch indicator end-point (blue color). The method can measure SO_3-S to a minimum detectable concentration of 2 mg/1.

The ASTM Book of Standards lists three titrimetric methods for SO_3-S in water. For SO_3-S over the range 0.1 to 6 mg/1, excess iodine chloride is added to oxidize SO_3-S to SO_4-S. The remaining (excess) iodine chloride is then measured by titrating with a standardized thiosulfate solution to an amperometric end-point. High results are caused by the presence of H_2S-S while NO_2-N will oxidize SO_3-S and cause low results. For SO_3-S concentrations greater than 6 mg/1, the reagent concentrations are adjusted. The end-point is detected amperometrically. The third method is similar to that in Standard Methods, 14th Edition, where the end-point is detected by starch indicator.

The EPA method for SO_3-S applies to fresh and waste waters; it is identical to the titrimetric methods given in Standard Methods and ASTM (Ref. 4).

Sulfide

The standard methods for H_2S-S are either volumetric (titration with iodine) or colorimetric using methylene blue. In the methylene blue method, paraaminodimethylaniline, ferric chloride and H_2S-S are mixed to form the methylene blue color. It is applied to concentrations covering the range 0.02 to 20 mg/1.

The titrimetric method is listed in Standard Methods, the EPA methods manual, and the USGS report. It may be applied to fresh, waste, and saline waters which have H_2S-S con-

centration above 1 mg/1. In this method, volatile sulfides are stripped from an acidified water sample by an inert gas (N_2, CO_2). The gas containing H_2S-S is bubbled through a solution containing dissolved Zn, to precipitate ZnS. Excess iodine and acid are added to the Zn solution to release H_2S-S, which reacts with iodine. The unreacted iodine is determined by titration with thiosulfate and is related to the quantity of H_2S-S.

Interferences include SO_3-S, thiosulfate and hydrosulfite. Care must be taken to exclude oxygen which will oxidize H_2S-S. The sample should be analyzed immediately, or it must be preserved with zinc acetate to prevent loss of H_2S-S.

Ion selective electrodes are available for sulfide monitoring.

SUMMARY AND RECOMMENDATIONS

Methods for monitoring nitrogen, phosphorus, and sulfur are given. Care must be taken in eliminating interfering substances and in the proper adjustment of parameters of the analytic procedure.

The Laboratory and field automated instruments should be investigated for use as continuous monitors and for reducing the time required for routine analyses.

E, ACKNOWLEDGMENT

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G. NPS-in-Water Instrument Notes

TABLE OF
ULTRAVIOLET AND VISIBLE ABSORPTION INSTRUMENTATION

Instrument	Wavelength Range (nm)	Wavelength Accuracy (nm)	Wavelength Resolution (nm)	Cost	Remarks
American					
DW-2™	200-825	±0.2	< 0.3	$19,900.	Wavelength scanning
Baird Atomic					
FM-200		10		$ 845.	
FP-100	220-770	2	2	$ 4,475.	Fluorometer Automatic or manual scannning
SF-100	220-700	2	2	$ 5,975.	Spectrofluorometer 2-speed wavelength scanning
Bausch & Lomb					
Spectronic® 20	340-950	2.5	20.0	$ 525.	Regulated model, $595.
Spectronic® 70	325-925	1.0	8.0	$ 795.	
Spectronic® 88	"	"	"	$ 1,195.	Concentration
Spectronic® 100	"	"	"	$ 2,195.	Digital readout, concentration
Spectronic® 200	190-800	±0.5	0.25	$ 4,895.	Wavelength scanning
Spectronic® 210	190-900	"	"	$ 6,000.	Digital, wavelength scanning, concentration
Spectronic® 700	200-950	1.0	2.0	$ 2,600.	Concentration
Spectronic® 710	200-1000	"	"	$ 3,000.	Digital, concentration

(Continued)

TABLE OF
ULTRAVIOLET AND VISIBLE ABSORPTION INSTRUMENTATION
(continued)

Instrument	Wavelength Range (nm)	Wavelength Accuracy (nm)	Wavelength Resolution (nm)	Cost	Remarks
Beckman					
24	340-700	±0.5	4.0	$ 2,730.	Wavelength scanning
25	190-700	"	0.2	$ 4,350.	Wavelength scanning
ACTA CII	190-800	±0.1	"	$ 6,680.	
ACTA CIII	"	"	"	$ 9,710.	
ACTA M-IV	190-3000	±0.5 (UV-Vis) ±2.5 (NIR)	0.02 (UV-Vis) 1.2 (NIR)	$14,445.	
ACTA M-VI	"	±0.1	< 0.05	$13,910.	
ACTA M-VII	190-800 800-3000	±0.1 ±0.5	< 0.05 < 0.30	$24,610.	
Model B	325-1000	±5.0	< 5.0	$ 2,140.	
Model DB-GT	190-700	±0.5	< 0.2	$ 3,890.	
Model DU-2	190-1000	"	< 0.3 (UV) < 0.1 (Vis)	$ 5,210.	
Brinkman					
1101-M	313-772			$ 3,010.	Fluorometer
GCA/McPherson					
EU-701-D	185-750 185-1000 (optional)	±0.1	0.1	$ 4,255.	
EU-707	"	"	"	$ 5,800.	
EU-721-D	"	"	"	$ 5,075.	

(Continued)

TABLE OF
ULTRAVIOLET AND VISIBLE ABSORPTION INSTRUMENTATION
(continued)

Instrument	Wavelength Range (nm)	Wavelength Accuracy (nm)	Wavelength Resolution (nm)	Cost	Remarks
Gilford 240	185-800			$ 5,366.	
Hitachi 101	220-900	< 2.5		$ 2,030.	
102	"	"		$ 2,700.	
181-7000		< 0.5		$ 2,750.	Model 181-7100, Tungsten only $2,350.
191	195-900			$ 3,350.	
Micromedic MS 2	200-700	±1.0	0.0003A	$ 4,400.	
Perkin-Elmer Junior Series	325-825	±1.0	20	$430 to $827	
54	330-835	"	±1	$ 1,654.	
Perkin-Elmer 55	325-800 200 (optional)	±1.0	2	$ 2,811.	
124	190-800			$ 4,382	Model 124D - $ 4,272.
156	190-900				
295	400-700	±1.0 @ 610 nm		$ 381.	
323	185-2500	±0.4 (UV)	0.2 (UV)	$15,200.	
356	185-850 185-1200 (optional)	±0.5	"	$17,000.	

*(Continued)

TABLE OF
ULTRAVIOLET AND VISIBLE ABSORPTION INSTRUMENTATION
(continued)

Instrument	Wavelength Range (nm)	Wavelength Accuracy (nm)	Wavelength Resolution (nm)	Cost	Remarks
402	190-850	±0.5 @ 200 nm ±1.0 @ 500 nm ±2.0 @ 750 nm	0.2 @ 210 nm 0.4 @ 390 nm 1.5 @ 600 nm	$ 8,480.	
Pye-Unicam SP 1700	190-700 850 (optional)	±0.5	0.1	$ 6,100.	Digital readout
SP 1800	"	"	"	$ 5,300.	Analog readout
Tektronix RSS	250-1100	±10 (150 1/mm) ±3 (1200 1/mm)	4 (150 1/mm) 0.4 (1200 1/mm)	$11,000.	Silicon vidicon detector
Turner 110	254-600	Blocking filters	Blocking filters	$ 1,195.	Filter photometer, manual
111	"	"	"	$ 1,735.	Filter photometer, automatic
330	335-710	±2.0	9.0	$ 595.	Spectrophotometer
350	"	"	"	$ 735.	"
430	300-700	"	15 (Excitation) 15 and 60 (Emission)	$ 3,990.	Spectrophotometer
510	Interference filters			$ 3,950.	Flame photometer
Varian Cary 17	186-2650	±0.4	0.1 (UV-Vis) 0.3 (IR)	$26,950.	Prism and grating

(Continued)

TABLE OF
ULTRAVIOLET AND VISIBLE ABSORPTION INSTRUMENTATION
(continued)

Instrument	Wavelength Range (nm)	Wavelength Accuracy (nm)	Wavelength Resolution (nm)	Cost	Remarks
Cary 118A	185-800		0.03 @ 200 nm 0.1 @ 350 nm	$10,900.	Manual
Cary 118B	"		"	$14,250.	Ratio recording
Cary 118C	185-800		0.02 @ 200 nm 0.1 @ 350 nm	$15,850.	Ratio recording scanning
635 M	190-900	>±0.5	0.2	$ 3,900.	
635 D	"	"	"	$ 4,950.	
Carl Zeiss PM2 D	200-1,000	1	10	$ 2,485.	
PMQ 3	185-2,500	< 0.05 @ 200 nm	0.03 (UV) 1.0 @ 600 nm	$ 6,800.70	

CONTENTS

FOR

DISSOLVED OXYGEN

INTRODUCTION

"The water environment can generally be characterized as a dilute aqueous solution, containing a large variety of inorganic and organic chemical species, dissolved and in suspension, and including a variety of plant and animal life" (Ref. 1).

Although water contains a number of dissolved gases, oxygen ranks first in importance, since it is essential for the survival of fish and all aerobic organisms. It is therefore the gas most commonly measured in aquatic environments.

Most water pollutants fall into two general categories: those that are biologically degradable, thereby consuming oxygen, and those substances that persist in the aqueous environment. The best known degradable pollutant is domestic sewage which includes both inorganic and organic degradable substances; but the combined organic wastes produced by industrial sources such as the food, pulp and paper, and chemical industries comprise by far the greater source of this pollution. Organic wastes may further be subdivided into three categories:

a) those that are used as an energy source by heterotrophic bacteria* (and therefore biodegradable);

b) those inert organic substances which are neither utilizable by the resident biota, nor toxic to them, for example, many many high molecular weight synthetic organic polymers;

c) toxic organics, such as the pesticides.

Some industrial plants produce huge quantities of organic pollutants. For example, a single pulp mill discharges wastes equivalent to the sewage load of a large city (Ref. 2).

When an effluent bearing a substantial load of organic wastes is expelled into an otherwise clean stream, a process known as aerobic degradation begins immediately. Stream biota -- primarily bacteria -- utilize dissolved oxygen and feed on the wastes, decomposing them to their inorganic end products (nitrates, carbonates, phosphates, sulfates), thereby furnishing the basic plant nutrients. This process, somewhat deceptively called "stream self-purification", consumes some of the dissolved oxygen (DO) present in the water. The depletion of oxygen is, however, offset by reoxygenation both via the air-water interface (a relatively slow process in still waters), and as a consequence of photosynthetic processes occurring in the aquasystem. If the waste load is not too heavy, the concentration of DO ([DO]) will first drop, and then rise again. This process is described mathematically by a characteristically shaped function known as the *oxygen sag* (Figure 1). If the concentration of organic wastes in the stream becomes high enough, however, the supply of DO may be exhausted. Degradation will then proceed via anaerobic processes through the action of bacteria capable of utilizing organically- and inorganically-bound oxygen. The gaseous byproducts of these anaerobic processes (CH_4, NH_3, H_2S) generally result in the emission of foul odors and the production of offensively brackish waters.

Plant nutrients resulting from the bacterial degradation of organic wastes may cause algae blooms. While these are not harmful in moderate abundance, even contributing to the food supply of the resident fish, they may pose problems for the resident biota if allowed to proliferate unchecked, because of ultimate DO depletion by algae decomposition. Streams in which the DO is consistently less than four to five ppm will not support some of the higher forms of fish life, such as the cold water varieties. Reduced levels of oxygen, even when not themselves lethal, increase the sensitivity of the fish to toxins. These problems are particularly important in comparatively quiet waters, such as lakes and estuaries, where the rates of reoxygenation are likely to be low. Here eutrophication from the build-up of inorganic nutrients can be a troublesome end result.

Wastewater in which the organic wastes have not been stabilized has a higher chlorine demand†, thereby making it more costly to

*Bacteria may also be viewed as degradable pollutants, since the enteric infectious variety does not survive long under in vitro (stream) conditions, and chlorination of the water supply effectively destroys them. Thus the traditional scourges of polluted water -- typhoid, paratyphoid, dysentery, and gastroenteritis -- are virtually unknown in American cities. On the other hand, viruses are less amenable to treatment. It is believed that viruses in our water supplies are associated with the spread of some diseases, but at less than the epidemic levels once attributable to bacteria.

†i.e., requires more chlorine to attain the free chlorine residual necessary to kill bacteria.

treat. An increase in temperature will accelerate a stream's degradation rate and reduce the DO content. A simple rule of thumb in chemical reaction kinetics is that a given rate of reaction will double for a 10°C rise in temperature. Heat therefore exacerbates the pollution problem. For this reason, the increasing number of stream electric power plants with their concomitant high heat output poses a serious problem.

1. Factors Influencing the Solubility of O_2

The solubility of oxygen in water is primarily a function of three variables: pressure (p), temperature (T), and salt content** or ionic strength (μ) of the solution. In natural waters the DO content is also dependent on the quantity of biodegradable organic material present, the diurnal cycle, and physical characteristics of the stream bed (e.g., gradient, rapids, pools, etc.)

1.1 Pressure Effects

Atmospheric oxygen dissolves according to Henry's Law up to four atmospheres pressure:

$$(1)\quad \frac{P_{O_2}}{P_{total}} = P = K\,[O_2], \text{ where}$$

P is the partial pressure of oxygen in the atmosphere, and K is the Henry's Law constant:

$$K = 5.98 \times 10^5 \text{ mm Hg/M/l}$$

At its partial pressure of 154 mm under STP conditions, oxygen is only sparingly soluble in pure water (2.56×10^{-4} moles/liter). However, the effect of hydrostatic pressure on the solubility of oxygen with depth has been calculated by Klotz using a thermodynamic treatment which assumes successive equilibria between the air dissolved in any given layer

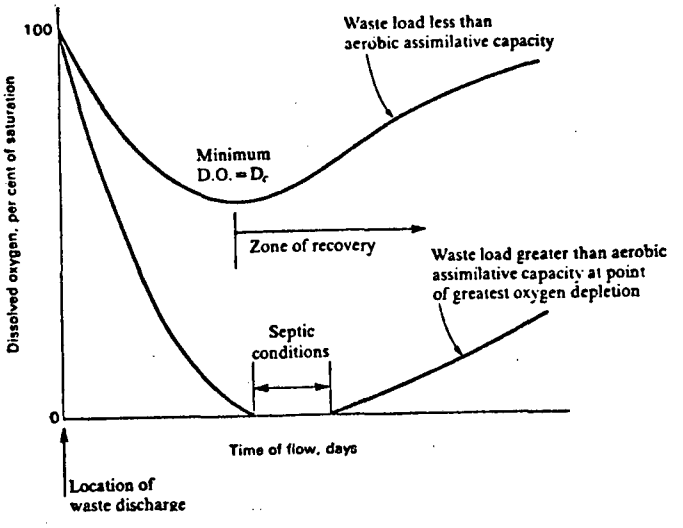


FIGURE 1+. Schematic primary oxygen sag curve for two different organic waste discharges, assuming waste enters a stream that is fully saturated with oxygen (from Ref. 3, p. 21).

+The oxygen sag equation is expressed as the difference between two kinetic processes:

$$\frac{dD}{dt} = K_1L - K_2D,$$

where L represents the oxygen demand at time t, and D the oxygen deficiency: K_1 and K_2 are proportionality constants for the deoxygenation and aeration processes, respectively (Ref. 4).

**The term salinity is generally employed in dealing with natural waters.

of water, dh, and that dissolved in the next adjacent layer (Ref. 5). Although the solubility of a gas may change considerably with depth, its partial molal free energy does not vary from one depth to another, being an intensive characteristic of the substance. Thus, the change in the solubility of oxygen with depth may be expressed as the following equation:

$$(2) \quad RT d\ln[O_2] = Mg(1 - \bar{v}\,\ell)dh, \text{ where}$$

h is the depth of the sample measured in a positive direction;
R is the gas constant (8.37×10^7 ergs/M/degree),
T is expressed in °K;
M is the molecular weight of the solute;
$\bar{v}$ is the partial specific volume of the solute, expressed in cc/gm;
ℓ represents the density of the solution in gm/cc, and
g is the gravitational constant (980 cm/sec^2).

Integration of equation (2) over the depth h leads to the following expression:

$$(3) \quad RT\ln\frac{[O_2]_y}{[O_2]_o} = Mg(1 - \bar{v}\,\ell)h.$$

Unlike nitrogen, for which Klotz' calculation using equation (3) showed a decrease in solubility with increasing depth, the solubility of atmospheric oxygen in water appears to be relatively independent of the depth, h (Ref. 5).

1.2 Temperature Effects

As with most other gases, oxygen has a negative temperature coefficient -- e.g., decreases in solubility with increasing temperature:

$$(4) \quad [O_2] = \alpha + \beta_1 T + \beta_2 T^2 + \beta_3 T^3,$$

where T is the temperature in °C and α and β's (1, 2 and 3) are constants.† For purposes of interpolating DO saturation values at working temperatures, an approximate form of the Clausius-Clapeyron equation may be applied:

$$(5) \quad \frac{d \ln [O_2]}{d (1/T)} = \frac{\Delta H}{R}, \text{ where}$$

ΔH is the heat of solution, in calories/mole. and R the gas constant (1.99 cal/M/degree). Since the temperature dependence of ΔH is slight, the application of this relationship over a limited temperature range is approximately linear. Integration of (5) yields:

$$(6) \quad \frac{[O_2]_2}{[O_2]_1} = \frac{\Delta H}{2.3R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

1.3 Electrolyte Effects

The addition of electrolytes to water generally decreases oxygen solubility, the amount of this decrease depending on the ionic strength of the solution. This phenomenon is known as the 'salting out effect' (Figure 2). The phenomenon of salting out is

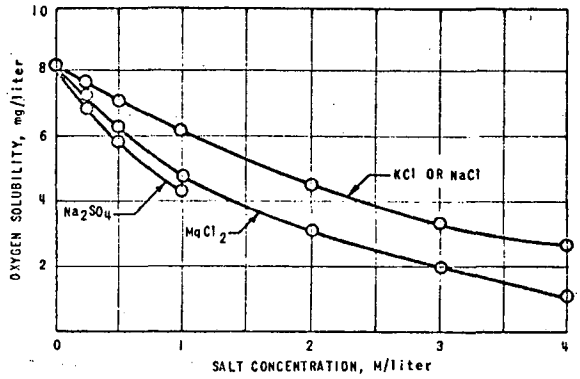


FIGURE 2. Oxygen solubility at various salt concentrations (from Reference 6, p. 6).

best understood in terms of activity coefficients*, and the effective concentration of the dissolved gas. The activity of oxygen in solution may be defined as follows:

$$(7) \quad a = \gamma C, \text{ where}$$

a = activity in moles/liter;
γ is the activity coefficient, and
C is the concentration in moles/liter.

The activity coefficient γ depends on the ionic strength of the solution:

$$(8) \quad \ln \gamma = K_s I, \text{ where}$$

$K_s I$ is the 'salting out' coefficient, and
I the ionic strength of the solution.

†α = 14.161; β_1 = -0.3943; β_2 = 0.007714; β_3 = 0.0000646

*For a discussion of the thermodynamic significance of activity coefficients, see appendix E, Reference 6.

Also,

(9) $I = \Sigma C_i Z_i^2$, where

C_i is the concentration of the ith salt component, and
Z_i is the ionic charge of the ith component.

For distilled water, I = 0 and ln γ is consequently 0 and γ = 1 (e.g., the activity is equal to the concentration).

A convenient equation for expressing the solubility of oxygen as a function of the concentration of a single salt is given:

(10) $\ln S = \ln S_o - K_s C_s$, where

S is the solubility of oxygen in the saline solution,
S_o its solubility in distilled water,
C_s is the concentration of the salt, and
K_s is a solubility constant.

A semilog plot of equation (10) is linear with a negative slope, $-K_s$. For solutions containing more than one salt, equation (8) must be used.

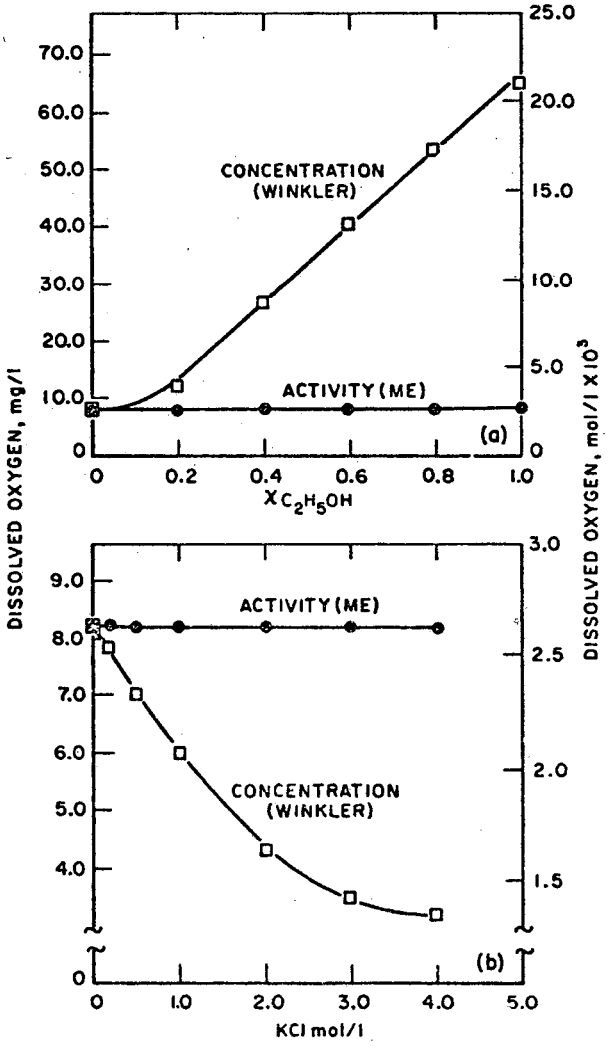


FIGURE 3. Effects of (a) salting-in and (b) salting-out. P^0_2 = 0.21 atmosphere, temperature = 25 ±0.5°C (from Reference 11, p. 314).

1.4 Effects of BOD* and Diurnal Variation

During daylight hours, photosynthesis produces O_2, and if its production exceeds the respiration rate, the concentration of DO [DO] will increase during the day. The entire biotic community requires O_2 at night, so that the minimum [DO] is reached just before dawn. The amount of diurnal variation is greater in organically enriched or polluted waters, where daytime supersaturation may be offset by oxygen concentrations approaching zero in the hours just before sunrise.

1.5 Other Effects

Water movement can have a significant effect on [DO] by accelerating the rate of loss at supersaturation and the rate of reaeration at low oxygen tension. Diurnal variation of DO is usually greatest in quiescent lakes and ponds, and least noticeable in rapidly flowing streams.

2. Analysis of Water for DO

Because of the constant demand for O_2 by the biotic community, the minimum $[O_2]$ and its duration are more important than measures of the average or maximum $[O_2]$. Measurements of the diurnal change of DO are useful in evaluating the overall metabolism within a body of water, encompassing both photosynthesis and respiration. Periodic measurement of this parameter often yields more information as to the condition of the body of water in question than the measurement of a large number of other environmental variables (Ref. 7).

The selection of an analytical procedure will largely depend on the objectives of the DO analysis. These may range all the way from (1) investigation of compliance with official standards, (2) evaluation of the environmental impact of a proposed water resource project, (3) assessment of the water treatment required in order to maintain a water quality level consistent with ongoing and/or proposed uses, to (4) simply providing some water quality control.

Differing objectives lead to the requirement of methods and instrumentation at varying levels of sophistication. Each analysis presents unique problems, not only in terms of the objectives of the analysis, but because water sample characteristics can vary widely, even within a given category of application. Thus, in addition to considering the needs for such characteristics as speed, accuracy, and continuity or frequency, the analyst must consider the unique character and limitations imposed by the specific water sample.

Methods used in the analysis of water samples for DO may be divided roughly into two categories:

a) Those traditional wet-chemical methods based on the Winkler test and more recent instrumental modifications of these (sections 2.2 - 2.4, inclusive);

b) Other methods based on the chemical and physical properties of oxygen and employing a wide variety of often quite sophisticated techniques and instrumentation (sections 2.5 ff.)

It is from category b) above that DO monitoring systems derive. These systems may be characterized as:

1) in situ† sensors or electrochemical transducers which perform measurments without altering the test solution, and

2) systems such as the Technicon Autoanalyzer which perform automated wet-chemical analysis.

Since in situ DO determination is so significant for ascertaining water quality, it is clear that emphasis should be placed on those methods which lend themselves to this kind of measurement. Such methods are invariably based on electrochemical reactions, with membrane electrode (ME) systems emerging as the most suitable vehicles for in situ DO analysis of natural and waste waters.

2.1 Sampling Methods for DO Analysis

Because of the diurnal variation in DO in natural systems, continuous monitoring of this parameter is desirable. If, however, continuous monitoring is not feasible, it is recommended that the [DO] should at the very least be measured twice daily -- at mid-afternoon and just before dawn.

*BOD = Biochemical Oxygen Demand

†in position -- generally (though not necessarily) in stream.

Samples for DO determination are generally collected in narrow-necked glass-stoppered (G.S.) flasks of 200 to 300 ml capacity, with flared rims, called BOD bottles. Great care must be exercised in the collection of samples for DO analysis to avoid agitation or post-sampling contact with air, in order to minimize the risk of oxygen exchange. The method of sampling is influenced by the source of the sample, the depth from which it is to be taken, and even the method of analysis to be used. King (Ref. 7) suggests the use of special samplers such as the Kemmerer water sampler or the Nansen water bottle for the collection of all water samples to be used in the determination of DO, in order to avoid oxygen exchange between the sample and the atmosphere. "Standard Methods" (Ref. 8) recommends the Kemmerer-type (Figure 4) sampler for all samples collected from depths of more than five feet. In the latter instance the sample is bled from the bottom of the sampler through a tube reaching to the bottom of a 250-300 ml BOD bottle. The bottle is filled to overflowing, then allowed to overflow for about 10 seconds, great care being exercised to avoid turbulence and bubble formation during the bottle-filling operation. Water temperature is recorded with the desired precision.

Depth sampling requires special precautions to eliminate effects of pressure and temperature changes. Techniques of sampling waters under pressure, as well as surface waters, are described in detail in references 9 and 10.

Selection of a sampling site is determined primarily by two factors: (a) the type of investigation, and (b) the degree of mixing in the body of water to be analyzed. Rainwater and Thatcher (Ref. 10) recommend the use of a 3-dimensional grid intersection method of sampling, with samples taken at various depths to provide a representative sampling. If only a single sample is to be taken, it should come from the center of the water mass.

Sampling frequency is determined by the variability of the source sampled. No important change in quality of the water should go unnoticed in an adequately planned sampling procedure. The U.S. Geological Survey follows the arbitrary rule for sampling once per day.

Sampling equipment is made from a variety of materials. Containers of hard rubber, polyethylene, and a few other plastics have been found satisfactory. No appreciable difference in the following characteristics was detected for pyrex vs polyethylene containers: silica content, Na^+, alkalinity, Cl^-, boron, specific conductance or pH, when water samples were stored for about five months.

Soda lime glass sampling bottles are, of course, not recommended when the samples are to be stored, because of the risk of sample contamination through leaching of ions from the glass and/or ion exchange between the glass and the water sample.

2.11 Post Sampling Preservation

The determination of DO in samples with an appreciable oxygen demand (OD) or iodine demand (ID) should be immediate -- preferably, on site. Samples which have no ID may be stored safely for several hours, provided that they are pretreated with the reagents used in the Winkler method of DO analysis, namely $MnSO_4$ solution followed by alkali-iodide solution and sulfuric acid. The pre-treated sample may then be safely stored in the dark before titration. For those samples which do have an ID and cannot be analyzed immediately, the addition of concentrated H_2SO_4 (0.7 ml) and 1.0 ml of a solution containing two grams of sodium azide (NaN_3) per 100 ml of distilled water will preserve them for four to eight hours. This treatment arrests the biological activity, thereby stabilizing the DO content, if the bottle is stored at its collection temperature, or, alternately, if it is water-sealed and stored at 10°-20°C (Ref. 8).

2.12 Post-Sampling Separation and Concentration

As with other dissolved gases, the DO in natural and waste water samples may be separated by vacuum degasification or by one of several stripping techniques. Stripping entails gas-liquid extraction by means of an inert carrier gas which is bubbled through the solution, entraining the dissolved gas from the solution into the vapor phase. The efficiency of the transfer process depends on such factors as the degree of mixing of the solution and carrier gas, and the area of the gas liquid interface.

Gaseous exchange separation of O_2 may by carried out continuously or in a batch process. In one design, a continuous mixed stream of the sample and carrier gas (N_2 or H_2) is forced through a nozzle under 50 pounds pressure. In another, the gas is stripped from the solution by means of multiple spinning discs rotating at high speed. The stripped O_2 may then be examined by gas-chromatography. By the choice of appropriate detectors, it is usually possible to analyze for a mixture of gases, including oxygen, in an aqueous sample (Ref. 11).

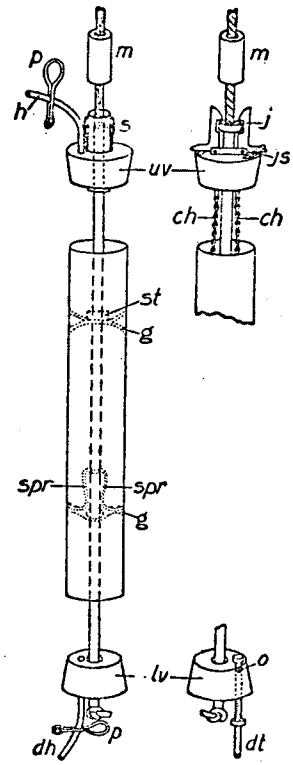


FIGURE 4. Modified Kemmerer sampler (from Ref. 8, p. 728).
Left: View of complete sampler with valves open.
Top right: another type of construction of upper valve and tripping device.
Bottom right: another type of construction of lower valve and drain tube.
Key: ch -- chain which anchors upper valve to upper interior guide;
dh -- rubber drain tube;
dt -- brass drain tube;
g -- interior guide fastened to inner surface of body of sampler;
h -- rubber tube;
j -- jaw of release;
js -- jaw spring;
lv -- lower valve;
m -- messenger;
o--- opening into interior of drain tube;
p -- pinchcock;
s -- upper release spring operating on horizontal pin, one end of which fits into groove on central rod;
spr -- spring fastened to lower internal guide and operating in groove on central rod to provide lower release;
st -- stop on central rod;
uv -- upper valve

2.2 Chemical Methods of DO Analysis

The most widely used analytical method for DO determination is that described by L.W. Winkler over 80 years ago (Ref. 12). It is based on the quantitative oxidation of manganous ion (MnII) by DO to the manganic state (MnIV) in alkaline solution. The Mn(IV) formed liberates iodine (I_2) quantitatively from potassium iodide under acid conditions. Titration of the liberated I_2 with a standardized thiosulfate solution in the presence of a starch indicator gives a measure of the DO present in the original sample. The following is a schematic representation of the reaction sequence of the Winkler test:

$$(11)\quad Mn(II) \xrightarrow{2OH^-} \underset{\text{(white ppt)}}{Mn(OH)_2} \rightarrow \underset{\text{(colloidal suspension)}}{MnO\cdot H_2O}$$

$$(11a)\quad MnO\cdot H_2O \xrightarrow[2H_2O]{O_2} Mn(OH)_4 + 2OH^-$$

$$Mn(OH)_4 \downarrow \text{ (brown)} \rightarrow Mn(IV)O_2\downarrow + 2H_2O$$

$$(11b)\quad Mn(IV) + 2I^- \xrightarrow{H_3O^+} Mn(II) + I_2$$

$$(11c)\quad 2S_2O_3^{=} + I_2 \xrightarrow[\text{indicator}]{\text{starch}} 2I^- + S_4O_6^{=}$$

Because of its reliability and sensitivity (±0.1 mg/l of DO) (Ref. 8), the Winkler test remains the basis for most of the current titrimetric methods.

2.21 Interferences in the Winkler Method

In applying the iodometric method to natural or waste waters, the analyst must be wary of other oxidants or reductants in the sample. The presence of some oxidizing agents other than O_2 will also liberate iodine from KI, resulting in positive interference. Reductants capable of reducing I_2 to I^- will lead to low DO values (negative interference). Surface active substances present in the water sample, such as detergents, may also interfere in the analysis by keeping the hydrated MnO_2 in suspension, hampering observation of the endpoint when a starch indicator is used. A number of modifications of the Winkler DO analysis have been developed to overcome these difficulties. The most commonly used of these are described briefly in Sections 2.22 to 2.25.

2.22 Azide Modification of the Winkler Method

This procedure was recommended by Alsterberg (Ref. 13) to eliminate interference from nitrites, commonly present in waste water samples. Nitrites are reduced by sodium azide in acid solution as shown:

$$(12)\quad N_3^- \xrightarrow{H^+} HN_3 \xrightarrow{NO_2^-,H^+} N_2 + N_2O + H_2O$$

2.23 Rideal and Stewart Modification of the Winkler Method (Ref. 14).

When both nitrates and organic matter are present in the DO sample, it is pretreated with an acid $KMNO_4$ solution which removes the following reductants:

$$(13)\quad 5NO_2^- + 2MNO_4^- + 6H^+ \rightarrow 5NO_3^- + 2Mn(II) + 3H_2O$$

$$(13a)\quad 5RCHO + MnO_4^- + H_3O^+ \rightarrow 5RCOOH + Mn(II) + 3H^+$$

$$(13b)\quad 5Fe(II) + MnO_4^- + 8H^+ \rightarrow 5Fe(III) + Mn(II) + 4H_2O$$

If more than 5 mg/l of ferric salts result after the permanganate treatment, ferric ion is removed as FeF_3. Excess permanganate is destroyed by potassium oxalate in acid solution. The Rideal-Stewart modification generally results in low accuracy and precision because of the manipulative complexity of the method.

2.24 Flocculation Modifications

Since suspended solids may result in positive interference in the Winkler test by the consumption of additional iodine, the solids are usually settled out first by means of flocculating agents. One method entails precipitation by the addition of alum and ammonium hydroxide (the Alum Flocculation Modification). Another is recommended for samples from biological treatment units, such as activated sludges. This precipitates the floc with a copper sulfate solution to which sulfamic acid, NH_2SO_2OH, is added to inhibit biological activity. The accuracy of this method is reportedly low (Ref. 6).

2.25 Other Modifications

The reader is referred to Chapter 3 of Reference 6, which lists approximately a dozen additional modifications of the basic Winkler approach, covering such exigencies as:

1. The hydrolysis of organic matter at high pH to create a false oxygen demand.

2. Analysis of "supersaturated" water samples.

3. A reversed reagent addition method.

4. A number of colorimetric variants.

2.26 Errors in the Winkler DO Method

The crucial step in analysis for DO by this method is determination of the quantitatively released free I_2 which may be carried out titrimetrically or colorimetrically. For the procedure recommended in the Standard Methods (Ref. 8), the reaction is represented by the oxidation of thiosulfate ion to tetrathionate ion and reduction of molecular I_2 to I^-:

(14) $I_2 + 2S_2O_3^= \rightarrow 2I^- + S_4O_6^=$

When the endpoint is determined visually by the blue color formed by starch and iodine, as little as 10^{-5}M molecular I_2 may be determined. However, there are two main sources of error in the direct titration of iodine: the first is due to (a) the low solubility of I_2 in aqueous solutions (1.33×10^{-3}M/1 @ 20°C), and (b) its high volatility. The second error is the susceptibility of iodide ion (I^-) to air oxidation. This latter reaction is strongly pH dependent, catalyzed by a number of ions (including Cu(II)) and may be photochemically induced as well.

The use of alternative instrumental methods of titration reduces the likelihood that these errors will occur.

2.3 Instrumental Variants of the Winkler Procedure.

Electrochemical endpoint detection in the Winkler titration procedure not only reduces the likelihood of the errors mentioned under section 2.26, but increases the precision, accuracy and sensitivity of the method.

2.31 Potentiometric Endpoint Detection

The endpoint of the iodometric titration in the Winkler DO procedure may be determined by means of a Pt wire electrode and a saturated calomel reference electrode. At the stoichiometric endpoint, the titration curve shows an inflection point (Figure 5).

2.32 "Dead Stop" Endpoint Detection

The "dead stop" endpoint is characterized by the cessation of current flow in the cell (see diagram, Figure 6a). The method utilizes a small potential difference between two identical smooth platinum electrodes (15 to 400 mV) placed in the solution (Figure 6b). In the course of the titration, faradaic current is measured at a fixed potential difference. While I_2 remains in solution as I_3^-, the chief

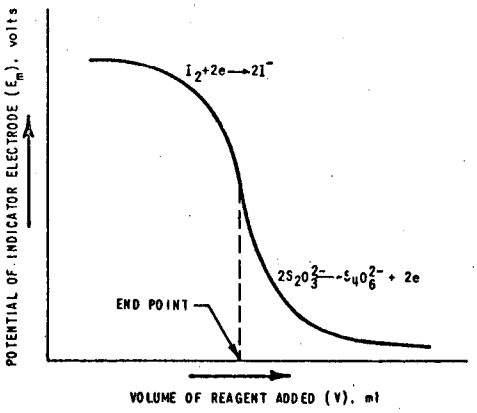


FIGURE 5. Potentiometric titration of iodine (from Ref. 6, p. 15).

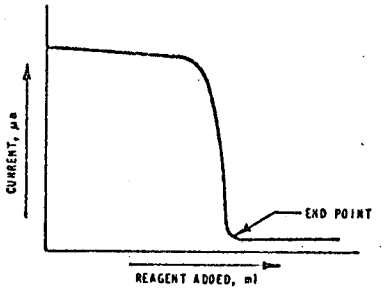


FIGURE 6a. Dead stop end point titration curve (from Ref. 21, p. 265).

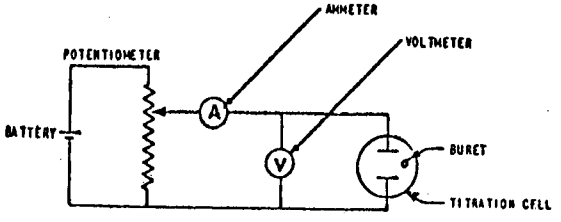


FIGURE 6b. Dead-stop end point circuit (from Ref. 21, p. 264).

electrode reactions are:

1) reduction of I_2 to I^- at the cathode, and

2) the oxidation of I^- at the anode.

At the endpoint, I_2 has been removed, precluding the I_2 to I^- reaction; therefore no current can flow. With the use of sensitive current detectors, the method is good to 1 part/10 billion (±0.01 ugm/100 ml).

2.33 Coulometric Titration

In a coulometric titration the reagent is electrolytically generated at the surface of the working electrode (anode) immersed in the solution (Figure 7). The amount of iodine generated may be calculated from Faraday's Law which states that, for the passage of one Faraday (96,500 coulombs) of current through the solution, one gram equivalent of I_2 will be produced:

(15) $W = \frac{qM}{nF}$, where

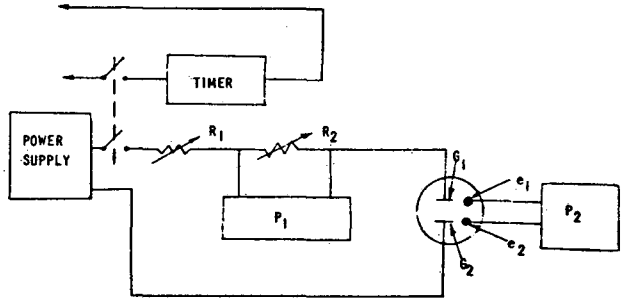
W is the weight of Iodine in grams,
M is the molecular weight of I_2 (253.8 g/mole)
q is the amount of current passed through the solution in coulombs
n is the number of equivalents per mole (or the number of electrons involved in the half-cell reaction).

In order to simplify the instrumentation and produce values directly proportional to time, most coulometric titrations are carried out at constant current. Under these conditions,

(16) $q = \int_0^t idt = it$, where

t is expressed in seconds, and i is the constant current in amperes x 10^{-6}. Figure 7 illustrates a typical constant current coulometer. The procedure for the coulometric determination of DO in a water sample involves the stepwise addition of $MnSO_4$, KOH + KI, and H_2SO_4, and, finally, an excess of $Na_2S_2O_3$. The iodine formed in the electrolytic reaction reacts with the excess thiosulfate present. Current is held constant by applying a high voltage through a large dropping resistor. The equivalence point may be conveniently detected by means of the dead-stop endpoint mentioned previously (section 2.32). The concentration of DO is then calculated from equations (15) and (16) above. Since i is kept constant, q may be determined by a substitution of the time t in the equation.

Coulometric measurement in the Winkler procedure has the advantage of great accuracy, and determinations may be made to within 0.02 µgm/l. Since the titrant is generated in situ, error due to contact with air is eliminated.



R_1, R_2 = Resistors

P_1 = Potentiometer for current measurement

P_2 = Potentiometer for end point detection

e_1, e_2 = Monitoring electrodes

G_1 = Generating electrode

G_2 = Auxiliary electrode

FIGURE 7. Constant-current coulometric circuit (from Ref. 21, p. 266).

2.34 Analysis for DO Using a Micro Winkler Adaptation

The Macro Winkler method described in in Standard Methods has been adapted to small volume samples, and for use in biological systems, where repeated DO measurements, each involving the removal of a small volume of sample are required. This modified micro method uses one to two ml of water and has an accuracy of 1 to 2%. The apparatus consists of a syringe type pipet (Figure 8), in which the sample and reagents are mixed. The liberated I_2 is then expelled for titration. For details of this procedure, see Appendix B, Reference 6.

2.4 Colorimetric Methods of DO Determination

The iodine liberated in the Winkler analysis may be estimated colorimetrically in a variety of ways: (a) The blue color of the starch-iodine complex can be measured photometrically (Ref. 15); (b) the liberated iodine may be estimated spectrophotometrically at 450 mμ (Ref. 16); (c) alternately, the free iodine may be extracted from the aqueous solution into CCl_4 and determined photometrically using disc comparators (Ref. 16).

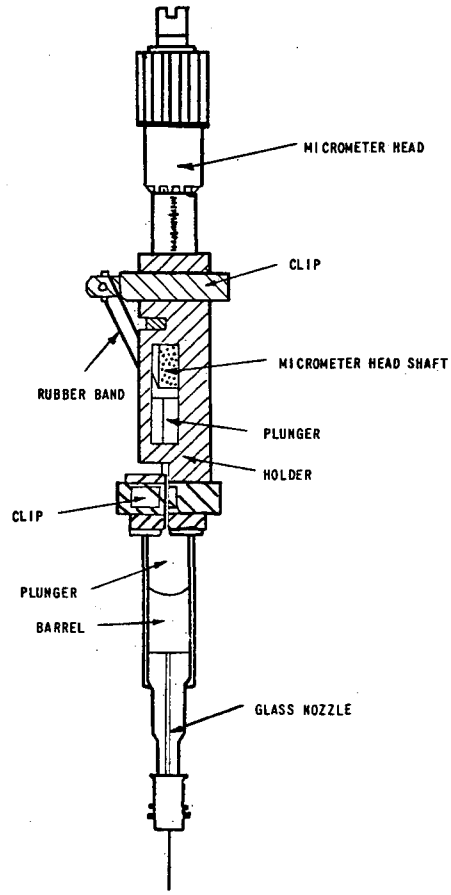


FIGURE 8. Micro-Winkler Test Syringe (from Ref. 6, p. 21).

2.41 Direct Colorimetric Methods of DO Determination

These methods generally depend on the the reaction of DO with a chromogen to give a color change. Oxidation-reduction indicators such as methylene blue, safranin T, and indigo carmine are employed (Ref. 6). The latter is the basis of an accurate method for DO analysis in boiler waters (Ref. 17).

2.42 Interferences with Colorimetric Methods of DO Analysis

Reportedly, nickel, copper (Cu(II)), and zinc do not interfere when present up to 1000 ppb, ferric ion up to 3000 ppb, and sulfite, 12 ppb. Ferrous ions do interfere, but may be removed on an ion exchange column (Ref. 18), although the oxidizing and/or reducing agents present in waste water precludes the use of a direct colorimetric aprroach. However, in comparatively clean surface waters, direct colorimetric methods can be useful.

2.43 Disadvantages of DO Direct Colorimetry

(1) When reduced indigo carmine is the indicator, 'anaerobic' sampling methods must be used to avoid exposing the sample to atmospheric oxygen. This poses difficulties in the field.

(2) There are no methods extant for in situ DO determination using direct colorimetry.

(3) Direct DO colorimetry does not lend itself to a continuous monitoring approach, and finally,

(4) Colorimetric methods are destructive.

2.5 Ion-Exchange Titrimetric DO Analysis

Inczedy (Ref. 19) describes an ingenious cation exchange resin method applicable to pure water only. The resin is first converted to the ferrous form with 0.1 N ferrous ammonium sulfate. The sample is then put through the column where it oxidizes an equivalent amount of Fe(II) to Fe(III). The column is treated with 6N H_2SO_4 eluting both ions. Titration of the remaining unoxidized Fe(II) with permanganate yields the value for DO by difference, since DO is equal to the equivalents of Fe(III) formed in the column by oxidation.

The following substances interfere with the test: (1) oxidants, (2) complexing agents, and (3) solids. The method is therefore only applicable in the analysis of water of high purity.

2.6 DO Analysis by the Gas Exchange (GE) Method

The determination of DO in the gas phase has the advantage of circumventing interferences often encountered in the original solution. A typical oxygen analyzer consists of (a) a gas exchange unit, and (b) an oxygen detector (Figure 9).

2.61 The Gas Exchanger

The gas-exchange unit usually consists of an aspirator followed by a separator. The water sample, along with a carrier gas inert to oxggen under conditions of the analysis (N_2 or H_2) is forced through a nozzle at about 50 lbs. pressure. Under these conditions intimate mixing of the gas and water droplets occurs and the DO is transferred to the gas phase. The efficiency of gas exchange will depend on the efficiency of the GE unit itself. Since equilibrium in the gas partition may not be obtained, the flow rates of the components must be constant in order to stabilize the rate of gas exchange. On leaving the GE unit, the carrier gas is passed through the detector and is either vented to the atmosphere or recirculated (Ref. 20). If the carrier gas is recirculated, equilibrium is eventually attained between the gaseous and aqueous phases, at which time the oxygen in the solution may be assumed to have been completely replaced by the carrier gas. (Ref. 22, 23).

2.62 The Oxygen Detector

The entrained oxygen may be detected by one of three methods: (a) by means of an oxygen-sensitive galvanic cell; (b) by a paramagnetic oxygen detector, or (c) by virtue of its thermal conductivity characteristics.

Method (a): Oxygen-sensitive galvanic cells consist of a base metal anode such as Zn, Pb, or Cd; the cathode may be a noble metal such as Au, Ag, or Ni; alternatively, a carbon cathode may be used. A highly conducting electrolyte in solution such as KOH is used. The carrier gas with entrained oxygen is bubbled through the solution by means of diffusers. The oxygen goes into solution and is depolarized at the cathode, generating an equivalent amount of current (Ref. 25). Measurement is generally with a micro-ammeter previously calibrated in terms of oxygen.

For an O_2-sensitive galvanic cell consisting of a Zn-C couple and KOH solution (1 M), the following half-cell reactions may be written:

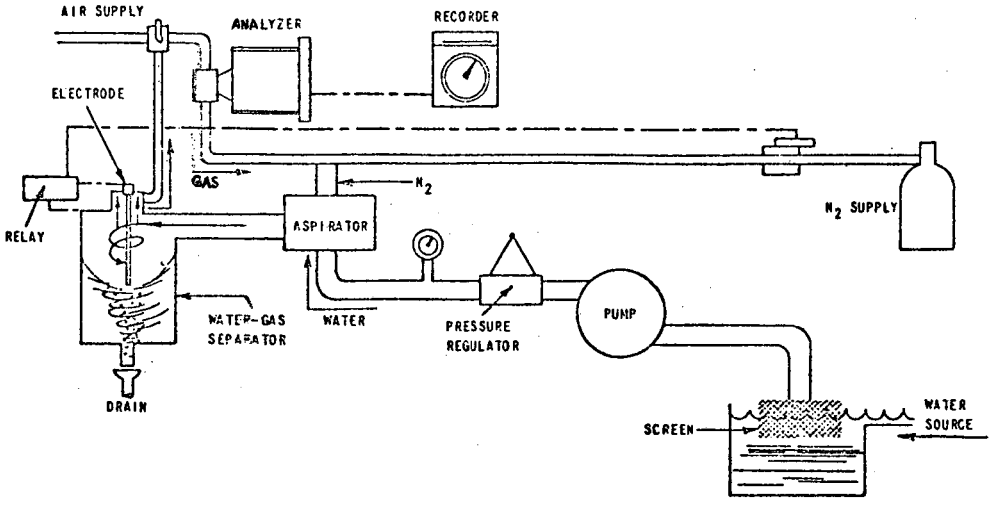


FIGURE 9. Gas-exchange analyzer (from Ref. 6, p. 25)

Anode: (17) $Zn \rightarrow Zn(II) + 2e$

(18) $Zn(II) + 4OH^- \rightarrow ZnO_2^{2-} + 2H_2O$

Cathode: (19) $1/2\ O_2 + H_2O + 2e \rightarrow 2OH^-$

Overall Cell Reaction:

(20) $Zn + 2OH^- + 1/2\ O_2 \rightarrow ZnO_2^{2-} + H_2O$

Method (b): Magnetic Oxygen Detector. Unlike most gases oxygen is strongly paramagnetic, making possible a detector based on the measurement of the magnetic susceptibility of the entrained gas mixture. In practice, the carrier gas leaves the exchange unit, passes through the oxygen detector consisting of a cell fitted with a permanent magnet and a spiral wire which is heated during operation (Figure 10). The heated oxygen gas loses its magnetic properties and is replaced inthe field by the cooler paramagnetic oxygen, thereby setting up a circulation of the O_2 gas in the vicinity of the heated wire. The change in resistance brought about by the flow of the cooler O_2 is proportional to the total amount of O_2 present in the carrier gas stream. This in turn depends on the DO present in the original test solution.

A second method for the magnetic determination of O_2 utilizes a small glass dumbbell suspended from a taut quartz fiber in a non-uniform magnetic field (Figure 11). In the absence of O_2, the force of the magnetic field and the torque exerted by the dumbbell

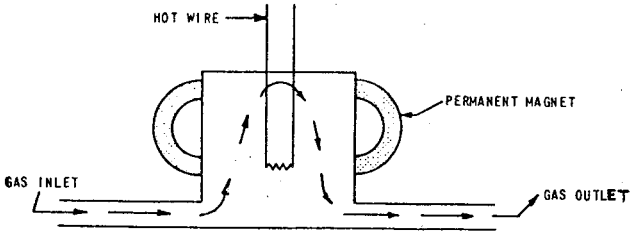


FIGURE 10. Paramagnetic analyzer cell (from Ref. 21, p. 270).

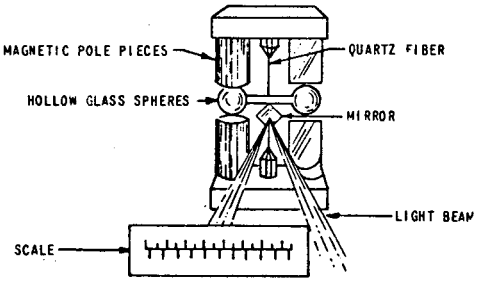


FIGURE 11. Oxygen-sensitive paramagnetic detector (from Ref. 21, p. 271).

remains stationary. On introduction of a carrier gas containing oxygen, the change in the magnetic field results in an imbalance of forces and the dumbbell rotates. The magnitude of the rotation is proportional to the change occurring in the magnetic field, the latter depending on the $[O_2]$. Thus the amount of O_2 in the carrier gas, and consequently the DO present in the original sample is determined.

Method (c): Thermal Conductivity Detector. A thermal conductivity type O_2 detector utilizes a wire which has a high temperature coefficient of resistance. The wire is stretched along the axis of a cylinder made of glass or metal, after which it is connected to a wheatstone bridge type circuit (Figure 12). Current passing across the bridge heats the wire, the equilibrium temperature of which depends on the thermal conductivity of the surrounding gas. Any change in thermal conductivity of the carrier gas produced by exchanged oxygen present will unbalance the bridge. This imbalance may then be measured either by a galvanometer or a potentiometer calibrated against standard DO solutions.

2.63 Merits and Disadvantages of GE Analyzers

Merits:

(1) Interferences are eliminated - in particular, those of salts and organics commonly present in waste waters.

(2) GE analyzers may be adapted for continuous monitoring of DO.

(3) The units described may be used in the field, whether on the bank of a stream or alongside an activated sludge unit.

Disadvantages:

(1) GE analyzers cannot be used for in stream determination of DO.

(2) They lack portability and are not sufficiently rugged to permit mounting the units in a boat. This precludes their use for river surveys.

(3) GE oxygen analyzers are not suited for discrete laboratory sample analysis.

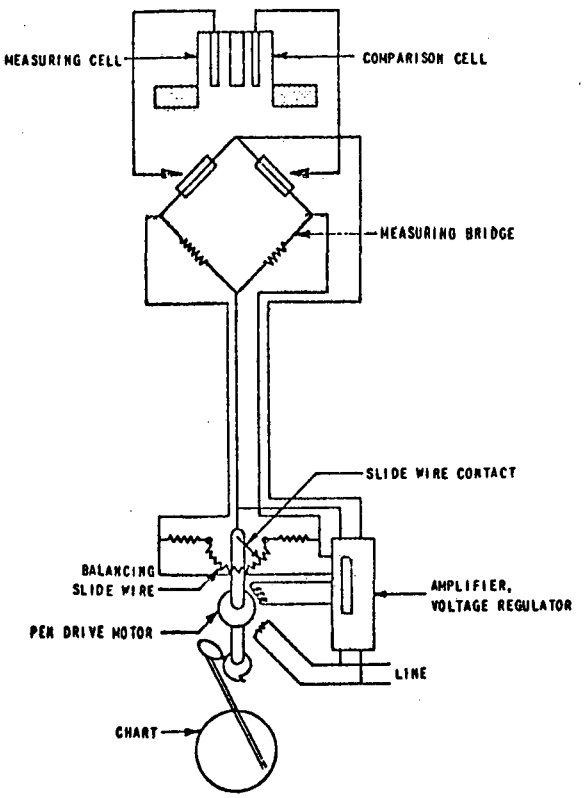


FIGURE 12. Schematic diagram of thermal conductivity oxygen analyzer (from Ref. 6, p. 28).

2.64 Performance of GE Analyzers

Oxygen analyzers of this type have accuracies of ±2 to ±5% of their full-scale readings. For DO values in the range of 0 to 5 mg/1, the expected accuracy for full-scale deflection is thus between 0.1 and 0.25 mg/1. Precision is of the order of ±1% of full-scale deflection.

2.7 Gas Chromatographic (GC) Methods of DO Analysis

In the GC determination of DO, the gas must first be stripped from aqueous solution by means of an inert gas. This is accomplished in a GE unit which is composed of a number of spinning discs capable of rotating at high speed while partially immersed in water. Such a unit has the capability of purging water of dissolved gases in a single pass over a wide range of inert gas-to-water flow ratios (See Figure 13).

From the GE unit, the gaseous stream passes through two GC columns arranged in series. The diagram in Figure 14 represents the Fisher gas partitioner (model 25). Chromatographic separation into the component gases is followed by passage of the gas through the detectors which are thermal conductivity cells. Elution curves are recorded by means of a 10 mV full-scale recorder.

The Fisher analyzer is calibrated as peak height (mm) vs gas volume ml/1. Using helium (He) as the carrier gas, good partitioning was achieved; however, the partitioner was unable to separate argon (Ar) from O_2. Another procedure entails the analysis of duplicate samples, in one of which O_2 is removed by catalytic combusion or absorption before column chromatography is used (Ref. 26). The difference between the samples is a measure of the oxygen present.

2.71 Evaluation of the GC Method for DO Analysis

GC has the following advantages for DO analysis:

(1) In common with other GE methods, it eliminates those interferences which cause analytical difficulties in aqueous DO analysis.

(2) The GC method is an on-stream one, and can be adapted for continuous monitoring.

(3) The method has multiparameter capability, enabling the analyst to determine other gases present in the original solution as well as O_2 (e.g., CO, CO_2, H_2, CH_4).

GC has these disadvantages for DO analysis:

(1) The instrumentation is delicate and complicated, requiring the attention of a specialist.

(2) In stream analysis for DO is not feasible.

(3) The GC Analyzer does not have the ruggedness or portability desirable in field use equipment.

2.8 Other Gasometric Methods of DO Analysis

Theriault and McNamee (Ref. 27) describe a modified gasometric method based on the Van Slyke* procedure which has since undergone some further modification (Ref. 28).

Prior to gasometry, gases are vacuum stripped from the solution to be analyzed, and transferred to a reaction vessel containing the Winkler DO test reagents. The mixture is then shaken for 15 minutes or more to complete the reaction, after which it is titrated with thiosulfate solution as usual. Details of this method are given in the Appendix C of Reference 6. McKeown and co-workers have made a study of the effects of a number of variables such as sample volume, stripping time and reaction time. There appears to be a good correlation between the Standard Winkler Test and the gasometric variant of it in distilled water samples with levels above 1.0 mg/1. Below the 1.0 mg/1 level considerable error may result from turbulence developed during sample transfer to the gasometer. The method has an accuracy of ±0.2 mg/1.

2.81 Advantages and Disadvantages of Gasometric DO Analysis

Gasometry is essentially a GE method, since the oxygen determination is carried out on the gas phase. As with other GE methods, it, too, avoids the pitfalls of interference by ionic species as well as non-volatile organics. However, volatile species such as H_2S, which interfere with the Winkler analysis are not excluded.

Chief disadvantages of the gasometric approach are:

(1) Gasometric equipment is not readily adaptable to a continuous monitoring process for DO, and

(2) The method is a laboratory analysis, not applicable in the field.

*A manometric procedure for the measurement of gases dissolved in blood. See Reference 29.

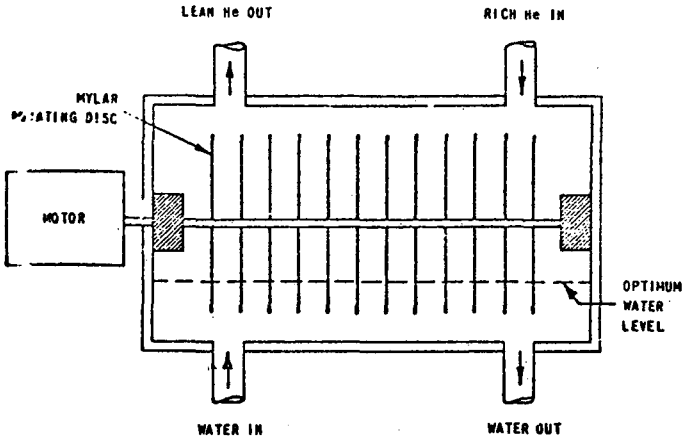


FIGURE 13. Gas exchange unit (from Ref. 6, p. 30).

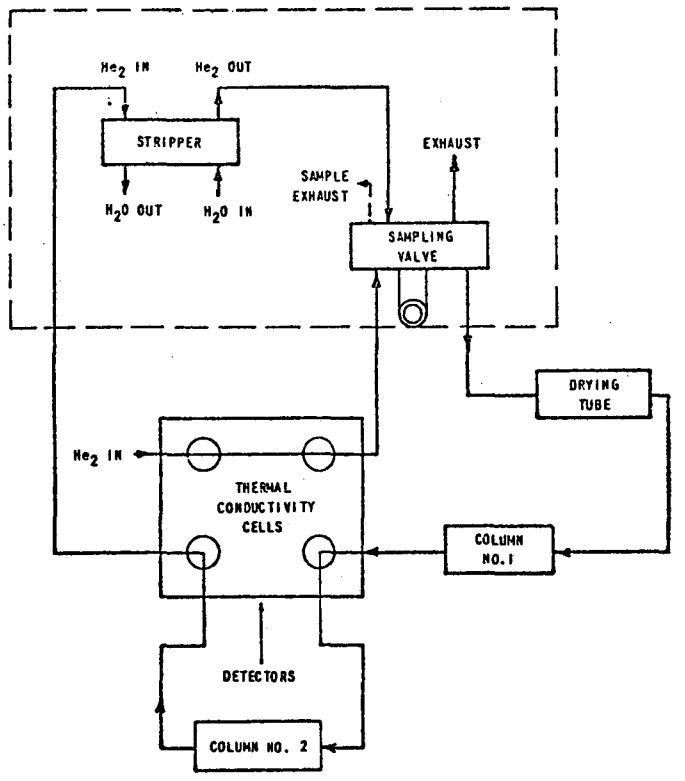


FIGURE 14. Gas chromatographic analyzer (from Ref. 21, p. 274).

2.82 Micro-Adaptation of the Gasometric Method

This adaptation permits the analysis of as little as 1 ml of a water sample. The method involves stripping of the dissolved gases in a specially designed pipet, after which the gases (in bubble form) are reacted with alkali to remove CO_2. Pyrogallol solution introduced into the syringe then absorbs the O_2. The change in bubble volume is equal to the volume of O_2 present (Ref. 30). See Figure 15 for an illustration of the microgasometric method equipment.

2.83 Advantages and Disadvantages of the Micro-Gasometric Method

The principle advantages of the method are that:

(1) The technique is adaptable to field use.

(2) Simultaneous analysis for O_2 and N_2 are an inherent feature of the method. With some simple procedural modifications CO_2 may also be determined, albeit with much lower accuracy.

(3) A number of substances generally present in polluted waters do not interfere.

However, the method has a number of limitations:

(1) It is not readily adaptable for continuous monitoring type analysis, and

(2) It is not applicable to *in situ* DO analysis.

2.9 Radiometric Analysis for DO

This method is based on the quantitative oxidation of the radioactive Tl^{204} by oxygen. Tl^{204} is a β-emitter with a 3.6 year half-life. Thus the sensitivity of this method is not greatly affected by a decay period of some months. Figure 16 illustrates the main features of the apparatus employed. It is essentially a column of Cu turnings on which Tl^{204} has been electro-deposited. Two Geiger-Mueller (G-M) flow counters, one preceding, the other following the column, count background and radioactive effluent, respectively.

The solution to be examined for DO is checked by the first G-M counter for background β-radiation, after which it is passed through the column and the eluate checked by the second counter. Oxidation of Tl^{204} takes place on the column, as shown below:

$$(21) \quad 4Tl_{(s)} + O_{2(aq)} + 2H_2O_{(liq)} \rightarrow \rightarrow 4Tl(I)_{(aq)} + 4OH^-_{(aq)}$$

One mg DO liberates 2.56×10^{-2} g of Tl^{204}, so that the counting rate and DO concentration are related by means of a proportionality constant.

2.91 Radiometric Method: Merits and Limitations

Merits:

(1) The method may be adapted to continuous monitoring of DO in effluents, and

(2) Instrumentation is relatively simple, although preparation of the column is a fairly complex procedure.

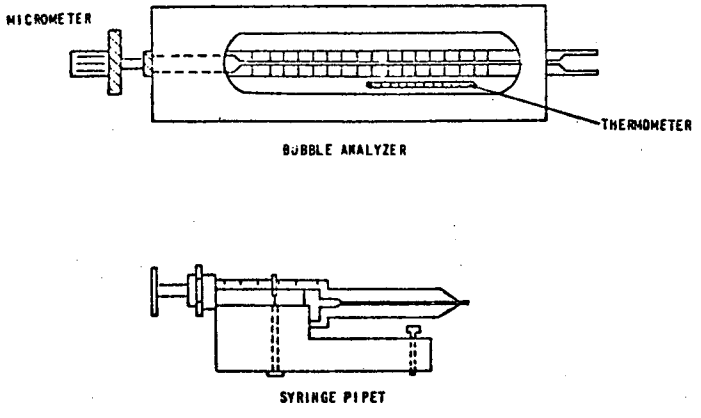


FIGURE 15. Microgasometric Equipment (from Ref. 6, p. 33).

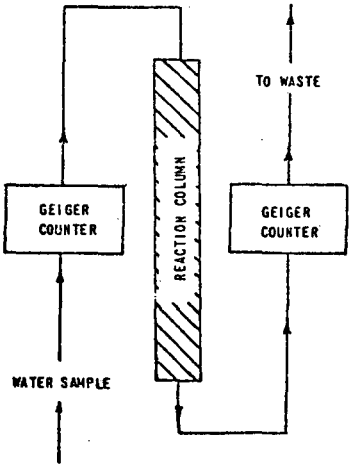


FIGURE 16. Radiometric Apparatus, employing thallium-204 (from Ref. 6, p. 34).

Limitations:

(1) Electrolytes in sea water interfere with the linear response of the G-M counter by affecting the solubility of Tl(I) on the column.

(2) The oxidation reaction Tl → Tl(I) is pH dependent.

(3) Other oxidants interfere markedly at low pH.

(4) With a column of specific activity ∿ 2.0 millicurie (mCi)/gram of Tl, sensitivity is ca. 0.2 mg/1; ie., a solution containing about 0.2 mg/1 of oxygen will have a counting rate equal to that of the background counter. Because of the random nature of radioactive decay, a precision of ±2% is about the best one can expect with this method (Ref. 31).

3. Electrochemical Methods of DO Determination

A number of electroanalytic methods have been employed in DO determinations, involving (a) conductimetry, (b) coulometry, and (c) (c) voltammetry (Table 1).

3.1 Conductimetry

The reaction of DO with chemical compounds to form ionic species results in increased conductivity of the solution. The addition of NO to a flowing water sample oxidizes NO as follows:

$$(22)\quad 4NO + O_2 + 2H_2O \rightarrow 4H^+ + 4NO_2^-$$

This reaction increases the ionic strength, μ, of the solution, and consequently, its electrical conductivity. The increase in conductance is directly proportional to the DO concentration of the original sample. Figure 17 depicts the flow diagram of a conductivity apparatus. The water sample is first passed through an ion-exchanger to remove bases and buffer salts which interfere. From there the solution goes through a reference cell to the reaction column where it reacts with the nitric oxide. The oxidation of NO by O_2 is instantaneous (Ref. 32). The treated sample then passes through the second conductivity cell, and the change in DO concentration observed is recorded as [DO].

In another method the anodic corrosion of Pb^{124} or Tl^{126} is utilized to analyse for DO:

$$(23)\quad Pb + O_2 + 2H_2O \rightarrow 2Pb(II) + 4OH^-$$

$$(24)\quad Tl + O_2 + 2H_2O \rightarrow 4Tl(I) + 4OH^-$$

Because OH^- is produced in these reactions, the pH of the solution plays an important part in the above reactions.

With $Tl(OH)_4$ (equivalent conductance 253), 1 mg/1 of DO will produce an increase in conductivity of 32 μmhos/cm. Surface waters may

TABLE 1.
(from Ref. 11, p. 324)
Electrochemical Sensors

Type	
a. Conductometric	$L = K_e \sum_i^n C_i \lambda_i z_i$
b. Potentiometric	$E_m = \text{constant} + \frac{RT}{z_i F} \ln \left[a_i + K_j a_j^{z_i/z_j} \right]$
1. Glass electrode	$pH = -\log a_{H^+}$
2. Inert metal electrode (redox potential)	$pE = -\log a_H / (2.3\ RTF^{-1})$
	Cationic = $pM^+ = -\log a_{M^+}$
3. Potentiometric membrane electrodes	Anionic = $pA^- = -\log a_{A^-}$
c. Voltammetric membrane electrodes (dissolved oxygen)	$i_d = \left[zFAP_m \frac{1}{b} a_{O_2} \right]$

L = specific conductance
K_e = cell constant
C_i = ionic concentration
λ_i = ionic equivalent conductance
z_i = ion valency
E_m = measured electrode potential
F = the Faraday constant
K_j = selectivity coefficient
i_d = diffusion current
A = electrode surface area
P_m = membrane permeability coefficient
b = membrane thickness

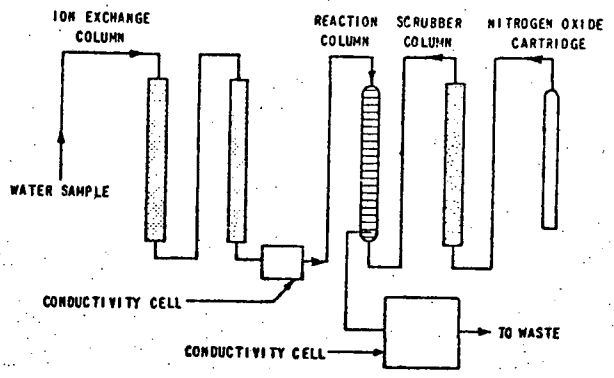


FIGURE 17. Conductivity Apparatus (from Ref. 6, p. 36)

vary in conductivity all the way from 100 to 1000 μmhos.

For minute amounts of DO, the water is first pretreated with ion-exchange resins to attain a pH ≥7, eliminating interfering carbonates and phosphates and reducing the initial sample conductance. The sample is then passed through the Pb or Tl column and the conductivity change noted. For convenience it is frequently expressed in [DO] units.

3.11 Merits and Demerits of Conductimetry in DO Analysis

The conductimetric method of analysis has been used in boiler water with considerable success. The following are advantages of conductimetry:

(1) The method has a relatively high sensitivity.

(2) Conductimetry may be adapted for continuous monitoring.

However, there are some disadvantages:

(1) The method does not lend itself to *in situ* monitoring.

(2) In all probability, ion-exchange pretreatment results in some DO loss as a result of reactions between it and the inorganic and organic constituents of the water sample on the large surface area provided by the ion-exchange column.

3.2 Constant Current Coulometric (CCC) Determination of DO

Water that has been saturated with air at 1 atmosphere and 25°C contains 8.18 mg/l of oxygen in solution. This has the appreciable coulometric equivalent of 0.1083 amp sec/g. Of the limited number of coulometric methods discussed in the literature, two have been selected for treatment here, both of which depend on the principle of constant current coulometry (Ref. 33, 34).

3.21 Electrolytic Reduction of Chromic Ions

The sample to be tested is treated with a deoxygenated solution of chromic ion. Chromous ion is generated during electrolysis, followed by the oxidation to Cr(III) by the DO present in solution. The end of the titration is signaled by the appearance of excess chromous ion in solution. Sensitivity of the method is of the order of .03 mg/l (in terms of DO present); accuracy is ±2%.

3.22 Electrolytic Oxidation of $Cu(NH_3)_2^+$

The cuprous-ammonium complex ($Cu[NH_3]_2^+$) is oxidized to the cupric ammonium state ($Cu[NH_3]_2^{++}$) by DO. Advantage is taken of this reaction to determine DO in solution. The oxidation step is followed by back-reduction of the complex to the cuprous state at a Pt cathode. The amount of current passed is a measure of the DO present in the test solution.

3.23 Limitations of CCC Methods

In general, coulometric methods for the analysis of DO (or other constituents) are only applicable to waters of high purity. Under these conditions the methods discussed above are both very accurate and highly sensitive.

3.3 DO Analysis by Voltammetric Methods

These methods depend on the electrolytic reduction of DO at an inert sensing electrode, thereby generating a current which is directly proportional to the (molecular) oxygen present in the solution. The electrode reaction is a function of (a) the nature of the electrode, (b) the pH of the solution, and (c) the imposed potential at the solution-electrode interface.

The usual voltammetric type of system has a large non-polarized* reference electrode and a polarizable micro-electrode, such as the dropping mercury (Hg) electrode. A typical voltammetric circuit is illustrated below (Figure 18). In it, a variable potential is applied to the system, and the current measured by a sensitive galvanometer.

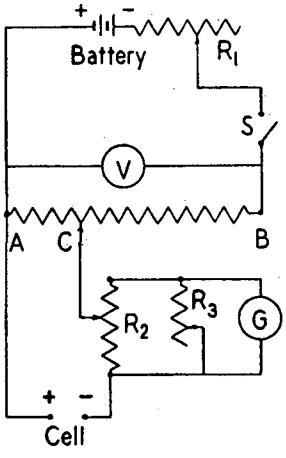


FIGURE 18. Schematic Voltammetric Circuit (from Ref. 39, p. 300).

Current flow at constant voltage is a function of parameters such as (a) the kinetics of the electrochemical reaction, and (b) the rate at which the reactant in question is transported to the electrode. Transfer of reactants may be effected by (1) diffusion, (2) convection, or (3) the migration of charged species. The migration factor may be virtually eliminated by conducting the electrolysis in the presence of a large excess of supporting electrolyte.

*A polarized electrode is one that has been forced to maintain a potential different from the equilibrium potential of the solution.

Because electrode reactions are generally fast, the concentration of the reactive species over a definite potential range is zero at the electrode surface itself. Under these conditions, the rate of mass transfer, and thus diffusion, becomes the rate-determining factor in the electrolysis.

The diffusion current i_d, of this system is proportional to the DO present. It is possible to obtain reproducible C-V curves provided the same cleaning procedures are maintained throughout the measurements.

A number of other hydrodynamic and diffusion-transport based systems have been described Ref. 36, 37, 38).

3.31 Mechanism of Electrolytic Reduction of Molecular Oxygen

The mechanism of the reduction process for oxygen has been investigated by many workers and is known to depend on the nature and surface properties of the cathode used as well as the pH and ionic strength of the solution. Such processes as the splitting of the molecular O-O bond, adsorption and desorption of O_2 on the electrode surface, and proton transfer, are all involved in the reduction process. In addition, the formation and disappearance of transient oxide films appear to be a factor with some metal electrodes (Ref. 35).

When classified according to the mechanism of mass transfer involved, voltammetric electrode systems fall into three main categories:

(1) Diffusion transport and hydrodynamic systems such as those utilizing a rotating Pt electrode;

(2) Semi-'infinite diffusion' transport systems of the polarographic type, such as the dropping Hg electrode; and

(3) 'Finite diffusion' transport systems exemplified by membrane electrodes.

3.32 The Rotating Platinum Electrode

Systems composed of a rotating electrode, or those utilizing a stationary electrode in a stirred solution belong to class (1) above. Rotating Pt electrodes have been in use for some years in DO analysis. The usual electrode assembly consists of a Pt wire which protrudes several millimeters through the wall of a glass tube. The latter rotates at some constant velocity such as 600 RPM. The bottom of the tube is filled with Hg and electrical contact is established by means of another Pt wire dipped into Hg (see Figure 19 below).

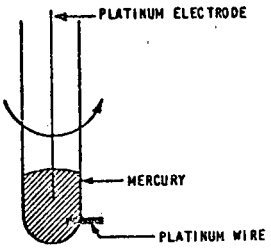


Figure 19. Rotating Platinum Electrode (from Ref. 6, p. 39).

3.33 Applications and Limitations of the Rotating Platinum Electrode

The rotating Pt electrode is usable in:

(1) in situ analysis for DO, and

(2) in the continuous monitoring of "clean" waters.

Limitations of this type of electrode system stem from:

(1) Electrode poisoning by any electroactive and/or surface active substances often present in waters and wastewaters which inhibit or totally interfere with the electrode-oxygen reactions.

(2) Difficulties encountered in obtaining constant speed of Pt electrode rotation, resulting in the distortion of the diffusion curves.

3.4 Polarographic Methods of DO Analysis

Polarography utilizes diffusion transport characteristics in "infinite" media. As such it constitutes a special category under voltammetry. Dropping Hg electrodes have been in use for a very long time to determine DO in water. The method was described in the 11th edition of Standard Methods (Ref. 40) as an alternative (and tentative) procedure when the Winkler method could not be employed -- as, for example, in the presence of high concentrations of industrial wastes. In a typical polarographic cell (Figure 20) a capillary tube attached to a vertical glass tube filled with Hg serves as the cathode. The anode may be a pool of Hg or the standard calomel electrode. A reservoir regulates the height of Hg in the cathode, and with it, the flow rate from the capillary. For DO analyses, a 3-4 second drop time is preferred. The steady supply of drops of Hg result in a continuous renewal of cathode surface. Figure 21 illustrates a typical C-V curve of an oxygen polarogram on Pt, showing the double wave of oxygen.

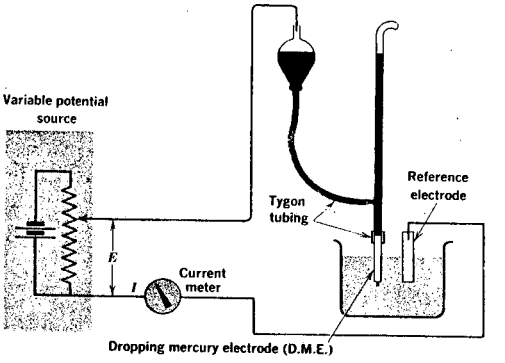


Figure 20. Schematic Polarographic Circuit (from Ref. 41, p. 51).

The oxygen content of the solution is related to the diffusion current i_d, by the following equation:

(25) $i_d = 607\ nm^{2/3}\ t^{1/6}\ D^{1/2}\ C$, where

n is the number of electrons participating in the electrode reaction/M of O_2,

m is the flow rate of the Hg in mg/sec

t is the drop time, in seconds,

D is the diffusion coefficient for molecular O_2 in cm^2/sec, and

C is the concentration of DO in mm/l.

Since n, m, t, and D are constant for any fixed system (S), the Ilkovic equation reduces to:

(26) $i_d = \phi C_S$, where

ϕ is the coefficient of sensitivity, in $\mu A/mm^{-1}$, and amperes = A

C_S is the concentration in a particular (fixed) system, S.

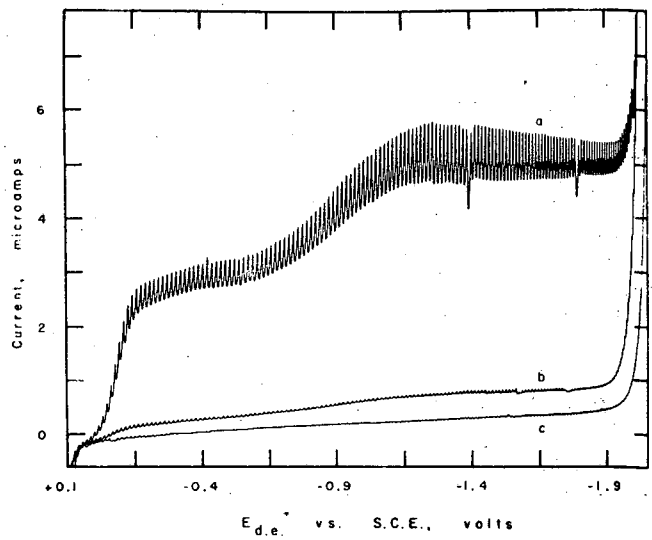


FIGURE 21. Polarograms of 0.1F potassium chloride (a) saturated with air, showing the double wave of oxygen, (b) partially deaerated, and (c) after complete deaeration (from Ref. 42, p. 136).

Instrument calibration is best done with the solution to be analyzed. Figure 22 illustrates a typical plot of the diffusion current in μ ampere compared with a DO determination using the Winkler method.

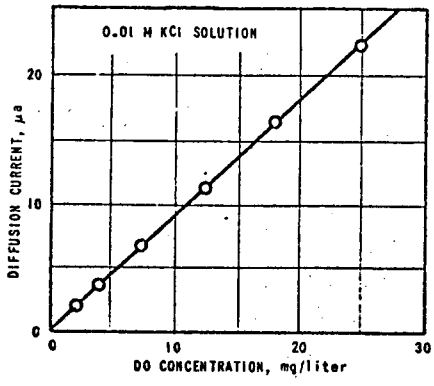


Figure 22. Calibration Curve (from Ref. 6, p. 43).

The selection of operating voltage for diffusion current measurements is important. It must be chosen to avoid interference from contaminants with the O_2 electrode reaction. A preliminary oxygen polarogram of the sample to be analyzed is useful for determining the applied voltage to be employed (Ref. 43).

Anionic surface active agents (surfactants) have been found to interfere with the electrode reaction corresponding to the first wave potential region, whereas cationic surfactants apparently interfere with those electrode reactions corresponding to the second wave potential (see Figures 23 a, b, c).

The use of a voltage corresponding to the second oxygen wave is preferable, since (1) the usual surface active agents present in waste water do not interfere, (2) the need for the addition of a maximum suppressor (a surfactant) is eliminated, (3) the interferences from the oxidation waves of sulfides and cyanides are eliminated, and (4) higher sensitivity is achieved because of the larger current.

The considerable number of attempts to adapt dropping Hg electrode procedures to the routine analysis of natural and waste waters have been generally unsuccessful because of difficulties encountered in continuous operations, particularly in heavily polluted waters (Ref. 44, 45). The so-called "wide bore" dropping mercury electrodes have had some success (Ref. 46, 47). This modification has an upward

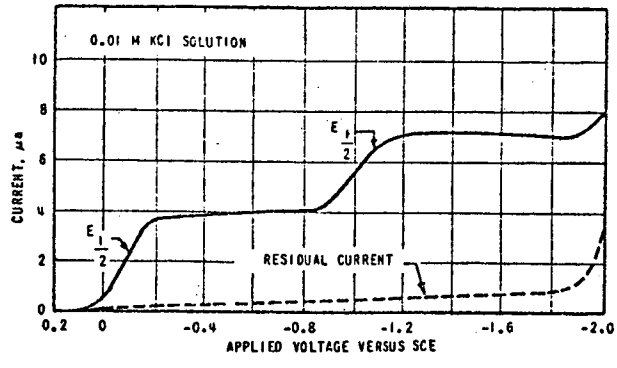


Figure 23 (a). Oxygen polarogram -- no surfactant (from Ref. 6, p. 42).

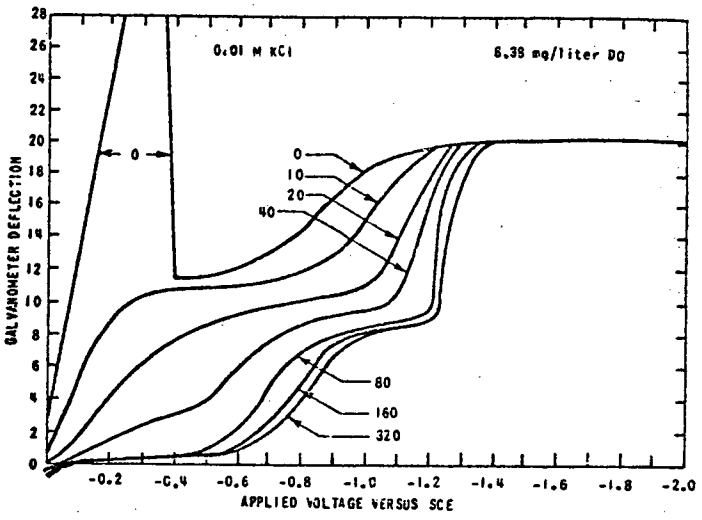


FIGURE 23 (b). Oxygen polarograms at different aerosol O.T. concentrations (mg/liter) (from Ref. 6, p.44).

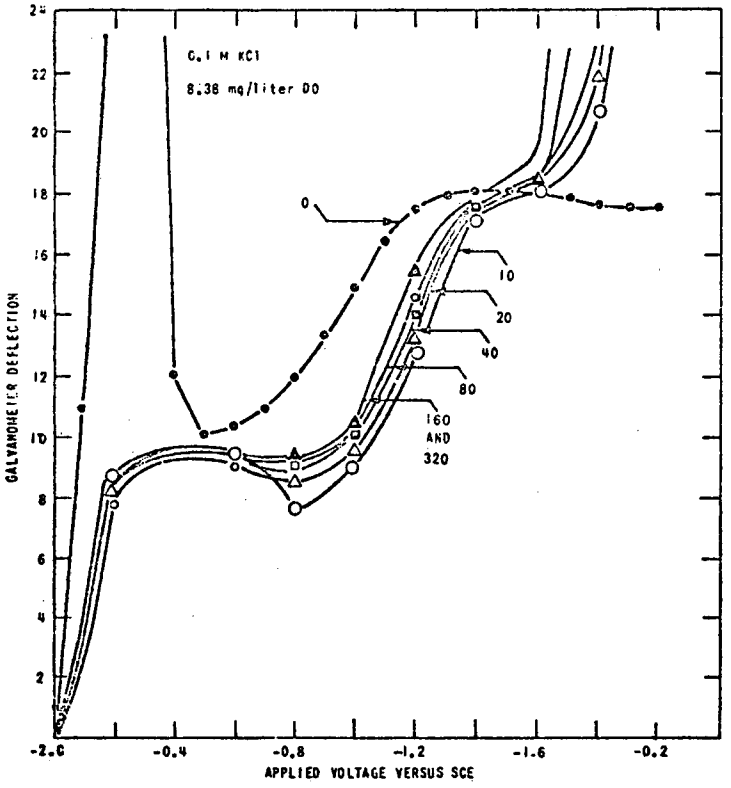
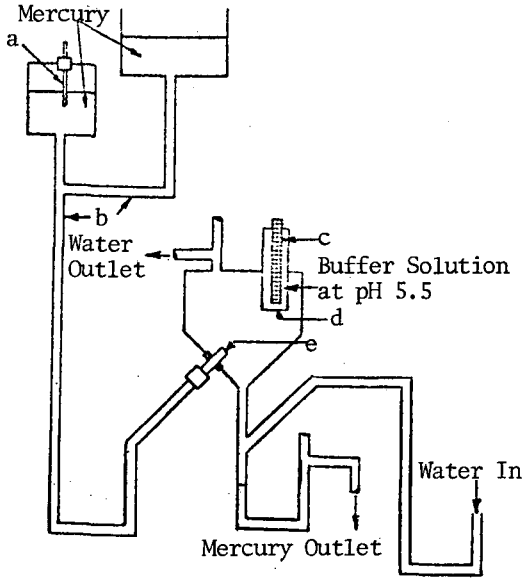


FIGURE 23 (c). Oxygen polarograms at different Roccal concentrations (mg/liter) (from Ref. 6, p. 45).

sloping capillary with an I.D. of 0.8 mm, and a Zn anode (Figure 24). The Hg flow rate is adjusted to about 7 mg/sec with a drop time of 0.2 to 0.3 seconds.



a = Platinum contact

b = Silicon Rubber Tubing

c = Zinc Electrode

d = No. 4 Sintered Glass Disc

e = Dropping-Hg Electrode

FIGURE 24. Rapid-dropping mercury electrode (from Ref. 6, p. 47).

3.41 Advantages and Limitations of Polarography for DO Analysis

The disadvantages of the small bore dropping Hg electrode have already been discussed under section 3.4. The reader is referred to the following additional references for information: References 48, 49.

Rapid dropping Hg electrodes have the following advantages:

(1) Their use minimizes the deleterious effects of surfactants on electrode reactions.

(2) They can be used with either ambient or stationary aqueous solutions.

(3) The nearly 10-fold increase in current in the short drop-time systems results in a considerable increase in sensitivity.

The limitations of polarography for DO analysis of natural and waste waters include:

(1) A lack of ruggedness and portability necessary in field instruments,

(2) Since the polarographic sensing electrode comes into direct contact with the solution, it is subject to the serious interference effects already discussed under 3.4.

(3) Toxicity of Hg to biological systems precludes polarography for respiration and/or oxygen uptake studies†.

The polarographic procedure used strongly influences the accuracy achieved. When interferences are absent, accuracy lies somewhere between 0.05 and 0.10 mg/1, with a precision of ±0.01 mg/1.

3.5 Galvanic Methods of DO Determination

Oxygen-sensitive galvanic cells have a long history. Prior to the invention of the Leclanche dry battery, cells using atmospheric oxygen were employed as sources of electrical energy. The traditional air cell consists of Zn anode(s) and a porous cathode immersed in a 20% sodium hydroxide solution. Unlike the Leclanche cell, the air cell participates conspicuously in the cell reaction, the cell eventually dying as the electrolyte is exhausted.

Special air cells have been designed in which the generated current is proportional to the $[O_2]$ which is in contact with the cathode (Ref. 50, 51, 52). Typical of these analyzers is that used by Hartmann and Braun (Figure 25) which was especially designed for the determination of DO. It employs a small circular Au or Pt cathode and a large area Zn anode which are dipped in a rapidly flowing stream of the test sample. (The stream velocity is maintained at 1 m /sec.) The electrodes are cleaned periodically by rotation against a scraper.

Since changes in conductivity affect DO measurements, a number of circuits have been designed which may be adjusted for variations in conductivity. For low conductivity water, gases such as CO_2, NH_3 and gaseous amines are added to increase the conductivity.

Galvanic methods for DO analysis have been in use for about 40 years. A number of different galvanic systems employing cathodes

†Waste mercury from laboratory uses is generally collected and reclaimed for economic reasons. The problem of Hg pollution is treated in the metals section of this Volume.

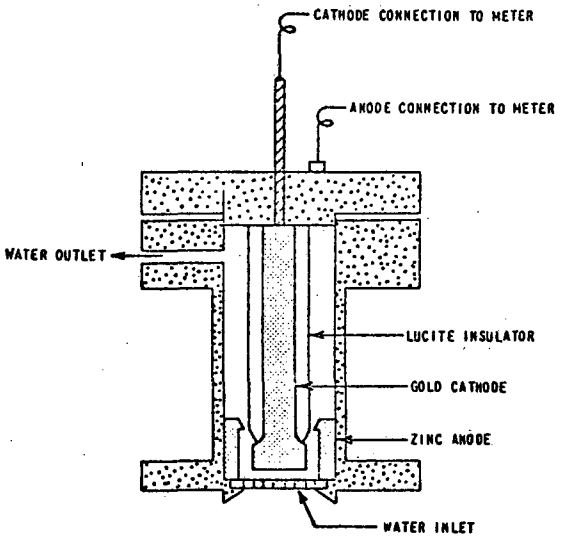


FIGURE 25. Hartmann and Braun Dissolved Oxygen Analyzer (from Ref. 6, p. 48).

of C, Au, or Pt have been used in Europe. Because these cells are susceptible to poisoning by their direct contact with the sample solution, they are of limited application. One method employed to avoid cathode incrustation in waste water analysis has been the addition of HCl to the water sample, using a dosing arrangement preceding the cell itself (Ref. 53).

3.51 Advantages and Disadvantages of Galvanic Methods of DO Analysis

(1) Galvanic methods are adaptable for in situ measurement in flowing streams.

(2) Galvanic methods may be employed in continuous-monitoring systems. However:

(a) Because the sensing element comes into direct contact with the test solution, the cathodes of galvanic cells are subject to poisoning by impurities which may adsorb on the cathode surface or react with the cathode material.

(b) Since the galvanic type analyzer is affected by changes in conductivity, any conductivity change experienced by a stream or estuary will affect the sensitivity of the galvanic cell.

3.6 Membrane Electrodes (ME) in DO Analysis

It is only within the last ten years or so that membrane electrode cells have been developed to a point where they can be of use in environmental monitoring of natural and waste waters. Those systems employed in DO analyses are electrochemical cells of the finite-diffusion type. The principle involved in their operation may best be understood by briefly examining the predecessor of these membrane systems - namely, polarography.

In polarographic-type cells the rate of diffusion of the active species is the sole determinant of the diffusion current. Since the volume of test solution is not fixed, the system is one in which the transport of active species may be viewed as occurring by a semi-infinite diffusion process.

Membrane electrode systems differ in that the diffusion current now depends only on the diffusion rate of the active species in a finite layer of the solution. This condition results from the use of a plastic membrane in close proximity to the electrode surface, thereby effectively separating the bulk of the test solution from the electrodes. Under these conditions the intervening membrane between solution and electrodes may be viewed as a strictly defined diffusion layer. As such its thickness will be independent of the hydrodynamic properties of the solution as a whole. In consequence, membrane electrode systems have more stable characteristics than those exhibited by the conventional polarographic systems.

3.61 Types of Membrane Electrode (ME) Systems

Finite diffusion type electrode systems fall into two main categories: (1) galvanic membrane electrode cells, and (2) voltammetric membrane electrode cells. These differ primarily in that galvanic systems generate their own EMF with the ion species to be analyzed involved as a reactant at one of the electrodes, whereas voltammetric membrane systems are driven by the external application of voltage thereby polarizing the indicator electrode. In this respect, voltammetric membranes resemble conventional polarography.

Descriptions of several systems developed for DO analysis may be found in References 54 and 55.

Mancy and coworkers have reported the successful use of a galvanic membrane electrode type probe in both waste treatment operations and in water pollution control programs (Ref. 56, 57, 58, 59).

The cell consists of a Pb-Ag couple. The lead anode is arranged annularly as shown in Figure 26. A disc shaped Ag cathode is located inside the anode. The couple is then fitted into a plastic collar and the tip of the assembly is covered by a polyethylene membrane between 0.5-1.0 mil in thickness. A small disc of lens paper between the membrane and the electrode tip saturated with 4M KOH, serves as the electrolyte. The system is disassembled periodically for cleaning the electrode surfaces, replenishing supporting electrolyte and replacing the plastic membrane with a new one.

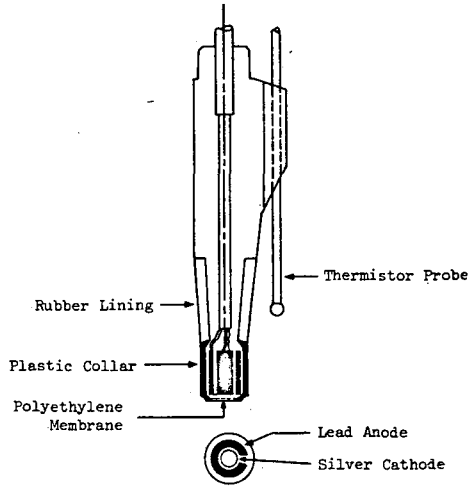


FIGURE 26. Galvanic Cell Oxygen Analyzer (from Ref. 21, p. 280).

The circuitry involved in galvanic sensor systems is relatively simple, requiring only a low impedance galvanometer or microammeter, and, if a recorder is desired, an inexpensive galvanometer-type recorder is generally adequate. Or, a known resistor may be used in the cell circuit and the potential drop then fed to a potentiometer-type recorder. It is a relatively simple matter to include such auxiliary equipment as an alarm, an integrator, or additional control equipment.

Sensitivity of the membrane electrode is not appreciably affected by the load resistance of the circuit because of the large polarization resistance of the sensing electrode with which it is in series. However, the current may be affected at high values of external load.

Johnson and coworkers have described a steam sterilizable galvanic membrane electrode which has been successfully employed in DO determinations in aerobic fermentation units (Ref. 60). The system consists of a Pb-Ag couple, with an acetate-buffer for the supporting electrode.

Galvanic type ME systems, in addition to being self-energized, are self-zeroing, which is advantageous. Voltammetric membrane systems, on the other hand, may exhibit background signals for either sign of an impressed voltage.

3.62 Principles of Oxygen Membrane Electrodes

Oxygen membrane electrodes operate in three principal stages:

(1) Molecular O_2 from the test solution permeates and diffuses through the membrane layer. This is a relatively slow process.

(2) The molecular oxygen then transfers through the electrolyte layer which is in contact with the electrode surface.

(3) Oxygen is electrolytically discharged at the Ag cathode, generating an equivalent amount of current.

In clarifying the principles involved in the oxygen membrane electrode, the reasonable assumption is made that the current generated involves linear finite diffusion only; e.g., the current is solely dependent on the rate of passage of the oxygen through the membrane to the surface of the electrode. This rate is in turn proportional to the oxygen concentration in the water in contact with the membrane. When the cell circuit is initially closed, the current will attain a maximum value representing the charging of the double layer's capacitance. Thereafter, there will be a diminution of current with time, the current-time curve now reflecting the mass transport rate of oxygen (Figure 27). The set of concentration profiles shown in Figure 28 illustrates the change in concentration of electroactive species with time in a cell of electrolyte film thickness A, and membrane thickness B. Measurement of the current at any time t, corrected for capacitance current, depends only on the concentration of electroactive species in the electrolyte film layer.

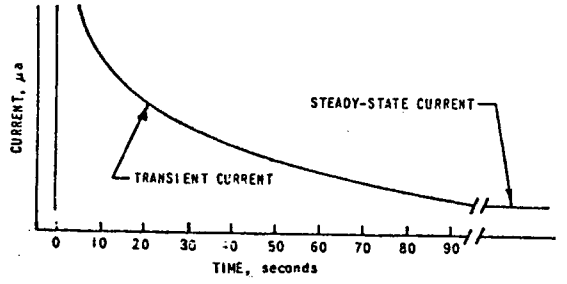


FIGURE 27. Current-Time Curve (from Ref. 6, p. 53).

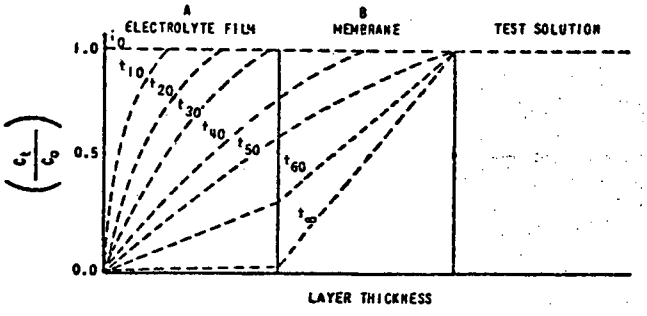


FIGURE 28. Concentration Profiles (from Ref. 6, p. 52).

For large values of t, where a steady state is attained, the following simplified expression holds for the oxygen membrane electrode:

(27) $i_\infty = nF\bar{a}\frac{Pm}{B}C$, where

n is the number of electrons exchanged per mole of reactant,

F is the Faraday constant (96,500 coulombs),

$\bar{a}$ is the surface area of the indicator electrode,

Pm is the membrane permeability coefficient (in cm^2/sec),

B is the membrane thickness, and

C the concentration of reacting species in moles/cc.

Here the rate-determining factor is transport of the active species through the membrane. Therefore, the current generated will be proportional to the rate at which molecular oxygen permeates the membrane. This depends on the oxygen dissolved in the test solution. Figure 29 illustrates a typical DO vs current calibration curve.

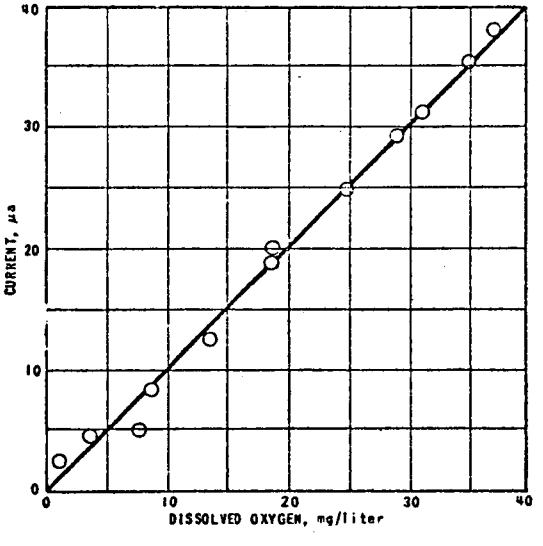


FIGURE 29. Calibration Curve at 25°C (from Ref. 6, p. 54).

The electrode reactions of the galvanic cell oxygen analyzer are as follows:

(a) Cathode reaction:

$$1/2\ O_2 + H_2O + 2e \rightarrow 2OH^-$$

(b) Anode reaction:

$$Pb + 2OH^- \rightarrow PbO + H_2O + 2e$$

(c) Overall cell reaction:

$$Pb + 1/2\ O_2 \rightarrow PbO$$

Although OH^- ions do not appear to be consumed in the overall cell reaction above, they are necessary in order to sustain the anode reaction. Therefore, there will be a deficiency of OH^- at the anode and an increase in OH^- in the electrolyte layer immediately adjacent to the central cathode and radiating toward the periphery of the anode.

For a more detailed treatment of oxygen membrane electrodes as a "2-film" system, the reader is referred to Reference 6, p. 51.

3.63 DO Probes: Some General Considerations

Oxygen membrane electrodes have three components: the membrane, the sensing element, and the electrolyte. Of these, the membrane is the unique feature of the system and has three separate functions:

(1) It acts as a protective barrier between the solution to be tested and the sensing element.

(2) It enables the supporting electrolyte to maintain contact with the electrodes.

(3) It constitutes a finite diffusion layer, with a thickness which is independent of the hydrodynamic properties of the solution bo be analyzed.

In order to qualify for use in a DO probe, a membrane:

(1) should have excellent oxygen permeability whilst remaining essentially impermeable to other species of the solution tested;

(2) should have permeability characteristics which are constant with time, and inert to the constituents of test solutions, and

(3) the membrane in question should be sufficiently resistant to tearing and/or breakage to enable one to apply it with ease to the electrode surface.

The following materials have shown good permeability characteristics for oxygen: polyethylene, polypropylene, synthetic rubber and teflon. In particular, polyethylene membranes which have low crystallinity show exceptional O_2 permeability (Ref. 61).

While Pt has been extensively employed as a sensing element for O_2 , Mancy et al (Ref. 58) have found that Au and Ag also have merit as cathodes for O_2 detection.

Electrolyte solutions in ME systems must be highly conducting aqueous solutions which do not affect the electrodes. For voltammetric systems, the nature of the electrolyte and its concentration is dictated by the reference anode. For example, with an Ag/AgCl reference electrode, the electrolyte of choice would be a 3% KCl solution.

3.64 Performance Characteristics of DO Probes

Figure 29 shows a typical calibration curve for a membrane oxygen electrode, in terms of the standard Winkler test.

For proper operation of the ME there must be adequate mixing in the test solution which is in contact with the analyzer tip. This is achieved in the laboratory by magnetic or motor-driven glass stirrers. In the field this movement may be provided by the natural stream flow, by towing the probe behind a vessel, or by manual up and down movement of the probe. In another method which has been employed, attachments with small battery-driven propellers are mounted on the tip of the probe to achieve the necessary movement.

The importance of stirring to obtaining maximum sensitivity in the DO probe is evident from Figure 30.

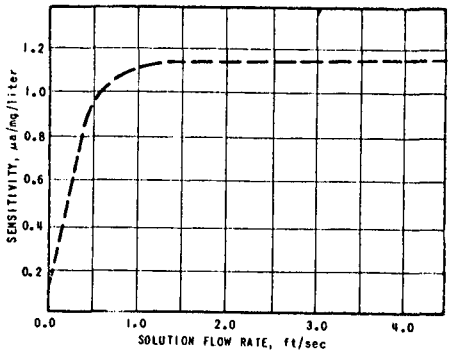


FIGURE 30. Effect of stirring on sensitivity (from Ref. 21, p. 286).

3.65 Temperature Coefficients of DO Probes

Voltammetric membrane electrodes have relatively high temperature coefficients (Figure 31), chiefly because of alterations in membrane permeabilities with changes in temperature. Electrode reaction kinetics and electrode potentials are essentially temperature independent, however,

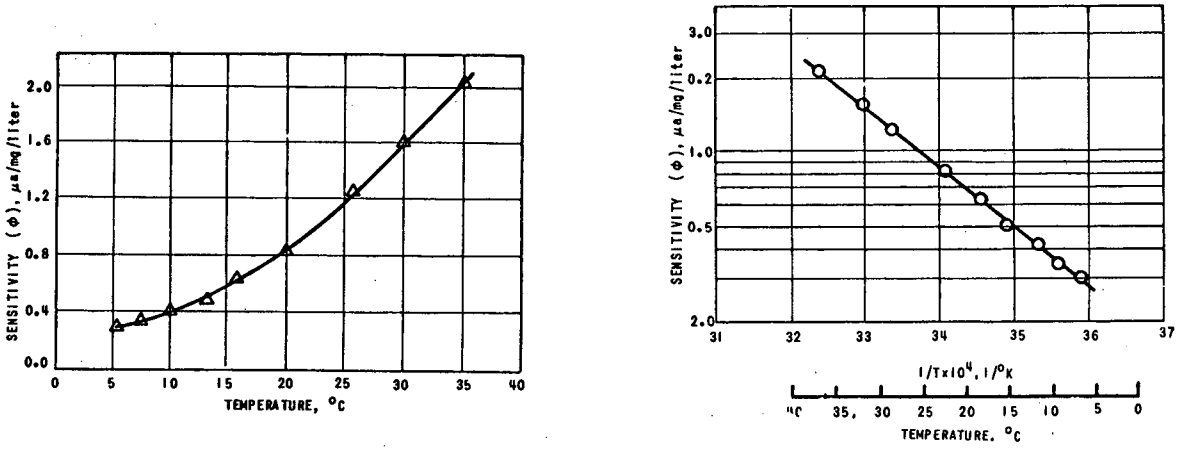


FIGURE 31 (a). Effect of temperature on sensitivity (from Ref. 21, p. 288).

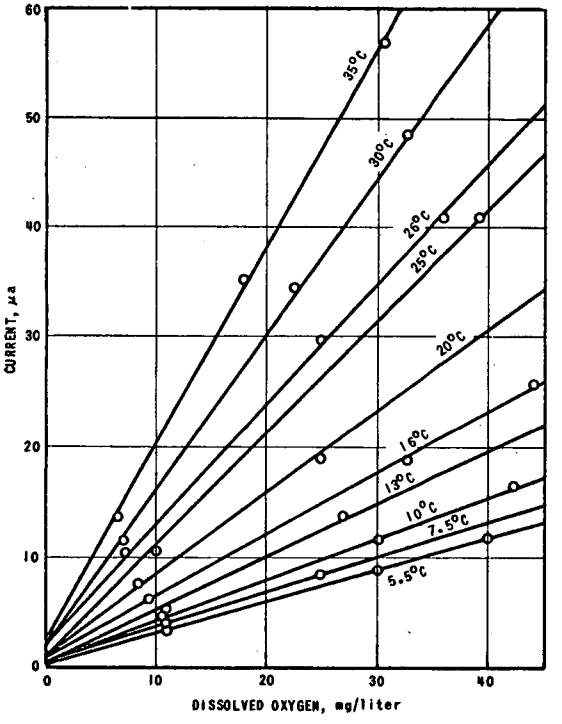


FIGURE 31 (b). Calibration curves for different temperatures (from Ref. 21, p. 287).

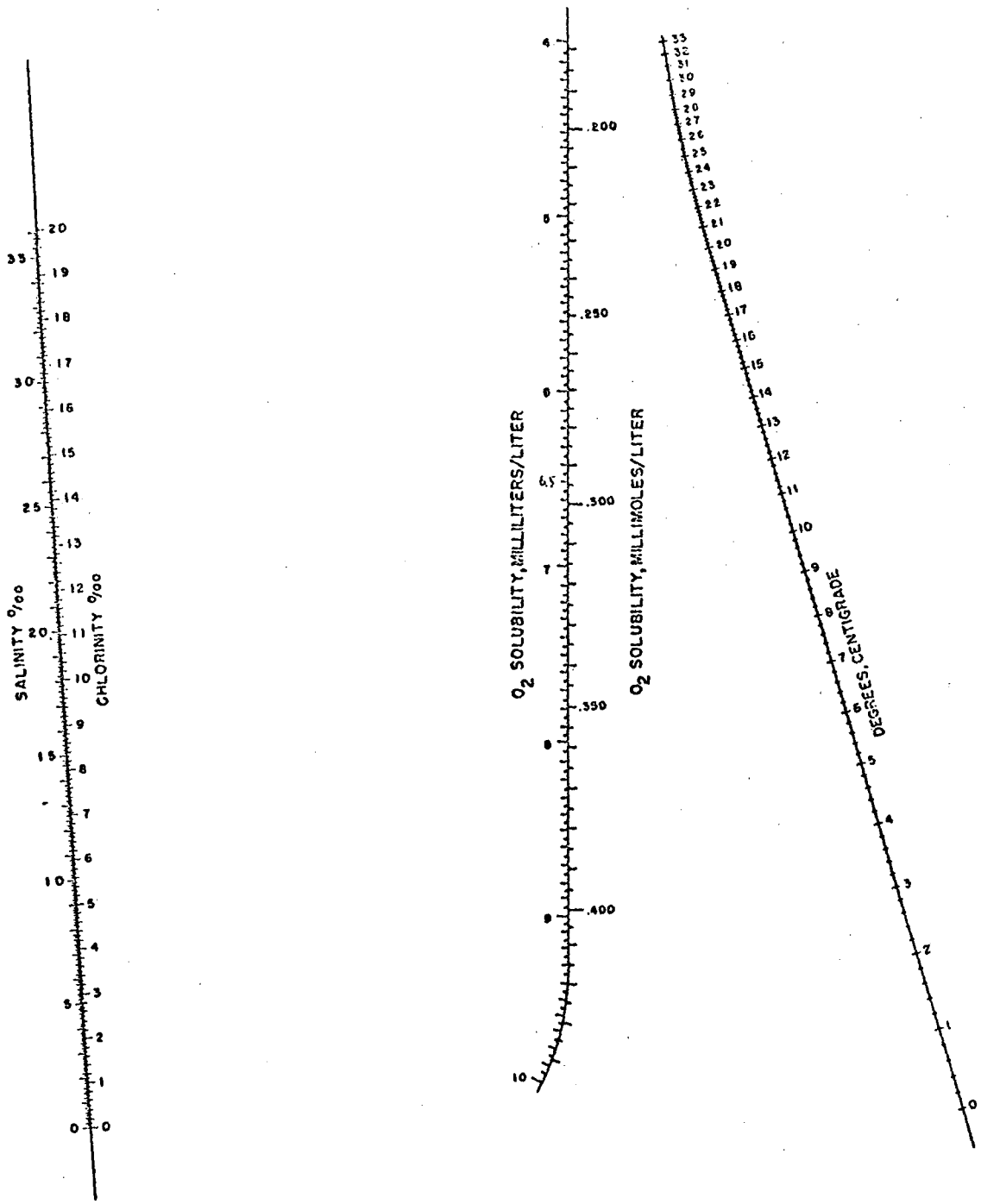


FIGURE 32. Oxygen solubility nomograph for seawater with respect to an atmosphere of 20.94% oxygen and 100% relative humidity. Prepared by William Gilbert, Department of Oceanography, O.S.U. Corvallis, Oregon 97331 (June 1967). (From Ref. 65).

The variation of sensitivity of DO probes with temperature is expressed by the equation:

(28) $\frac{d\phi}{dT} = m^\circ \frac{\phi}{T^2}$, where

d is the sensitivity in μA/mg/l

T is the temperature, expressed in °K, and

m° is the temperature coefficient in °K.

A plot of log ϕ vs 1/T is linear with a slope equal to $-m^\circ/2.303$ and an intercept b:

(29) $\text{Log } \phi = -\frac{m^\circ}{2.303}\frac{1}{T} + b$

Once m° has been determined, it is possible to calculate the instrument sensitivity at any desired temperature (Ref. 58). Nomographic temperature correction charts may be constructed (Figure 32). These calibrated charts should be used when high accuracy is desired. For lesser accuracy, ME systems with a thermistor setting incorporated in the circuit may be used (Ref. 64).

3.66 Interpretation of Data Obtained from ME Systems

An examination of the similarities between glass membrane electrodes used in measurement of pH, and pNa, and oxygen membrane electrodes may be illuminating.

In glass electrode systems, the asymmetry potential across the membrane is directly related to hydrogen ion activity. Similarly, in oxygen ME systems, the measured diffusion current is a function of the difference in chemical potential across the membrane of the reactive species. Thus both systems measure intensive properties of the solutions rather than extensive ones, such as those measured in a Winkler titration, or the titration of an acid with a standard alkaline solution. The values of the diffusion currents obtained from ME systems will be a linear function of concentration under ideal conditions only. The real diffusion equation for ME's is more correctly written:

(30) $i = (nF\bar{a}\frac{Pm}{B})a = \phi_a a = \phi_a \gamma C$, where

ϕ_a is a sensitivity coefficient related to activity and expressed in μA/mole/cc,

γ is the activity coefficient of molecular oxygen,

n is the number of electrons exchanged/mole of reactant,

F is the Faraday constant (96,500 coulombs),

$\bar{a}$ is the surface area of the indicating electrode, in cm^2

B is the membrane layer thickness in cm,

Pm is the membrane permeability coefficient in cm^2/sec,

a is the activity of molecular oxygen in moles/cc, and

C is the concentration of molecular oxygen in moles/cc

Diffusion current depends on ionic strength of the solution:

(31) $i = (e^{K_s I}\phi_a)C$, where

K_s is a salting-out coefficient and I the ionic strength of the solution. The above equation correlates diffusion current with the molecular oxygen concentration in solution; the latter is a function of ionic strength. For distilled water I = 0, and

$$e^{K_s I} = 1.$$

Therefore, equation (31) reduces to equation (30). By means of the last two equations, one can determine the important activity coefficients, γ, and salting-out coefficients, K_s, in salt solutions such as $CaCl_2$, KCl, and Na_2SO_4. Figure 33 correlates the sensitivity ϕ_a with ionic strength.

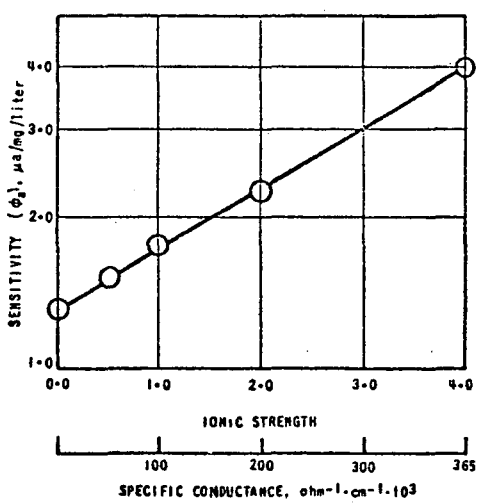


FIGURE 33. Effect of ionic strength on sensitivity (from Ref. 6, p. 60).

It has been shown that the temperature and salt effects in ME systems may be compensated. The effect of temperature may be expressed as:

$$(32)\quad i = \phi_{o,t} e^{-\frac{E_p}{R}\Delta\frac{1}{T}} C, \text{ where}$$

$\phi_{o,t}$ is the sensitivity (current, amperes; DO concentration moles/l) at a reference state, with respect to t in °C,

E_p is the activation energy for membrane permeation (cal/mole),

T is the temperature in °K,

R is the gas constant (cal/mole/°K), and

C is the molecular oxygen concentration in moles/l.

The corresponding salt effect on sensitivity is:

$$(33)\quad i = \phi_{o,s} e^{K_s \Delta I} C, \text{ where}$$

$\phi_{o,s}$ is the sensitivity at a reference state with respect to the ionic strength of the solution (units: amp/mole/l).

The ionic strength, μ, of any solution may be accurately determined from conductance measurements:

$$(34)\quad L = \Theta + \lambda I - \delta I^2 + \Gamma I^3, \text{ where}$$

L is the specific conductance in $ohm^{-1}cm^{-1}$; and Θ, λ, δ, and Γ are constants. The non-linear expression above may be approximated by:

$$(35)\quad \Delta L = K_i \Delta I, \text{ where}$$

K_i is a proportionality constant.

This approximately linear relationship of conductance to ionic strength holds in most surface waters, including estuaries, but fails for industrial waste waters with high salt concentrations. Combining equations (33) and (35), we obtain

$$(36)\quad i = \phi_{o,s} e^{K'_s \Delta L} C, \text{ where}$$

$K'_s = K_s K_i$.

The exponential terms in equations (33) and (36) reflect temperature and ionic strength effects, respectively. It is possible to compensate for these effects to some extent by employing the electronic compensator diagrammed in Figure 34.

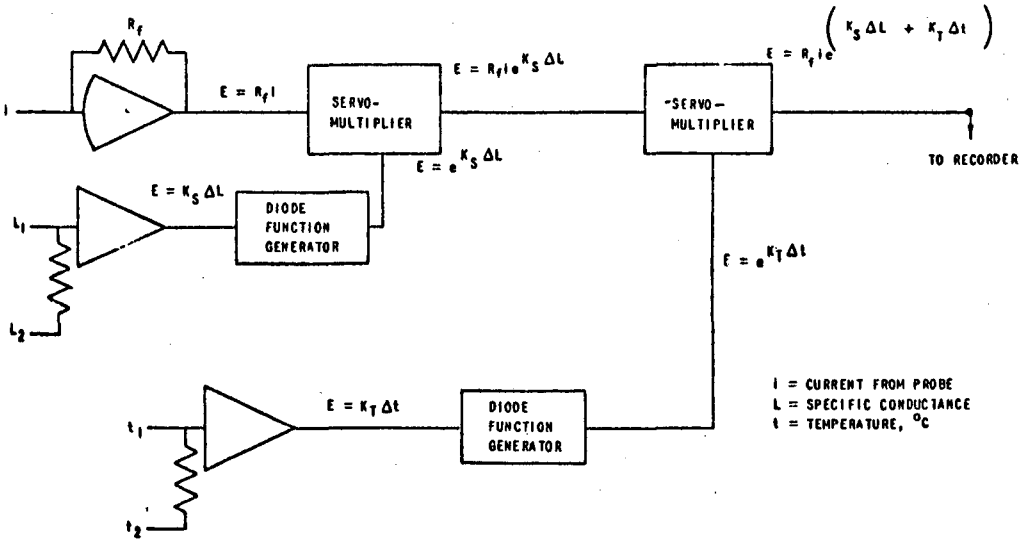


FIGURE 34. Compensator for temperature and salinity (from Ref. 6, p. 63).

3.67 Merits of ME Systems

(1) Molecular oxygen activity and concentration can be determined with ME systems. Activity measurements are of particular interest where one is concerned with making environmental measurements or in the examination of biochemical systems.

(2) Because of the presence of the membrane in ME systems, analysis is feasible in contaminated water samples containing ionized salts and organics.

(3) The ability of the membrane to function as a diffusion layer independent of hydrodynamic properties in the main body of the test solution results in more stable performance of ME systems in flowing conditions, compared with other electrode systems.

(4) ME systems are uniquely qualified for measuring DO in a variety of states from aqueous and non-aqueous solutions to the gas phase.

(5) ME systems are uniquely suited to field measurement; they are rugged, portable, easy to operate and maintain, and are ideal for the measurement of DO under adverse conditions.

(6) ME systems are completely submersible, and they may be adapted for measuring DO in situ, sometimes at great depths.

(7) ME systems, in common with other electrochemical systems, can be used in continuous monitoring.

3.68 Some Limitations of ME Systems

The procedures used in ME-DO analyses are generally quite simple. Nevertheless, a number of difficulties have been encountered:

(1) One of these probably results from a lack of knowledge of the fundamental principles involved in the successful operation of ME's. Because there is no continual renewal of ME surface (as is the case in polarographic analyses), adequate renewal of the active species at the electrode must be insured by the stirring or other means of motion provided. An inadequate flow across the surface of the membrane will result in erratic response. It is therefore essential to maintain a threshold mixing value in the solution.

(2) It is possible to contaminate the sensing element during recharging, and considerable care must be exercised to avoid this pitfall.

(3) Other gases which are reduced at the potential of the sensor, such as the halogens, or SO_2, may cause erroneous readings if they permeate the selective membrane. Fortunately, these are rarely present in the free state in the samples tested. CO_2 and H_2S are other potential contaminants; they interfere either by reaction with the electrolyte, or by poisoning the sensing element.

3.69 Some Applications of Oxygen Membrane Electrodes

Oxygen sensors of the ME type have already been widely employed in the environmental field for such applications as the monitoring of lakes and rivers, studies concerned with DO consumption in domestic sewage, and a number of aeration studies (Ref. 57, 59, 67).

Oxygen ME's have also been employed in studies involving fermentation processes (Ref. 68), the continuous monitoring of activated sludge processes, a number of oceanographic investigations (Ref. 70, 71), and as a substitute for the Warburg gas apparatus.

4. Some Suggested DO Criteria for Natural Waters

The following recommendations were made by the National Technical Advisory Committee with regard to the preservation of native biota (Ref. 72):

(1) For a diversified warm-water biota, including game fish, DO concentration should be above 5 mg/l, assuming normal seasonal and daily variations are above this concentration. Under extreme conditions, however, they may range between 5 and 4 mg/l for short periods during any 24-hour period, provided that the water quality is favorable in all other respects. In stratified lakes, the DO requirements may not apply to the hypolimnion. In shallow unstratified lakes, they should apply to the entire circulation water mass.

These requirements should apply to all waters except administratively established mixing zones. In lakes, such zones must be restricted so as to limit the effect on the biota. In streams, there must be adequate and safe passageways for migrating forms. These must be extensive enough so that the majority of plankton and other drifting organisms are protected (see sections on zones of passage).

(2) For the cold-water biota, it is desirable that DO concentrations be at or near saturation. This is especially important in spawning areas where DO levels must not be be below 7 mg/l at any time. For good growth and the general well-being of trout, salmon, and their associated biota, DO concentrations should not be below 6 mg/l. Under extreme conditions, they may range between 6 and 5 mg/l for short periods provided the water quality is favorable in all other respects and normal daily and seasonal fluctuations occur. In large streams that have some stratification or that serve principally as migratory routes, DO levels may range between 4 and 5 mg/l for periods up to 6 hours, but should never be below 4 mg/l at any time or place.

(3) DO levels in the hypolimnion of oligotrophic small inland lakes and in large lakes should not be lowered below 6 mg/l at any time due to the addition of oxygen-demanding waste or other materials.

The EPA has issued an updated compilation of Federal/State criteria for dissolved oxygen. Because of the difference in criteria from one state or territory to another, the reader is referred to the original digest for information on DO criteria of the individual states (Ref. 73).

5. Summary and Conclusions

Dissolved oxygen has long been recognized as an important parameter for the measurement of water quality. Until quite recently the methods of DO determination were largely wet-chemical, the Winkler procedure and its variants being the method of choice in most laboratories concerned with water quality measurement. However, wet-chemical methods of DO analysis, while sensitive, suffer from two major disadvantages:

1) They are relatively slow and not suited to on-line monitoring.

2) They may not reflect accurately the in-stream conditions at the precise time of sampling.

The development of DO sensors within the past ten years has kept reasonable pace with the demands of the growing environmental market. There is now a plethora of DO sensors available, some of which are designed for continuous on-line monitoring. Most are intended for in-stream or in situ use, and the portable varieties are the instruments of choice for field work. However, it is important to recognize that the proper maintenance and calibration of field instruments is necessary to insure their reliability.

The National Oceanographic Instrumentation Center is engaged in a long-term study concerned with the evaluation of DO sensors. To date, one detailed evaluation of five sensors presently in use has been published (Ref. 74). Another such survey has been initiated, but is still in the early stages (Ref. 75). Public water quality control laboratories, such as those administered by the California Regional Water Quality Control Board and the EPA have occasionally carried out independent evaluations of instruments for specific uses. It would be desirable to have more of these studies published in the open literature to avoid duplication of effort and the obvious logistic difficulties faced by the individual user attempting to make the best choice for a specific purpose.

The sensors presently available can vary quite widely in such characteristics as temperature sensitivity, flow sensitivity, effect of depth, stability and response characteristics, ease of recharging with electrolytes and replacing of membranes, useful life of replaceable parts, and initial and replacement costs.

There is still sufficient room for improvement in the areas of flow sensitivity, temperature-compensated direct read-out type instruments, and the development of membranes with imporved characteristics and specificities to warrant a considerable research effort in these areas.

In the following instrument notes we shall address outselves to these questions of performance and characteristics insofar as the information is presently available. It is to be hoped that the potential user of DO probes will find these notes of considerable help in locating those instruments best adapted to fill the specific demands of a particular job, thereby narrowing the field to a point where the selection of an appropriate sensor becomes a less confusing and frustrating experience.

6. Acknowledgments

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8. Appendix: Notation

A = Amperes; also thickness of the electrolyte solution film, cm

a = Activity, molar units

$\bar{a}$ = Surface area of indicator electrode, cm^2

B = Thickness of the membrane layer, cm

C = Concentration of dissolved oxygen, moles/liter

C_s = Salt concentration, mg/liter

D = Diffusivity coefficient, cm^2/sec

E_m = Measured electrode potential, V

E_o = Standard electrode potential, V

E_p = Activation energy of permeation of membrane, cal/mole

F = The Faraday (96,500 coulombs)

G = Free energy

$\bar{g}$ = Acceleration, cm/sec^2

g = Weight in grams

H = Henry's Law constant, 5.89×10^5 mm Hg/mole/liter

h = Depth (cm)

I = Ionic strength

i = Current, A

i_d = Diffusion current, A

J = Flux of molecular oxygen, $moles/cm^2\text{-}sec$

K_i = Conductance proportionality constant

K_s = Salting-out coefficient

K'_s = Modified salting-out coefficient

L = Specific conductance, $ohm^{-1}cm^{-1}$

M = Molecular weight, g/mole

m = Rate of flow of mercury, mg/sec

m° = Temperature coefficient, °K

n = Number of electrons transferred per mole in redox

N_i = Number of gram moles of solute

P = Partial pressure of oxygen, 154 mm Hg at sea level

P_m = Permeability coefficient, cm^2/sec

q = Number of coulombs passed in electrolysis

R = Gas constant = 0.0821 L -atm/mole/°K = 1.99 cal/mole°

S = Oxygen solubility, mg/liter

S_o = Oxygen solubility in distilled water, mg/liter

T = Absolute temperature, °K

T_c = Temperature, °C

t = Time

V = Volume

v = Velocity of molecular oxygen, cm/sec

$\bar{v}$ = Partial molal volume of solute, liter/atm

X = Mole fraction

x = Distance, cm

Z = Ionic charge

α = Constant

β = Constant

Γ = Constant

λ = Constant

δ = Constant

γ = Activity coefficient

ρ = Density of solution, g/cm^3

ΔH = Heat of solution, cal/mole

Ψ = Electrostatic charge

μ = Chemical potential, cal/mole also μ = micro

$\bar{\mu}$ = Electrochemical potential

θ = Constant

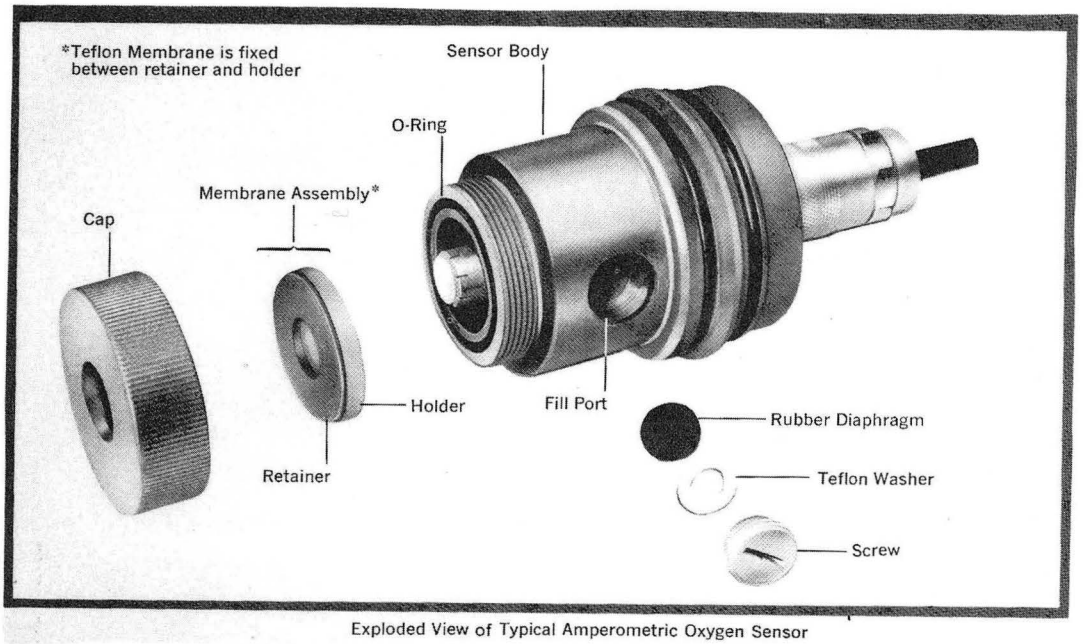
ϕ = Sensitivity coefficient, μA per unit concentration

INSTRUMENTATION
FOR ENVIRONMENTAL
MONITORING

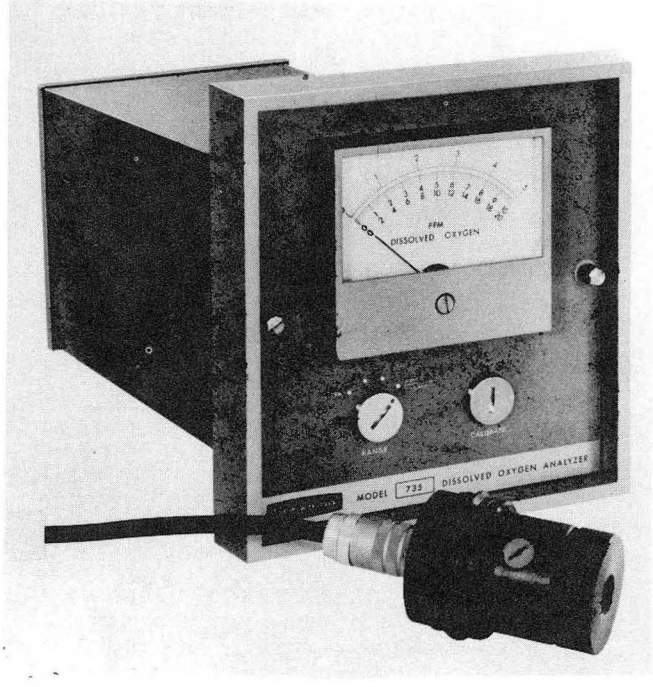
H2O-BIO
Field: DO
Beckman 1
Sept. 1975

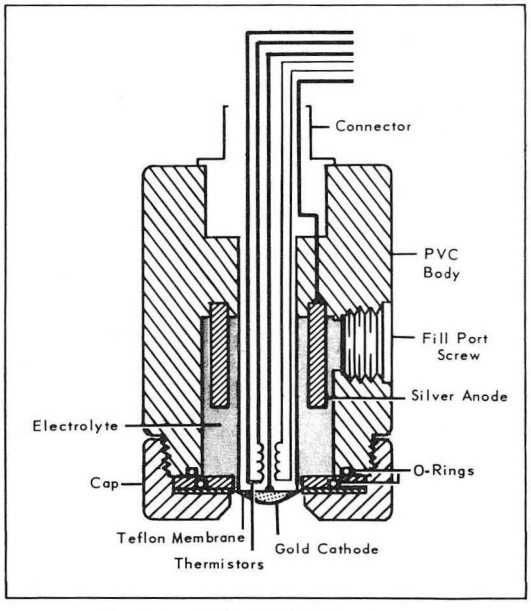
Dissolved Oxygen Analyzer

Beckman Model 735, Catalog No. 191600



Exploded View of Typical Amperometric Oxygen Sensor





Amperometric Oxygen Sensor

Class	Continuous-Sensor, Laboratory/Field
Categories of Water	Fresh or Waste (May be used in salt water by use of correction factors for oxygen solubility)
Principle of Operation	Polarographic oxygen sensor with a large silver anode and gold cathode; electrodes are protected from the solution by a thin Teflon membrane. An aqueous KCl solution confined by the membrane serves as the electrolyte. Oxygen diffuses through the (semi-permeable) membrane to the cathode where it is reduced when an appropriate voltage (.725 V) is applied across the electrodes. The magnitude of the resulting current is proportional to the amount of oxygen present in the sample. Electrode reactions: Anode $4Ag + 4Cl^- \rightarrow 4AgCl + 4e$ Cathode $O_2 + 2H_2O + 4e \rightarrow 4OH^-$
Minimum Detectable Sensitivity	1.0% of full scale
Range	0-5, 0-10, 0-20 ppm by weight of dissolved oxygen
Range Correlation:	±0.25% of full scale for recorder output in going to a less sensitive range
Interferences	Halogens, H_2S, NO(X), SO_2, mercaptans
Multiparameter Capability	Not applicable
Sampling	Method: In situ; continuous flow, 1.5 ft/sec minimum Pressure: 0-50 psig Volume: minimum depth, ; maximum depth, 100 ft Maximum Temperature Input: 55.55°C (132°F) Collection Efficiency: Not applicable Maximum Number of Sample Sources: Limited to <1000 ft from amplifier location (by length of longest specified cable)
Performance	System Accuracy: (a) ±1% of full scale at calibration temperature (recorder output) (b) Sensor accuracy compensated to 6% of reading over full range 0-43.33°C (32-110°F) Reproducibility: ±1% of reading for any temperature, in 24 hrs Linearity: a) Sensor: ±.75% of reading at any given temperature b) Electronics: ±.25% of reading at any given temperature Noise: <±0.5% of F.S. Lag Time: ≤2 sec Rise Time: <20 sec to 90% of final response Retention Time: Not Applicable Fall Time: <20 sec to 90% of final response Zero Drift: <1% in 24 hr at constant temperature Span Drift: <1% in 24 hr at constant temperature Response Time: 90% in 20 seconds or less at constant temperature
Operation	Ambient Temperature Range: -28.89 to 50°C (-20 to 122°F) (Amplifier only) Sample Temperature: 0°-43.33°C (32°-110°F) Temperature Compensation: Two thermistor compensators; one corrects for temperature effect on the sensor itself, the second compensates for the change in solubility of oxygen with temperature Relative Humidity Range: Up to 100% R.H.

Operation (Contd)

Calibration: a) Partial pressure calibration for oxygen in air is achieved by exposing the sensor to air, turning the Range switch to calibrate, and adjusting the Calibrate control so that the meter reads the value for total atmospheric pressure: 760 mm at sea level (7.6 on the scale)
b) Alternately, the instrument may be calibrated by a standard method such as the Winkler. Calibration at least once a month is recommended.

Procedure: Instruction manual supplied with each instrument

Unattended Period: Depends on application - normally 1 to 4 weeks

Maintenance: Depends on process conditions:
Membrane change: every 30 days to 3 months. Membrane need not be removed to replenish electrolyte.
Service period: 3 to 6 months for an average application.

Requirements

Power: a) 115 ±15 volts, 50/60 Hz (cps)
b) 230 ±30 volts, 50/60 Hz (cps)

Weight: Sensor: .227 kg (0.5 lb); Electronic unit: 7.27 kg (16 lbs)

Dimensions: Amplifier: 20.33 cm H x 22.35 cm W x 32.77 cm D (8" x 8-8/10" x 12-9/10" maximum)
Sensor: 8.57 cm diameter x 18.74 cm H (3-3/8" x 7-3/8")

Features

Output: a) Meter readout scales correspond directly to ppm of oxygen: 0-5, 0-10, and 0-20 ppm
b) Potentiometric: 0-10 mV, 0-100 mV or 0-1 V

Training: Sensor may be recharged in the field by non-technical personnel.

Options: Alternate Model, Catalog No. 191601 is available; like 191600, except for additional outputs for current recorders of 0-5, 1-5, 4-20 and 10-50 mA

References

Beckman, Bulletin 4092A, "Dissolved Oxygen Analyzer" and communications, 3/73
For an in-use evaluation see Reference 74 of text.

Cost

Model 735, Catalog No. 191600		$810
Model 735, Catalog No. 191601 (See under options.)		930
Replacement parts:	191605 Sensor	194
	191755 Recharge Kit	39

Accessories:

193661	Cable (1000 ft. maximum, including amphenol connector and loose spade lugs) 20 ft.	$ 38
193662	All other lengths	26 + 0.60/ft.
190705	Submersion assembly	108
190708	In line flow assembly (Pressure compensated)	114
70999	Field mounting kit (for pipe, rail or wall mounting)	27
81778	Instruction manual (1 supplied)	7

Remarks

1) Output signal from solid state amplifier is compatible with virtually all current or potentiometric recorders and controllers, data reduction devices, telemetering systems, and computers.
2) Sensor: The anode, cathode, thermistors and all leads are molded into a PVC body.
3) Note: Each instrument includes: a) Amplifier, b) Sensor P/N 191605, c) Recharge kit P/N 191755, d) Instruction manual P/N 81778. Cable must be ordered separately to length (See Accessories).

Address

Beckman Instruments, Inc.
Process Instruments Div.
2500 Harbor Boulevard
Fullerton, CA 92634
Attn: Lee Braun - Product Line Manager
or
Robert Buchanan - Process Instruments Div. (Ex. 1454)

Dr. Ette Geiger - Sales Analyst (for catalog and price information) (Ex. 1330)
(714) 871-4848

INSTRUMENTATION
FOR ENVIRONMENTAL
MONITORING

H2O-BIO
Field: DO
Delta 1
Sept. 1975

Dissolved Oxygen Analyzer

Delta Model 2110

Class	Laboratory/Field/Portable
Categories of Water	Fresh/Waste
Principle of Operation	The passive type probe has a gold cathode and silver anode connected by a reservoir containing a buffered potassium chloride solution as the electrolyte. A semipermeable (Teflon) membrane confines the electrolyte, and separates it and the electrodes from the solution to be tested. Oxygen from the test solution diffuses through the membrane at a rate proportional to its concentration producing a corresponding flow in the measuring circuit. Temperature effects on oxygen diffusion rates are automatically compensated by the thermistor. Electrode Reactions: Anode $4Ag + 4Cl^- \rightarrow 4AgCl + 4e$ Cathode $O_2 + 2H_2O + 4e \rightarrow 4OH^-$
Minimum Detectable Sensitivity	0.02
Range	0-2, 0-10, 0-20 ppm (mg/l); F.S. adjustable for 0-1, 0-5 ppm
Interferences	Halogens in molecular form, H_2S, mercaptans, NO_X, SO_2
Multiparameter Capability	BOD; temperature

Sampling

Method: Probe in situ
Volume: Min. depth - 1/2 inch
Max. depth - 300 ft
Maximum Temperature Input: 50°C
Collection Efficiency: N/A
Maximum Number of Sample Sources: Unlimited except for 300 ft depth limitation

Performance

Accuracy: Meter - 1% F.S.
Reproducibility: ±1%
Linearity: Linear response
Noise: Negligible
Lag Time: Maximum 30 seconds
Rise Time: Maximum 30 seconds
Retention Time: N/A
Fall Time: Maximum 30 seconds
Zero Drift: Negligible
Span Drift: Negligible

Operation

Ambient Temperature Range: -5° to 50°C; temp. readout provided.
Temperature Compensation: Automatic compensation between -5° and 50°C
Other: Built-in depth and altitude compensation
Relative Humidity Range: Up to 100%
Calibration: Air calibration cable provided
Depth compensation by means of a pressure gland permits submersion up to 300 ft without calibration adjustment.
Procedure: Set mechanical zero, set electrical zero; calibrate unit using a known standard. Using the 0-20 ppm range, immerse probe in sample, agitate sample so that a minimum flow of 1 ft. per second of sample passes over membrane. If reading is lower than 10 ppm, switch to the 10 ppm scale, or lower than 2 ppm, switch to the 0-2 ppm scale.
Unattended Period: May be operated 6 to 9 months without attention
Maintenance: Electrolyte change requires about 2 minutes.
Membrane: Torn membrane may be replaced in about 1 minute.
Other: Replacement kit provides 10 membranes (1 mil) and 2 oz of buffered potassium chloride solution.

Requirements

Power: Rechargeable batteries
Weight: Net weight 9 lbs. (includes battery charger provided with instr.); shipping weight ~ 15 lbs.
Dimensions: 28 cm H x 33 cm W x 20.3 cm D (11" x 13" x 8")

Features

Output: Dual output 0-10 mV; 1) proportional to DO; 2) proportional to temp.
Training: Manual provided with the instrument; see also under Maintenance above.
Options: See under Cost.
Other: Probe is waterproof and submersible to 300 ft. Probe is insensitive to shock, vibration, or changes in temperature and/or pressure within the recommended operating range.

References

Manufacturer's bulletin 2010-AP, May 1971
Additional information provided by Mr. David Anajovitch.

Cost

Model No.	Description	Price
2110-00	Do Analyzer (Price for meter includes battery charge and recorder output connector)	$495
2110-25	Combination DO-temperature probe with 25-ft cable	195
Options:		
2110-100	Probe with 100 ft cable	220
2110-300	Probe with 300 ft cable	290
1010-10	Remote Stirrer on 100 ft cable	190
1010-103	Remote Stirrer on 300 ft cable	215
1010-112	Sample Agitator on 25 ft cable	175

Remarks

Manual salinity compensation; 0 to 40 parts/thousand salinity.
A one-year warrantee against defects in materials or workmanship is provided with the 2110 Series analyzer and probes.

User information is available on request.

Output signal may be used to operate proportional control valves or feeders; or for conversion of analog to digital form for input to computer telemetry, and data acquisition systems.

Model 2110 is shipped with a service kit which includes replacement membranes and enough electrolyte for over a year of normal usage.

Address

Delta Scientific Corp.
122 E. Hoffman Ave.
Lindenhurst, NY 11757
Attn: John Becker— Sales Coord. for Laboratory Instr.
or
Robert Mankes—Vice President of Sales
(516) 884-4422

Portable Oxygen Analyzer

Edmont Wilson Model 60-620

Class	Continuous/Portable
Categories of Water	Fresh/Waste
Principle of Operation	The analyzer consists of a gold cathode, silver anode, temperature compensating thermistor, a source of polarizing voltage and a readout. The electrodes are connected by means of a conductive gel of cellulose-base containing potassium chloride. They are separated from the gas or liquid sample by a semi-permeable Teflon membrane which shields the electrodes from contamination. When a potential of 0.8 volts is applied between the electrodes, oxygen (O_2) passing through the membrane is reduced at the cathode, generating a current, the magnitude of which is proportional to the amount of oxygen present. Since the diffusion rate of oxygen passing through the membrane increases with increasing temperature the instrument is equipped with a thermistor (resistance thermometer) which compensates for changes in temperature. Temperature changes between 59-122°F are thus automatically compensated to within ~2% of the reading indicated.
	Electrode Reactions: Anode: $2Ag + 2Cl^- \rightarrow 2AgCl + 2e$ Cathode: $1/2O_2 + H_2O + 2e \rightarrow 2OH^-$
	Sensitivity of the sensor is reduced in water by virtue of the increased effective thickness of the Teflon membrane, due to an adsorbed film of water. This increases the distance which O_2 must traverse to the electrode. Diffusion of O_2 in liquids is so much slower than in gases, that the sensor must be in motion in order to replenish even the minute quantity of O_2 consumed by the sensor.
Minimum Detectable Sensitivity	0.1% O_2
Range	0-25% oxygen

Interferences

SO_2, F_2, Cl_2, Br_2, I_2 and NO_X (<0.25% = 2500 ppm). Mercaptans and H_2S ($\geq$1%) poison sensor.

Multiparameter Capability

Measures oxygen in air between 0-25%

Sampling

Method: In situ probe, 2-3 ft/sec minimum flow
Volume: Minimum depth = 0.25 inches
Maximum Temperature Input: 68.3°C (155°F)
Collection Efficiency: N/A
Maximum Number of Sample Sources: Unlimited

Performance

Accuracy: ±0.2% oxygen in calibration and temperature range
Reproducibility: ±0.1 ppm in water
Linearity: ±1% O_2 from 0-100% O_2, over compensated temperature range
Noise: N/A
Lag Time: N/A
Rise Time: 90% in 10 sec in air; 90% in 10 sec in H_2O
Retention Time: N/A
Fall Time: N/A
Zero Drift: Negligible
Span Drift: <1% O_2 in 2 weeks, when adjusted for atmospheric pressure changes

Operation

Ambient Temperature Range: Sensor: -2.2 to 68.3°C (28 to 255°F)
Analyzer: 0 to 68.3 °C (32 to 155°F)
Temperature Compensation: Sensor compensated between 15-50°C (59-122°F)
Relative Humidity Range: 0-100%, non-condensing
Calibration: Air calibration
Procedure: The sensor is placed in the stream for several minutes to allow equilibration of internal sensor temperature with that of the stream of liquid sample. The sensor is then withdrawn and all water droplets shaken off, leaving the film of moisture on the membrane itself. (This compensates for decreased sensor sensitivity in water.) The instrument is then calibrated in air to 20.9% oxygen and re-inserted into the liquid for reading.

A stirrer may be used to keep renewing the sample at the sensor-liquid interface. In the field this movement may be accomplished in a variety of ways such as siphoning stream water past the sensor. In industrial applications, the sensor is generally installed as an integral part of a pipeline through which the liquid flows. Flow must exceed 2 to 3 ft/second to prevent film formation which results in lower O_2 reading.

Unattended Period: N/A
Maintenance: Sensor must be recharged every 30-60 days

Requirements

Power: 9 V battery (alkali or Hg) included
Weight: .455 kg (1 lb)
Dimensions: 7.6 cm x 12.7 cm x 12.7 cm (3" x 5" x 5")

Features

Output:
Training: Instruction manual provided
Options:

60-601	Replacement Oxygen Sensor with six-foot cable	130.00 ea.
60-602	Disposable Recharge Kits (Box of five)	17.50 box
60-603	6-Foot Sensor Extension Cable	25.00 ea.
60-604	50-Foot Sensor Extension Cable	45.00 ea.
60-605	Carrying Case for Oxygen Analyzer Models #60-600, 60-620, 60-625	5.00 ea.
60-607	Oxygen Nomographs, Pad of 50, 8-1/2 x 11	5.00 ea.

Also available: Model 60-600 - same as 60-620 except with with a 0-50% O_2 scale. Includes O_2 sensor 60-601 and two disposable Recharge Kits. $275. ea.

References — Operating instructions for Edmont Oxygen Analyzers and Monitors, Aug. 15 (1972)

Cost — Analyzer 60-620 includes sensor, case, and 2 disposable recharge kits — $310.

Remarks — Sensor is fitted with a patented disposable discharge cap which operates at temperatures up to 68.3°C (155°F), and is not damaged by freezing, thawing, mud, oil, or "gummy process chemicals", according to manufacturer's claim. Manufacturer provides a limited 1 year warranty ("provided connector, electrodes and critical surfaces are not worn or damaged in any way.") Warranty does not include batteries.

Instruction booklet includes the following conversion tables:

a) A nomograph from conversion of Edmont $\%O_2$ to partial pressure in mm Hg or ppm of O_2 by weight.

b) A table: Effective Oxygen by Weight Adjusted for Elevation Above Sea-Level (between 0-6000 ft; 50°F only).

Address — Edmont-Wilson
Coshocton, Ohio 43812
(614) 622-4311
Attn: Mike Sweet, Manager of Market Development for Instruments

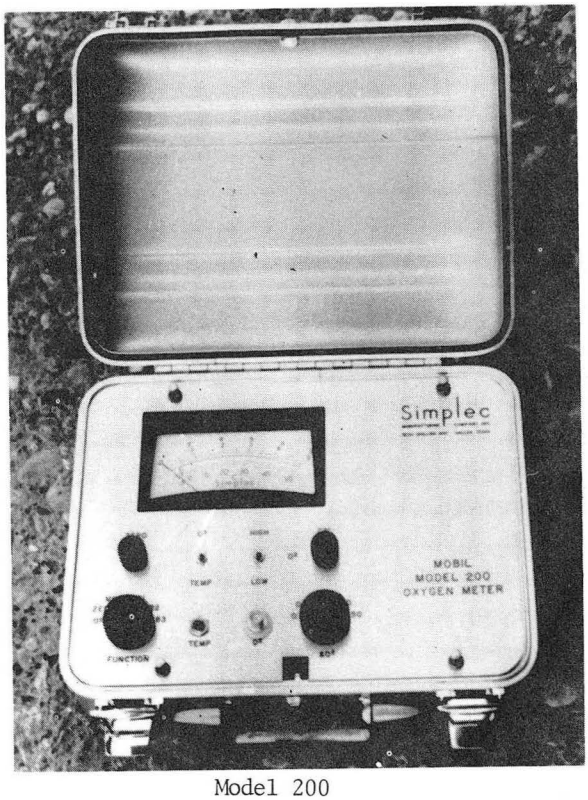
INSTRUMENTATION
FOR ENVIRONMENTAL
MONITORING

H2O-BIO
Field: DO
Fincher 1
Sept. 1975

Dissolved Oxygen

Fincher Oxygen Meter Mobil Model 200

Model 100RT



Model 200

Class	Portable probe
Categories of Water	Fresh/Waste/Salt
Principle of Operation	Amperometric measurement of oxygen by cathodic reduction in a membrane-covered electrolytic cell. An impressed constant voltage reduces all oxygen that diffuses through the membrane to the cathode; the electric current is therefore a measure of the rate of diffusion through the membrane which in turn is proportional to the concentration of oxygen. Polarographic cell consists of a gold cathode and silver anode immersed in electrolyte (KCl). The electrodes are isolated from the liquid or gas sample by a fluorocarbon membrane secured by an O-ring. A constant voltage (0.6 V) is impressed on the electrodes. Electrode reactions: Anode: $4Ag + 4Cl^- \rightarrow 4AgCl + 4e$ Cathode: $O_2 + 2H_2O + 4e \rightarrow 4OH^-$ Overall: $4Ag + 4Cl^- + O_2 + 2H_2O \rightarrow 4OH^-$
Minimum Detectable Sensitivity	5 ppb in solution
Range	.01% to 50% in gases; concentrations in liquids corresponding to equilibrium with gas phase; H_2O, .05 to 25 ppm at 21.1°C (70°F). Range may be expanded to 100% in gases and 50 ppm in H_2O by calibration to a proportional reading.

Interferences

High concentrations of hydrogen sulfide and some gases that can be electrolytically reduced.

Multiparameter Capability

Measures gaseous oxygen and temperature

Sampling

Method: In situ, flowing stream or stirred batch
Volume: 20 cc/min or 400 cc batch
Maximum Temperature Input: 50°C (122°F)
Collection Efficiency: 100%
Maximum Number of Sample Sources: One

Performance

Accuracy: ±.010 ppm in solutions; ±.02% in gases
Reproducibility: 1% of full scale
Linearity: 1%
Noise: Zero without interferences
Lag Time: Less than 10 seconds
*Rise Time: Less than one minute
Retention Time: Zero
*Fall Time: Less than one minute
Zero Drift: 0.1% of full scale per °C
Span Drift: 0.01% of full scale per °C

Operation

Ambient Temperature Range: -5 to +50°C (23-122°F)
Temperature Compensation: Thermistor in probe senses sample temperature which may be displayed by means of the temp-02 switch.
Relative Humidity Range: Zero to saturated
Calibration: Set to 20.8% in air for most applications; for very low concentrations, a reading at zero oxygen is required which is obtained in an auxiliary cell supplied with the instrument.
Procedure: The sensor is calibrated in air and in the zero cell; direct readings are then made in a flowing sample or stirred batch.
Unattended Period: 1000 hours with internal power.
Maintenance: Battery change after 1000 hours operation; occasional membrane and electrolyte change (about 15 minutes required for change).

Requirements

Power: 10 Hg batteries, 1.35 V (Mallory RM12R or equivalent)
Weight: 3.2 kg (7 lbs)
Dimensions: 22.9 x 30.5 x 12.7 cm (9" x 12" x 5"). Lid detachable.

Features

Output: Triple scale meter-- (Gas mixtures) 0-50%; 0-10%; 0-5%; 0-1%; 0-0.5%; 0-0.1%
Training: Manual
Options: Model 100RT (with recorder) $1,275. FOB Houston TX

References

1) Manufacturer's Brochure
2) E.S. Snavely and F.E. Blount, "Rates of Reaction of Dissolved Oxygen with Scavengers in Sweet and Sour Brines," Corrosion 25, 397-404 (1969).
3) E.S. Snavely Jr., "Chemical Removal of Oxygen from Natural Waters," J. Pet. Techn. 23 (4), 443-6 (1971).
4) F.E. Blount and E.S. Snavely, "Use of Oxygen Meter in Corrosion Control," paper no. 44, NACE National Conference, Houston, TX, March 1969. See Proc. 25th Conf. NACE, pp. 193-200, Mar. 10-14, 1970.
5) Manufacturer's Booklet, "Galvanic Probes for the Drilling Industry"

*Electrical rise and fall times are about 0.6 seconds; however, the rise and fall times of the oxygen sensor depend on the magnitude of the change in oxygen concentration; less than one minute is required for 95% of the total rise or fall, but up to 5 minutes may be required for complete equilibrium.

Cost	Model 200	$675. FOB Houston, TX
Remarks	Manufacturer also markets galvanic probes suitable for oxygen monitoring in corrosion control (See Ref. 5).	
Address	Fincher Engineering Co. 6826 Addicks-Fairbanks Rt. 9, Box 909 Houston, TX 77040 Attn: Dorsey R. Fincher, P. E.; Natalie Zolan, Exec. Asst.; J. J. Marr, Engineer; Dr. James W. Ward, Consultant (713) 466-4164	

INSTRUMENTATION
FOR ENVIRONMENTAL
MONITORING

Dissolved Oxygen Analyzer

Enviro Monitor Model 1012

Class	Field/Continuous
Categories of Water	Fresh/Waste
Principle of Operation	A passive type polarographic oxygen sensor with a gold cathode and a silver anode, detects oxygen which diffuses across a Teflon membrane and is reduced at the cathode. The magnitude of the current produced is proportional to the partial pressure of oxygen. Electrode reactions:

$$\text{Anode:} \quad 2Ag + 2OH^- \rightarrow Ag_2O + H_2O + 2e$$
$$\text{Cathode:} \quad 1/2O_2 + H_2O + 2e \rightarrow 2OH^-$$
$$\text{Overall:} \quad 1/2O_2 + 2Ag \rightarrow Ag_2O$$

Minimum Detectable Sensitivity	.05 ppm (5% of F.S.)
Range	0-5, 0-10, 0-20 mg/1 (0-5, 0-10, 0-20 ppm)
Interferences	Strong oxidizing and reducing agents (e.g., HOCl, HF, SO_2, H_2S)
Multiparameter Capability	Up to seven in one monitor
Sampling	Method: In situ or online Volume: Continuous flowing sample Minimum Stream Velocity: 1.5 ft/sec (1/2 gal/min suggested inline flow) Minimum Depth: 8" Maximum Depth: 25' Maximum Temperature Input: 43°C (110°F) Collection Efficiency: N/A Maximum Number of Sample Sources: N/A

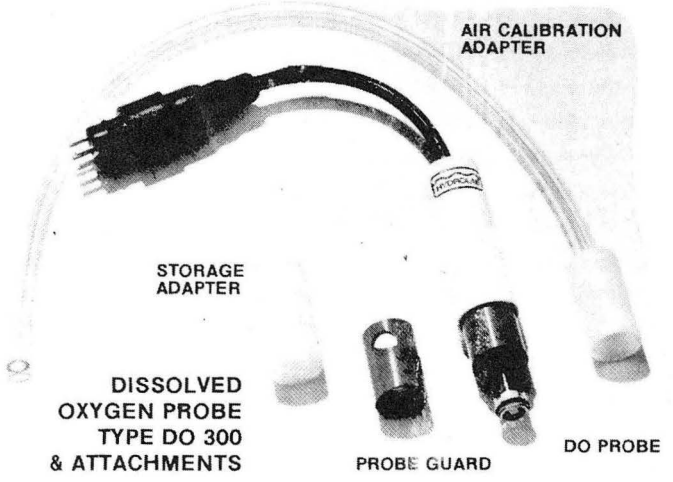
Performance	Accuracy: ±1% FS Reproducibility: ±1% of reading at any given temperature/24 hrs Linearity: ±1% of reading at any given temperature/24 hrs Noise: ±0.5% Response Time: 20 sec Lag Time: 12 sec Rise Time: 8 sec Retention Time: Flow dependent; volume = 150 cc in chamber Fall Time: 10 sec Zero Drift: ±1% FS at any given temperature/24 hrs Span Drift: ±1% FS at any given temperature/24 hrs
Operation	Ambient Temperature Range: Electronics: -29°C to 55°C (-20°F to 130°F) Sensor: 0°C to 43°C (32°F to 110°F) Temperature Compensation: Sensor accuracy compensated to 6% of reading over full 32°F to 110°F span Relative Humidity Range: Electronics to 98% Calibration: Air calibrate Procedure: A jet of sample stream is directed against the membrane Unattended Period: 1-8 weeks depending upon application Maintenance:
Requirements	Power: 115 Vac, 60 Hz, 3 A max Weight: 15.9 kg (35 lbs) Dimensions: Electronics: Single channel instrument (Model 512), 25.4 x 25.4 x 17.8 cm (10" x 10" x 7") Multiparameter (Model 1012) Electronics Package, 27.94 cm^3 (11 in^3) Sensor diameter 7.67 cm (3"); length ∿12.7 cm (5")
Features	Output: Current: 0-1 ma/1-5 ma/4-20 ma/10-50 ma Potentiometric: 0-10, 0-100 mV; 0-1, 0-5 V Training: Available Options: 1) Plug in alarm module. Adjustable over full range with selected hysteresis. SPDT alarm contacts wired to back terminal board. 2) Maximum cable length 2000 ft. Others: Sensor housings have PVC and stainless steel construction throughout
References	Enviromonitor Bulletin 1012 Information provided by the manufacturer (telephone conversations with Mr. Trawick, 6/5/74 and 6/11/74)
Cost	Includes housing, transmitter, sensor, E to I converter and 25 ft of cable $1050.
Remarks	Assembly can be mounted in-line in a flow-through housing with entrance and exit ports on opposite sides. The sensor is supplied by a pipe connected to the top of the housing. The monitor is threaded through the pipe to the sensor. The DO monitoring assembly is supplied with a standard 25' cable. Other cable lengths available on request.
Address	Gam Rad Inc. 16825 Wyoming Avenue Detroit, Mich. 48221 Attn: William Helke, General Manager for Sales of Industrial Products; Dan Mapes, Applications Engineer (313) 864-6006

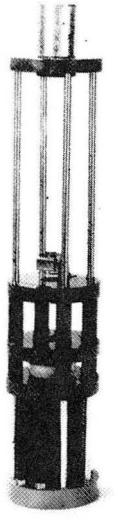
INSTRUMENTATION
FOR ENVIRONMENTAL
MONITORING

H2O-BIO
Field: DO
Hydrolab 1
Sept. 1975

Dissolved Oxygen Temperature Meter

Hydrolab Model TDO-2





MODEL 71 SELF CIRCULATING UNDERWATER SONDE

Class	Field: In situ sensor/portable
Categories of Water	Fresh/natural waters
Principle of Operation	A passive gold-silver/polarographic cell is fitted with a gas-permeable (1 mil Teflon) membrane through which oxygen from the surrounding medium may diffuse into the probe and be reduced at the cathode. The current required by the probe for reduction of the diffusing oxygen is linearly proportional to the partial pressure of the oxygen present in the medium.

Electrode reactions:

Anode: $4Ag + 4Cl^- \rightarrow 4AgCl + 4e$

Cathode: $O_2 + 2H_2O + 4e \rightarrow 4OH$

Minimum Detectable Sensitivity	.05 ppm
Range	0-10 (100 Divisions), 0-20 ppm (or mg/1), 0-100% saturation
Interferences	SO_2, H_2S, halogens poison the silver electrode.
Multiparameter Capability	Temperature not recorded separately.
Sampling	Method: Automatic sample-circulating sonde Volume: Minimum depth - sensor: 1/2 inch/not recommended sonde: 8-10 inches Maximum depth: 100 meters (330 ft) Maximum Temperature Input: 45°C Collection Efficiency: N/A Maximum Number of Sample Sources: Limited by maximum cable length to 100 meters/setting; otherwise unlimited

Performance

Calibrated DO Accuracy: Output data signal: ±2% of reading
Meter: ±2% of reading to 0.5% of range
Temperature: ±0.5°C

Reproducibility:
Linearity: Meter: 0.5%
Noise:
Response Time: 10 sec to stepchange in DO
30 sec to stepchange in temperature
Lag Time:
Rise Time:
Retention Time:
Fall Time:
Zero Drift:
Span Drift:
Readability: 0.1 ppm for 0-10 ppm setting of water

Operation

Ambient Temperature Range: -5° to 45°C
Temperature Compensation: Membrane dependence and oxygen solubility temperature coefficient are automatically compensated.
Relative Humidity Range: Up to 100% relative humidity
Calibration: Dissolved oxygen: Air, or Winkler standardized oxygen solution
Temperature: May be verified against an internal standard
Procedure: In operation, the sonde and probe are lowered at the end of an underwater cable to a desired measuring depth and the DO concentration and temperature of the water at that depth are read directly from the instrument meter. The output may be recorded as DO or partial pressure as a function of time.
Unattended Period: Minimum one week and up to six weeks
Maintenance: Depends on use. In fresh water the analyzer may run 24 hours/day for approximately 2 weeks prior to preventive maintenance. Time required to load and purge probes -- about 30 seconds.

Requirements

Power: Instrument: Three TR-132R or E-132N mercury batteries
Voltage: 2.7 V; stirrer - 9 V lantern battery
Battery Life: About 500-600 instrument hours
Sample Circulation: 130 mA, 6 or 9 Vac (lantern type battery), depending on cable length
Weight: Surface Unit: 2.7 kg (6 lbs)
Sonde: 1 kg (2.2 lbs)
Cable: 1.5 kg (3.3 lbs)
Probe: ca. 6 oz
Dimensions: Inst. Encl.: 30 x 19 x 16-1/2 cm (12 x 7-1/2 x 6-1/2 in.)
Sonde: 39 cm (15-1/2 in.)
Cables: Standard lengths: 10, 20, 50, 100 m
(See also Summary for optionals)

Features

Output: Data signal: 0-10 millivolts
Output resistance: 500 ohms
Training: Manual provided.
Membrane change may be done by non-technical personnel.
Options: For continuous recording the TDO-2 may be used in conjunction with a Hydrolab Model 400-M recorder which records DO vs time for periods up to 7 days.
Other: Controls, electronics, batteries and readout meter are protected from outside air and moisture by means of the TDO-2 case which is fitted with gasket or o-ring seals at all openings.

Instrument unit may be floated in water.

Controls extend via shaft seals through a heavy plastic viewing window for total water sealing during instrument operation.

References

Hydrolab Model TDO-2 Brochure and information provided by Mr. Jim Flynn of Hydrolab Corporation.

Cost

Basic package includes the instrument, one cable, and a maintenance kit (electrolyte, 30 membranes, and o-rings)

Model TDO-2, surface unit	$570
Probe	270

Remarks

The Model TDO-2 is used in conjunction with a type 10 CS underwater cable, a DO-3 oxygen-temperature probe and a type 71 sonde for making in situ measurements of DO.

Cables are type 10C multiconductor, urethane jacketed with oceanographic subsurface connectors and environmental surface connector; breaking strength, 300 lbs.

Measurements at different depths permit construction of DO-temperature profiles.

Electrolyte: Half-saturated KCl solution

Summary

Part (type)	Weight		Dimensions	Cost
	kg	(lb)		
Standard cables: (urethane)				
10C-10	1.135	2.5	10 m (33 ft)	$250
10C-20	2.043	4.5	20 m (66 ft)	270
10C-50	4.767	10.5	50 m (165 ft)	340
10C-100	9.307	20.5	100 m (330 ft)	450
Field case (sealed, waterproof)	2.7 kg (6 lb)		30 x 10 x 16.5 cm (12 x 7.5 x 6.5 in)	110
Sonde model	1 kg (2.5 lb)		39 cm L x 8.5 cm diam. (15-1/2 x 3-1/4 in.)	260

Address

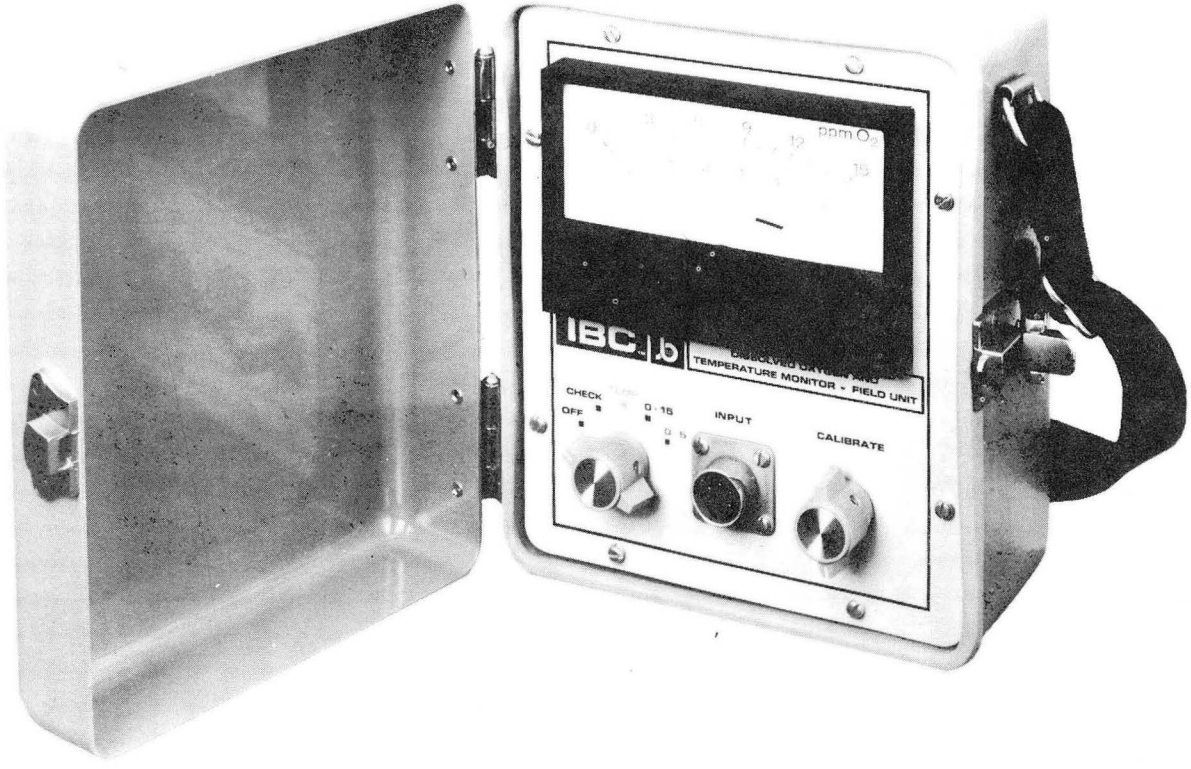
Hydrolab Corporation
P. O. Box 9406
Austin, Tx 78766
Attn: Mr. Jim Flynn or Ms. Tess Peterson
(512) 837-2050

INSTRUMENTATION
FOR ENVIRONMENTAL
MONITORING

H20:BIO
Field:DO
IBC 1
June 1975

Dissolved Oxygen and Temperature Monitor

IBC Model 490-051



Class	Field/Laboratory/Portable
Categories of Water	Fresh/Saline/waste
Principle of Operation	The oxygen sensor consists of a polarographic cell which measures partial pressure of O_2 in a gas or liquid. The anode, cathode and electrolyte gel of the sensor are separated from the sample by a semi-permeable teflon membrane (1 mil) across which the oxygen may diffuse. A polarization voltage (V) is applied across the electrodes. In the absence of oxygen, no current flows, but when O_2 is present in the sample, it will diffuse across the membrane at a rate proportional to its partial pressure (P_{O_2}) in the solution and be reduced at the cathode. Current flow is a linear function of the P_{O_2}. Overall reaction:

$$O_2 + 2H_2O + 4\varepsilon \rightarrow 4OH^-.$$

Thus for every molecule of O_2 reduced at the cathode, 4 electrons are given up by the cathode and 4 hydroxyl anions (OH^-) are formed and migrate to the anode.

For O_2 measurement, the instrument operates as a current amplifier for current generated in the sensor. The amplified current drives the indicator meter. Polarizing potential is supplied by a separate circuit.

Since polarographic sensors have temperature coefficients, current output increasing with temperature for a given P_{O_2}, and the O_2 solubility shows appreciable temperature-dependence, automatic temperature compensation which controls amplifier gain is built into the sensor by means of a temperature sensing thermistor.

Minimum Detectable Sensitivity

Range	0-5, 0-15 ppm.
Interferences	Free Halogens, H_2S, NO_x
Multiparameter Capability	Temperature, BOD
Sampling	Method: In situ sensor Volume: N/A Minimum Depth: 0-12 inches, depending on sensor. Maximum Depth: 500 ft. Maximum Temperature Input: 50° C Collection Efficiency: N/A Maximum Number of Sample Sources: N/A
Performance	Accuracy: ±0.1, 0-5 ppm; ±0.2,10-15 ppm, ±1° C Reproducibility: Better than 0.1 ppm Linearity: D.O.: ±1% F.S.; Temperature: ±1° C max. error Noise: Lag Time: 1 sec Retention Time: N/A Fall Time: See response time Response Time: 90% in 30 sec. Zero Drift: +0.1 ppm max. Span Drift: Negligible between calibrations
Operation	Ambient Temperature Range: 0-50° C Temperature Compensation: ±0.1 ppm max. error when calibrated within ±5° C of sample temperature Relative Humidity Range: 0-100%

Calibration: Since individual sensor cartridges vary, each must be calibrated. In addition, long term sensor drift requires periodic calibration. Calibration should be repeated every 24 hours, even under constant operating conditions.

For the greatest accuracy, polarizing voltage should be applied to the sensor for a minimum of 15 minutes before calibration. Simple and accurate calibration may be accomplished by exposing the sensor to ambient air. Correction tables are supplied in the operating manual for total pressure, salinity altitude, and humidity. The corrected reading will be equal to that of water saturated with air under identical conditions.

Calibration may also be accomplished by measurement of a water sample that has been prepared in a tonometer with a known gas, or a Winkler titration for dissolved oxygen may be used for calibration.

Procedure: The appropriate sensor is connected to the assembly through the front panel INPUT connector. The "CALIBRATE" knob on the face of the instrument is tuned to bring the meter reading into agreement with the calibration medium. Although recalibration every 24 hours is suggested, long term in situ monitoring may be accomplished with any required corrections applied at the end of the monitoring period.

The temperature reading requires no calibrations or preliminary warmup.

Once calibrated, the sensor may be placed in the water to be analyzed. Two scales are available, 0-5 and 0-15 ppm dissolved oxygen and the applicable scale should be selected.

Fast equilibration time permits rapid readings even under highly variable conditions. Stirring is provided on Deep Diver

and BOD Sensors and is optional on the Shallow Diver.
A rotary switch has the following operating positions:

(1) OFF: all power is disconnected;
(2) CHECK: monitors battery voltage:
(3) TEMP: Indicates temperature on the red scale (0-50° C)
(4) 0-15: Dissolved Oxygen (D.O., 0-15 ppm) on the black scale
(5) 0-5: Dissolved Oxygen (0-5 ppm) on the green scale

The CALIBRATE control is active only in the D.O. measuring positions and adjusts the gain (span) of the instrument to calibrate the sensor. (See under calibration)

Unattended Period:

Maintenance:

Requirements:

Power: 4 "C" size batteries (Eveready E93 or equivalent) and one mercury cell (Mallory RM502R or equivalent)
Weight: 2 Kg(4.4 lb)
Dimensions: 17.8 x 15.2 x 11.4 cm(7"x6"x4½") (HxWxD)

Features:

Output: To meter read out. See under options.

Training: Instruction Booklets
Options: May be used with D.O. Sensor(with stirrer) Cat. no. 501-001 Deep Diver and/or with BOD sensors 410-001 and 410-011. The monitor may also be used with DO Sensor 600-01, Shallow Diver (10 ft lead standard)
Lead lengths are available in multiples of 25 feet up to 50 ft.
A splashproof recorder output is available on special order, 0-1 V.

References:

IBC Instruction Booklet: "IBC Dissolved Oxygen & Temperature Monitor Field Unit" (Cat No. 490-051)
IBC Dissolved Oxygen Sensor With Stirrer (Cat. No. 501-001)

Cost:

490-051	Field Model (price without electrodes) batteries included	$450.00
500-051	BOD, DO and Temperature Analyzer	380.00
Options:	Laboratory Model	
300-061	Compact Model	230.00

Instruments and Sensors with Waterproof Connectors for use with Models 490-051, 500-051, and 300-061 Analyzers

410-001	BOD Sensor, 5 ft lead	$170.00
412-001	Replacement Cartridge, BOD	25.00
600-001	Shallow Diver, DO, 10 ft lead	120.00
600-021	Shallow Diver, DO, 50 ft lead	135.00
620-001	Stirring Unit, Deep and Shallow Diver	125.00
501-001	Deep Diver, DO, with Stirrer, 25 ft	280.00
501-011	Deep Diver, DO, with Stirrer, 50 ft	290.00
501-021	Deep Diver, DO, with Stirrer, 75 ft	300.00

Other lengths up to 500 ft available in multiples of 25 ft. Please specify length desired and add $10.00 for each 25 ft ordered.

526-001	Replacement Cartridge, DO	25.00

Remarks:

This instrument uses battery-powered integrated circuitry, and is packaged in a "splash-proof" case. It is specifically designed for "reliable operation under adverse conditions".

The instrument as originally shipped is equipped with long-life alkaline power batteries(Eveready E93 or equivalent) and a mercury reference battery (Mallory RM502R or equivalent). Reference batteries should be 1.30-1.35V at room temperature.

The following sensors are recommended for use with this assembly:

1) IBC DO sensor with stirrer, Cat. No. 501-001.
2) IBC Biological oxygen Demand Sensor, Cat. No. 410-001.

Both sensors are designed to use replaceable sensor cartridges.

Readings from the Model 501-001 Deep Diver and 600-001 Shallow Diver are both pressure and temperature compensated.

In-line measurements of temperature and D.O. are available with special sensor modifications.

Instruments and sensors (except cartridges) warranted against defects in materials (essentially PVC) and workmanship for one year. Cartridge life is in the range of 4-6 months and is dependent on care outlined in the operating manual.
Both sensors are designed to use replaceable sensor cartridges.

Address:

International Biophysics Corporation
2700 DuPont Drive
Irvine, CA 92664
Attn: Robert E. KLees
Vice President of Marketing

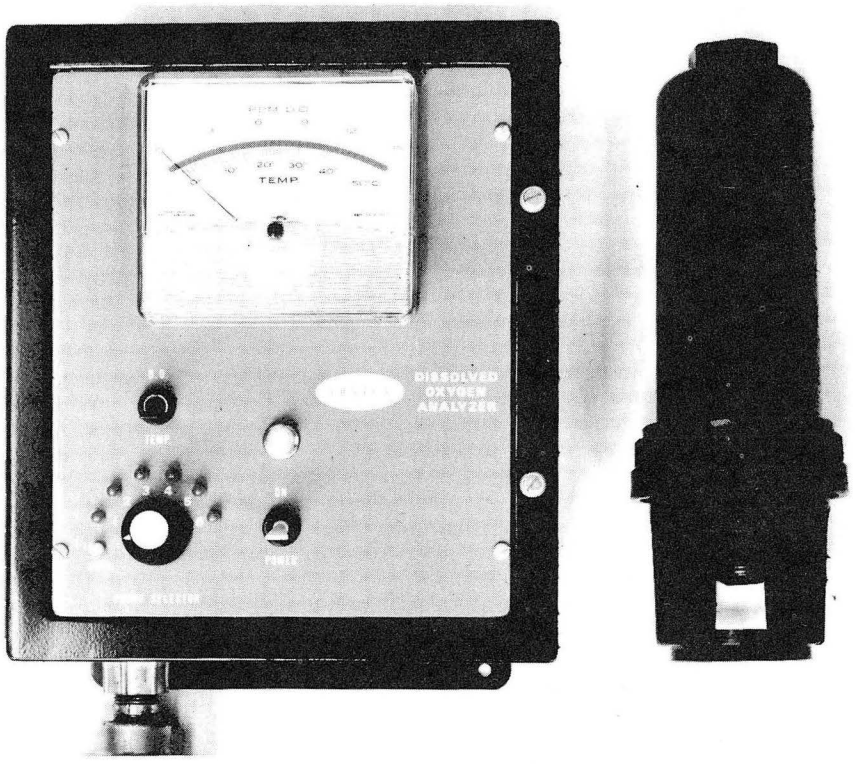
Gilbert M. Bockhaus, Sales Manager
(714)833-3300

INSTRUMENTATION
FOR ENVIRONMENTAL
MONITORING

H2O-BIO
Field: DO
Ionics 1
Sept. 1975

Dissolved Oxygen Analyzer

Ionics Model 1131S



Class	Continuous online
Categories of Water	Waste (Designed primarily for the measurement and control of Dissolved Oxygen concentration [DO] in activated sludge aeration basins)
Principle of Operation	The corrosion potential generated between an exposed Tl metal electrode and a reference electrode is proportional to [DO]. Electrode reactions: Anode: $4Ag \rightarrow 4Ag^{+} + 4e$ Cathode: $O_2 + 2H_2O + 4e \rightarrow 4OH^{-}$ Overall: $4Ag + O_2 + 2H_2O \rightarrow 4AgOH$
Minimum Detectable Sensitivity	0.1 ppm
Range	0.5-5 ppm, 1-10 ppm, 1.5-15 ppm; optional ranges up to 15 ppm DO and 50°C available on special order
Interferences	Large conductivity changes
Multiparameter Capability	Temperature
Sampling	Method: In situ, continuous flow; 5 ft/minute, minimum Volume: Depth up to 25 ft. For greater depths, consult manufacturer Minimum Depth: 1 ft Maximum Temperature Input: 50°C Collection Efficiency: N/A Maximum Number of Sample Sources: 6 Maximum Distance to Analyzer: 1000 ft. Sample Flow Rate: minimum 5 ft/min.

Performance

Accuracy: DO: ±0.3 ppm or ±3.0% of reading, whichever is larger (at constant temperature)
Temperature: ±1°C
Reproducibility: ±2%
Linearity: Direct linear readout of ppm DO and temperature in °C
Noise: N/A
Lag Time: N/A
Rise Time: DO: 15 second max. for 95% F.S. @ constant temperature. A sensor damping filter increases response time to 1 minute maximum.
Temperature: 3 min max. for 95% step change
Retention Time: N/A
Fall Time: N/A
Zero Drift: DO: 0.1 ppm/30 day period
Temperature: 0.3°C/30 day period
Span Drift: <1%/month

Operation

Ambient Temperature Range: 0-50°C
Temperature Compensation: Compensated between 10-50°C
Relative Humidity Range: 0-85%
Calibration: Winkler titration

The following procedure is recommended when starting up a new analyzer, or adjusting the analyzer to changing conditions.

A. Temperature Calibration
1. Measure the temperature of the water at the probe with an accurate thermometer.
2. Switch temperature - DO switch located on the front of the control cabinet to TEMP.
3. For a multiprobe unit, select the proper probe with the probe selector switch (front panel).
4. Remove the plexiglas cover plate located inside the analyzer and adjust the temperature - adjust control for the probe to be calibrated. This procedure is repeated for all probes. For a multiprobe instrument the temperature test reading will be the same for all probes.

B. Dissolved Oxygen
1. Place the probe in the flowing stream.
2. For multiprobe analyzers place the probe selector switch in the position corresponding to the correct probe.
3. Switch the temperature-D.O. switch to D.O.
4. Switch AC power on and allow for warm-up (i.e., the indicating meter shows no drift).
5. Collect one gallon of water in a bucket from the stream and bubble air into the sample to maximum D.O. (saturation).
6. Position the probe in the bucket.
7. Determine the actual D.O. content of the sample by an appropriate modification of the Winkler procedure.
8. Adjust the input zero control so that the meter will indicate the D.O. value.
9. Repeat the Winkler calibration until values differ by < .25 ppm and the D.O. value in the sample is steady, readjusting input zero control to get correct meter readings each time.
10. This completes the calibration and the probe may be returned to the flowing stream for measurements.

Unattended Period: 1-5 weeks depending on sample
Maintenance: Once every 6 weeks;trim electrodes

Requirements

Power: 0.1 A @ 115 V ±10 Vac, 50/60 Hz (220 V available on request)
Weight: approx. 4.5 Kg (10 lbs.)
Dimensions: 27.3 cm H x 23.5 cm W x 14.6 cm D (10-3/4" x 8-1/4" x 5-3/4")
Maximum Distance of Sensor from Analyzer: 1000 ft
Environmental Conditions: Analyzer: Should be sheltered from direct exposure to weather
Sample: Output may be affected by changes in conductivity and/or flow rate.
Materials in contact with sample: Tl metal, epoxy, polypropylene, glass ceramic, stainless steel and neoprene

Features

Output: 0-50 mV potentiometric or 0-50 μA; 1000 ΩDC recorders
Standard Outputs:

Meter: DO: 5 ppm F.S., 10 ppm F.S., 15 ppm F.S.
Temperature: 0-50°C

Options: Probe is also available in a flow chamber configuration which may be inserted into a pipeline by means of 3/4-inch pipe connections.

1131 AS Electronics for multiple switching unit. $1250.00
Permits automatic or manual switching of the single inputs of up to six probes. May be used with multipoint recorder model 1131 MPR. Probes separate.

1131 025 Probe assembly. $300.00
Includes thallium and reference electrodes in a polypropylene housing designed for standard submersible use. Cable separate.

Output Options: Any F.S. voltage up to 5 volts
Meter: Other scales available limited to 15 ppm maximum.
Current Output: 1-5, 4-20, or 10-50 mA current outputs are also available.
Optional Accessories:

1) 1131 MPR - 6 point multipoint recorder $1525.00
2) 11310 2F - In-Line Probe Assembly. The sensors are available in in-line flow configuration having 3/4" NPT inlet and outlet fittings. 325.00
3) DO/Temperature Switching Unit: Allows DO and temperature to be recorded from the same analyzer using either a single- or multipoint pen recorder. 395.00
4) Mounting Brackets: A number of suggested arrangements are available:
   1131 P - panel mounting kit for mounting electronics 25.00
   1131 BRK - mounting bracket for waste treatment plant aeration basin 65.00
5) 1131 NIV - Dust Proof water-tight enclosure for electronics. 175.00

References

1) Ionics Bulletin "Dissolved Oxygen Analyzer Model 1131"
2) Ionics Instruction Manual, Series 1131, Dissolved Oxygen Analyzers
3) Manufacturer's letter of May 10, 1974

Cost

Model 1131S (Single probe unit) $695.00

Remarks

Self-cleaning sensor consists of metallic thallium electrode, reference electrode, and temperature sensitive resistor.

The electrodes, and a temperature sensor, are mounted in a plastic probe fitted on top with a terminal strip for cable connections. The connector is protected by a gasketed watertight probe housing threaded on top to receive 1-inch conduit or pipe which supports the probe in the water and provides access for the shielded cable connecting sensors with the analyzer cabinet.

Automatic or manual switching units can handle signals from up to six separate probes.

Address

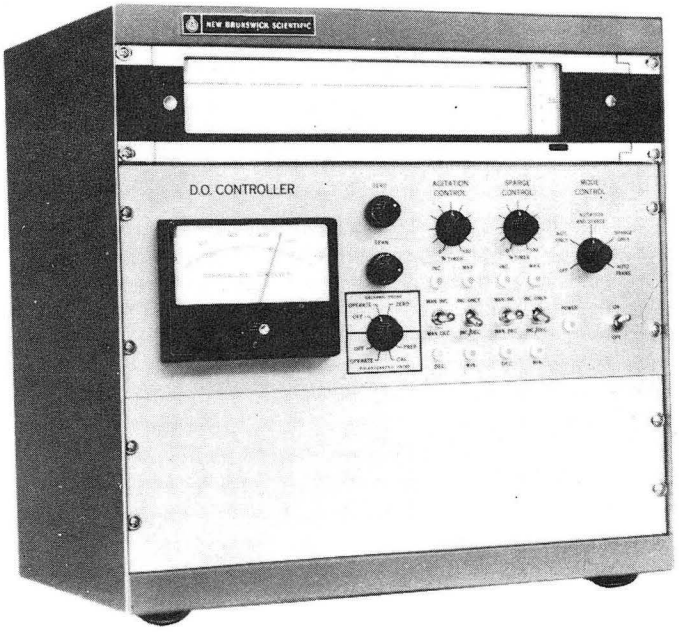
Ionics
65 Grove St.
Watertown, MA 02172
Attn: Floyd H. Meller, Technical Director, Instrument Division, or
Steven A. Michalek, Instrument Division, Applications Manager
Elizabeth Greene, Sales
(617) 926-2500

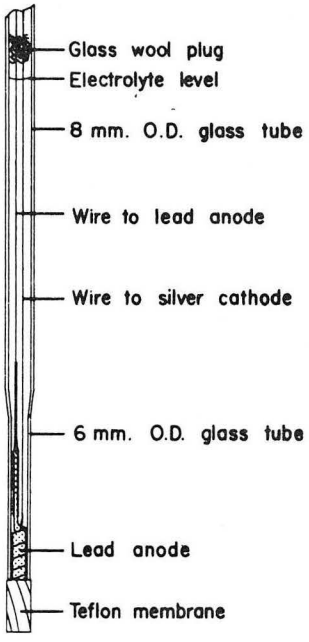
INSTRUMENTATION
FOR ENVIRONMENTAL
MONITORING

H2O-BIO
Field: DO
NBS 1
Sept. 1975

Dissolved Oxygen Controller

New Brunswick Scientific Model DO 81





Probe

Class	Batch/Continuous (Laboratory/Industrial)
Categories of Water	Fresh/Waste
Principle of Operation	A galvanic type electrode uses a silver cathode and lead anode with acetate buffered electrolyte (5 M HAc + 0.5 M NaAc + 0.1 M $Pb(Ac)_2$) confined by a Teflon membrane permeable to O_2. Inside the membrane the O_2 content is kept very low by the electrochemical reaction. Thus the rate-determining step for oxygen reduction is in effect the rate of oxygen diffusion across the membrane. The latter rate depends on the partial pressure of oxygen (oxygen tension) in the solution in contact with the membrane. Electrode reactions:

$$\text{Anode} \quad Pb \rightarrow Pb^{++} + 2e$$

$$\text{Cathode} \quad 1/2O_2 + H_2O + 2e \rightarrow 2\ OH^-$$

$$\text{Overall} \quad Pb + 1/2O_2 + H_2O \rightarrow Pb(OH)_2 \xrightarrow{[2CH_3COOH]} Pb(Ac)_2 + 2H_2O$$

Minimum Detectable Sensitivity	0.00002 Atm. O_2
Range	0-100% O_2 saturation
Interferences	sulfide conc. should be less than 40,000 Mg./ml.
Multiparameter Capability	N/A.
Sampling	Method: Batch/Continuous Volume: Varies with length of probe Maximum Temperature Input: 60°C Collection Efficiency: N/A Maximum Number of Sample Sources: One

Performance

Accuracy: ±2.0% of O_2 saturation
Reproducibility: ± 1% O_2 saturation
Linearity: Response linear from <0.00002 to >0.2 atm O_2
Noise: Not detectable
Lag Time: Instantaneous
Rise Time: 90% response in 45 seconds; probe, 99% response in ~3 minutes
Retention Time: Instantaneous
Fall Time: 90% response in 45 seconds; 99% response in ∿ 3 minutes.
Zero Drift: 0.2 MV.
Span Drift: Not more than 1%/week
Zero Current: <0.1% of O_2 saturation

Operation

Ambient Temperature Range: 20-60°C
Temperature Compensation: None
Working Pressure: Up to 50 psig
Relative Humidity Range: 0-100% O_2 saturation
Calibration: Probe is calibrated in air (after wetting so that membrane has a film of H_2O) and in air-saturated water.
Procedure: The micro-sized probe is readily mounted in a small vessel, either by insertion into a rubber stopper or compression fitting. It may be mounted vertically or sloped. Larger probes are sheathed in stainless steel housings. A variety of adaptors and probe mountings are available.
Unattended Period: 1 year with repeated autoclaving
Maintenance: Maintenance-free for long periods

Requirements

Power: Analyzers and controllers - 115 V, 60 Hz or 220 V, 50 Hz 1 phase, AC
Weight: ∿ .23 - 1.4 Kg (∿ 1/2 lb - 3 lb.)
Dimensions: Probe: 8 lengths available (see table under Options)
Cable: 6 ft
Controller:

Features

Output: 10 mV, 1000 Ω
10 μA @ 30°C and 100% O_2 saturation
Zero current <0.1% of O_2
Training: Operating Manual

Options: Probe lengths from 8" to 53"

PROBE SPECIFICATIONS

ELECTRODE BODY	Glass electrode permanently encapsulated in a type 316 stainless steel immersion holder of 5/16" diameter				
HOLDER SIZE	3/8" N.P.T.				
MEMBRANE	Teflon				
PROBE LENGTHS*	Overall	Immersion Depth	Vessel Size	Cost	
M1016-0200	8"	5"	2 L.	$140	
M1016-0202	12"	9"	5 L.	140	
M1016-0201	17"	14"	7.5 & 14 L.	140	
M1016-0203	20"	17"	28 L.	180	
M1016-0204	25"	22"	50 L.	190	
M1016-0205	31"	28"	75 & 130 L.	210	
M1016-0206	40"	37"	150 & 250 L.	230	
CABLE	6 ft. length			15	

Features (cont'd.) Options:

O_2 ELECTRODE (Less Cable and Adapters)

PART NO.	DESCRIPTION				FOB PRICE
	COMPONENTS	OVER-ALL LENGTH†	IMMER-SION DEPTH	FERMENTOR SIZE	
M1016-0202	O_2 Electrode Steam-Sterilizable with Immersion Holder and Shorting Jack	12"	9"	5 Liters	$140
M1016-0201		17"	14"	7.5 & 14 Liters	$140
M1016-0203		20"	17"	20 Liters	$180
M1016-0208	Dissolved O_2 Glass Electrode, repeatedly autoclavable, (less connecting cable) 17.5 cm immersion depth				$115

CONNECTING CABLE

P0720-2010	6 ft. length* with amphenol plug for connection to electrode, and pin-jack terminals.	$15

*Additional lengths available at 50¢ per ft. additional.

O_2 ANALYZERS & CONTROLLERS (LESS ELECTRODE)

Please Specify Size of Culture Vessel and Electrical Service

MODEL NO.		DESCRIPTION	ELECTRICAL SERVICE	FOB PRICE
1	DO-40	O_2 Indicator	115 V 60 Hz and 220 V 50 Hz, 1 Phase, A.C.	$525
2	DO-50	O_2 Indicator and Recorder		$825
3	DO-81	O_2 Indicator, Expanded View Recorder and Exponential Controller for bench scale equipment		$3,340
3	DO-82	Same as above but panel-mounted in pilot plant fermentors		$3,340
PO540-1010		Chart Paper, O_2 recorder, (31-day) calibrated in % O_2, 6 rolls/ctn. 1 carton supplied with DO-50 and DO-80 series.		$40/ carton of 6

References

a) Manufacturer's Brochure "Dissolved Oxygen Electrodes and Control Systems"
b) M.J. Johnson, J. Borkowski, and C. Engblom, "Steam Sterilizable Probes for Dissolved Oxygen Measurement", Biotechnology and Bioengineering VI, pp. 457-68 (1964); *ibid.* IX (4), "Communications", pp. 2-6 (1967) (NBS reprint booklet).

Cost

Model DO 81 (less electrode)	$3340

Remarks

Probe life expectancy manufacturer claims in excess of 1 year of continuous use with repeated sterilization. Can be used with three different instruments for O_2 measurement and control.

The model DO-81 dissolved Oxygen Controller was designed primarily for use with NBS fermentation equipment. For other applications the Model DO-40 Dissolved Oxygen Indicator or the Model DO-50 Indicator/recorder are recommended by the manufacturer. (See table 1, p. 3.)

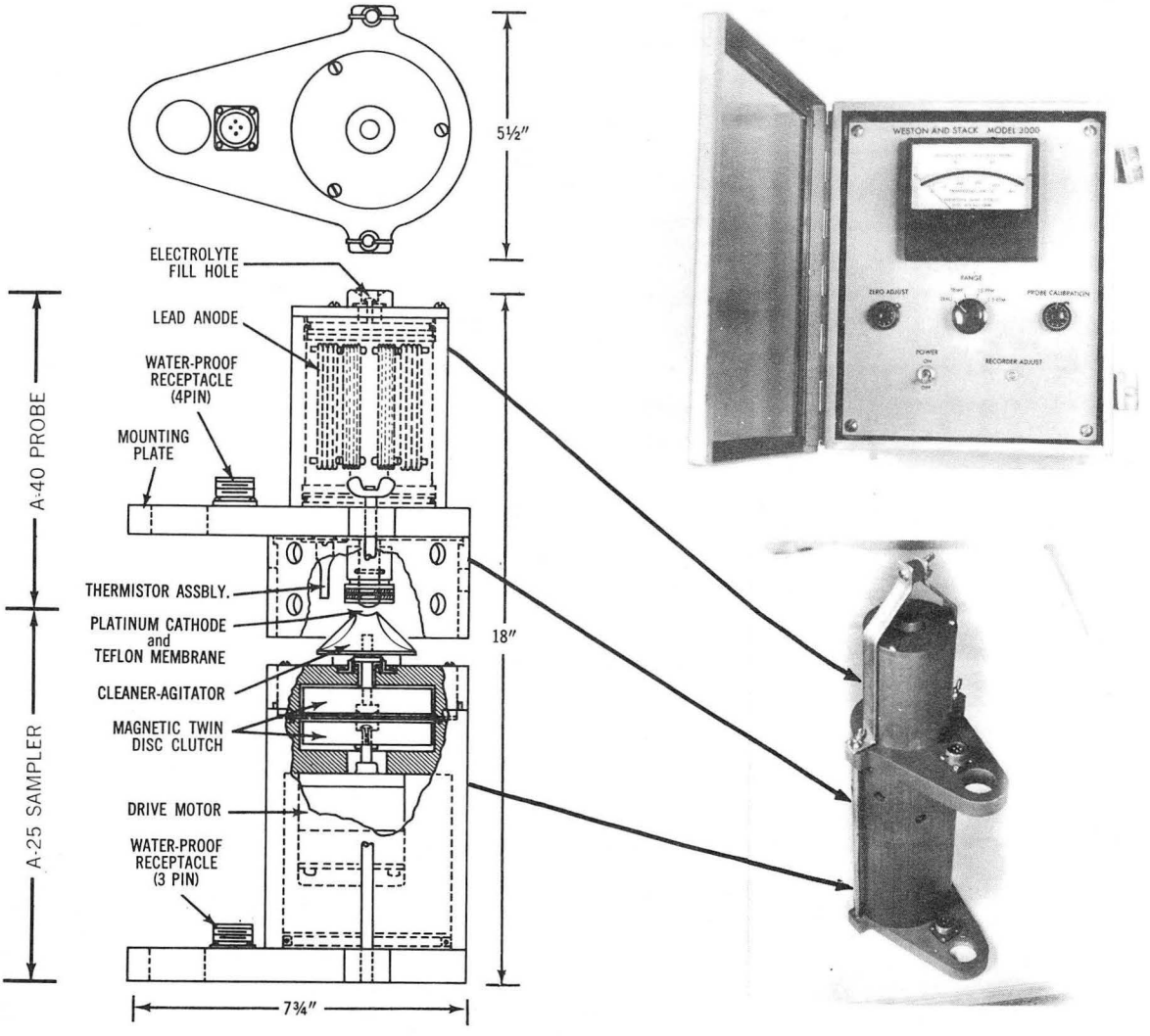
Address

New Brunswick Scientific Co., Inc.
1130 Somerset Street
New Brunswick, NJ 08930
Attn: Ezra Weisman, Sales Manager
Tel: (201) 846-4600

INSTRUMENTATION
FOR ENVIRONMENTAL
MONITORING

Dissolved Oxygen Analyser

Weston and Stack Model 3000



Class	Continuous-sensor, stationary
Categories of Water	Fresh/Saline/Waste (sewage - activated sludge)
Principle of Operation	A polarographic cell consisting of a lead anode and platinum cathode functions galvanically, producing 0.6 volts potential. The probe is separated from the sample by a semipermeable membrane. For a given set of physical conditions the rate of diffusion across the membrane is directly related to the concentration of oxygen in the sample.
	Electrode Reactions: Anode: $Pb + 2OH^- \rightarrow PbO + H_2O + 2e$ Cathode: $1/2\ O_2 + H_2O + 2e \rightarrow 2OH^-$ Overall: $Pb + 1/2\ O_2 \rightarrow PbO$
Minimum Detectable Sensitivity	.05 ppm on 0-15 ppm scale .005 ppm on 0-1.5 ppm scale
Range	0-1.5, 0-15 mg/1 (ppm); 0-50°C ±1°C
Interferences	Limited to gases to which the membrane is permeable, and which can be reduced by hydrogen at -0.578 V (e.g., free chlorine gas and NO_x). Not affected by H_2S

Multiparameter Capability

Direct temperature readout, 0°-50°C

Sampling

Method: Continuous
Volume:
Maximum Temperature Input: 50°C
Collection Efficiency:
Maximum Number of Sample Sources: Probe may be placed at any desired point in the system.
Minimum Flow Rate: None. Pumping and agitation is built in.

Performance

Accuracy: 1% of reading on either DO scale; limited by meter movement
Reproducibility: Better than 0.1 ppm on the 0-15 ppm scale; 0.5% with recorders
Linearity:
Noise:
Lag Time:
Response Time: Function of membrane thickness

Up scale	Down scale
1/2 mil - 15 sec	1/2 mil - 20 sec
1 mil - 30 sec	1 mil - 90 sec
2 mils - 1 min	2 mils - 180 sec

Retention Time:
Fall Time:
Warm-up Time: Approximately 15 min
Zero Drift: <.05 ppm long term drift
Span Drift: <.01 ppm/°C drift
Depth: 350 ft (maximum tested); minimum - about 4 inches

Operation

Ambient Temperature Range: 0-50°C ±1°C
Temperature Compensation: Thermistor compensates within ±2% over the temperature range (0-50°C); ±1% within 10°C span of probe.
Relative Humidity Range: Up to 100%

Calibration: a) Recommended procedure: Remove probe from aeration basin, rinse to remove accumulated solids, and place it in a bucket of tapwater. The DO concentration is determined first by the Winkler titration. Sample water should be slightly warmer than ambient temperature and nearly saturated with oxygen so that the DO level does not change significantly during calibration.

b) Alternate procedure: Remove probe from aeration basin and expose it to air for about 15 minutes. As the probe dries, the assembly approaches ambient temperature and the output is equivalent to that of water saturated with oxygen at ambient temperature. The ambient temperature is obtained by switching the selector knob to the temperature position and the appropriate DO value may then be read from a table of saturation DO values for pure water. Note: This method is not suitable for waste water containing >1,500 mg/l dissolved solids.

Procedure: The assembly, including the A-40 DO probe and the A-25 cleaner-agitator, is submerged in the activated sludge mixed liquor. Cables with waterproof connectors bring power to the motor in the cleaner-agitator unit and transmit signals from the probe and thermistor to the DO analyzer.

Unattended Period:
Maintenance: Varies with use: Based on an uninterrupted (unruptured) membrane under normal conditions the analyzer may run as long as 6 months, but preventive maintenance is recommended every 30 days.

Requirements

Power: Sampler: 110 Vac or battery operated with high efficiency inverter 10 watts power drain by motor at 280 rpm
Weight: Analyzer-- 10 kg (22 lb). A40 Probe/A25 Agitator -- 6.4 kg (14 lb)

Requirements (Cont'd) Dimensions: Model 3000-1-A--Wall Mount JIC Type--30.5 cm x 20.7 cm 14 cm (12" x 10-1/2" x 5-1/2")
Model 3000-1-B--Rack Mount Panel--48.3 cm x 22.2 cm x 33 cm (19" x 8-3/4" x 13")
Model 3000-1-C--Panel Mount, Slideout Chassis--15.25 cm x 15.25 cm x 43.2 cm (6" x 6" x 17")

Features

Output: Recorder: 0-1 V full scale output for both ranges
Current output recorder: 0-10, 4-20, 10-50 ma
Probe: Zero at zero DO, repeatable

Training: Factory-trained service technician is furnished to supervise initial operation of the system and instruct plant personnel in operation and maintenance. Membranes are simple to replace.

Options: W & S RC-1 Remote readout and calibration unit
Strip chart single pen recorder (multipoint type)
For multipoint systems: W & S Model S-6 switching box, plus the proper number of probes (max. cap. - 6 probes).

Materials and Design:
1) Cleaner-agitator is made of silicone rubber and may be set to provide continuous wiping of membrane under extreme fouling conditions, as in the presence of oil and greases.
2) Membrane: 2 mil Teflon - life about 1 month when used with cleaner-wiper
3) Supporting electrolyte: Potassium Iodide - 325 ml (solution used: 50 mg KI/100 ml)
4) Pb anode: Minimum 430 sq cm exposed to electrolyte

Other: Connections and mounting: Extension cords available as follows
a) two water proof cords - 2-conductor for power, one 4-conductor for signals
b) Y-adaptor and one 6-conductor power cable
Mounting holes provided for fastening to standard 1" pipe (Pipe mounting fixtures are available)

References

1) Weston and Stack Design Manual - Monitoring and Control of Dissolved Oxygen in Activated Sludge Systems
2) Weston and Stack Bulletin 3000 - Continuous Oxygen Monitoring: Dissolved Oxygen Analyzer

Cost*

Analyzer: W & S Model 3000-1-A (or 3000-1-B)**	$700
W & S Model A40 Probe Comes with a supply of 24 membranes	335
W & S Model A-25 cleaner-agitator-sampler	355
W & S Model RC-1 Remote readout and calibration unit (optional)	300
Standard 25 ft Y-adaptor 6-conductor cable unit (Lengths up to 2,000 ft are feasible)	90
Maintenance kit for probe includes complete set of o-rings, 24 membranes (1 mil & 2 mil), 32 oz. of electrolyte, a fill screw washer kit, fill-cap assembly, and membrane holder assembly.	70
Agitator maintenance kit: 0-rings shaft, sleeve bearing, thrust button & washer kit, grit seal & impeller wiper assembly.	50
Special Mounting Bracket, including standard lower and upper mounting plates	125
Current output recorder (Optional)	75
Instruction Manual for operation and maintenance provided. Additional manuals	5.50

* Price breakdown is informational only. Products are priced and sold on a systems basis only including start-up, etc.

** A - Denotes enclosure is a JIC Box
B - Denotes enclosure is a Relay Rack
1 - Denotes a single channel system

Remarks

Direct contact of cleaner-wiper with membrane is required in the presence of oil or grease.

Conductors carrying probe signal need not be shielded. Long conductor lengths are feasible.

Separate recorder output calibration adjustment.

Information obtained from manufacturer's literature or supplied by manufacturer on request.

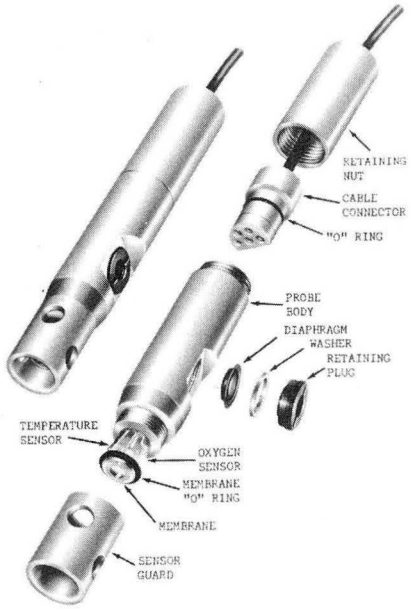
Address

Rexnord Instrument Products
446 Lancester Avenue
Malvern, PA 19355
Attn: William Wilkins–Market Manager
or
Edward Woytowicz–Sales Manager

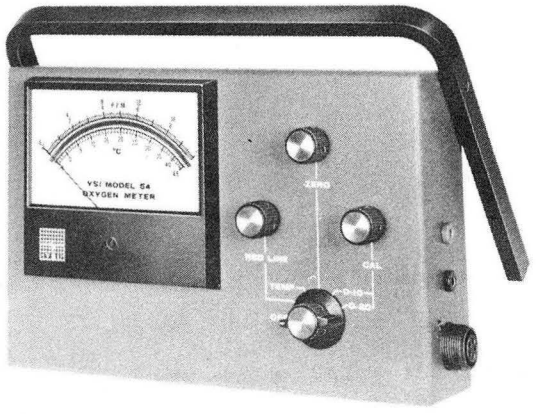
INSTRUMENTATION
FOR ENVIRONMENTAL
MONITORING

Dissolved Oxygen Analyser

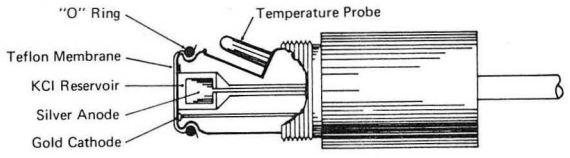
YSI Model 54A



YSI 5739 Dissolved Oxygen Probe



YSI Model 54A Dissolved Oxygen Meter



Class	Field/Lab/Portable
Categories of Water	Fresh/Waste
Principle of Operation	The YSI oxygen probe is a Clark type polarographic electrode system consisting of an annular gold cathode imbedded in a lucite block, and a silver anode recessed in a central well. The interior is filled with an aqueous solution of KCl. A thin Teflon membrane permeable to gases stretched across the end of the sensor isolates the sensor elements from the environment. When a suitable polarizing voltage of 0.65 to 0.8 volts is applied across the cell, oxygen will be reduced at the cathode, causing current to flow in an amount proportional to the partial pressure of oxygen at the membrane surface. Since oxygen is consumed at the gold cathode, the oxygen pressure inside the membrane is effectively zero, and the force causing oxygen to diffuse through the membrane is therefore proportional to the absolute pressure of oxygen outside the membrane. Thus a linear relationship is established between cell current and external oxygen pressure. Electrode reactions: Anode $2Ag + 2Cl^- = 2AgCl + 2e$ Cathode $1/2O_2 + H_2O + 2e = 2OH^-$
Minimum Detectable Sensitivity	0.05 ppm on 0-10 scale 0.10 ppm on 0-20 scale
Range	0-10 and 0-20 ppm scales 0-5 and 0-10 ppm with YSI 5937 High Sensitivity Membrane
Interferences	Halogens, H_2S, NO_x
Multiparameter Capability	Temperature

Sampling

Method: In situ probe
Volume:
Maximum Depth: 600 ft
Minimum Depth: None
Maximum Temperature Input: 45°C
Collection Efficiency: Not Applicable
Maximum Number of Sample Sources: Unlimited

Performance

Accuracy:
Meter: ±0.1 ppm on 0-10 scale; ±1% F.S. at temperature of calibration
Temperature: ±0.7°C (including probe)
Automatic Temperature Compensation: See under "Temperature Compensation"
Amplifier and Circuit: ±0.05%
Readability: 0.05 ppm on 0-10 ppm scale; 0.10 ppm on 0-20 ppm scale; Temperature readable to 0.3°C
Reproducibility: Instrument temperature stability, 2% of reading for each 25°C change of instrument temperature
Linearity: cell current is directly proportional to oxygen pressure under fixed conditions.
Noise: Not Applicable
Lag Time: Not Applicable
Rise Time: 30 sec for 95%
Retention Time: Not Applicable
Fall Time: 2 min for 99% to zero
Zero Drift: Trimable to zero
Span Drift: Negligible between calibrations

Operation

Ambient Temperature Range:
Probe: -2° to +45°C
Instrument: -5° to +45°C with NiCd batteries (54 RC)
+5° to +45°C with Hg batteries (54 BP)
Temperature Compensation: Automatic temperature compensation for membrane coefficient and solubility of oxygen in water:
±1% of reading within ±5°C span of probe temperature;
±3% of reading over entire range of -2° to +45°C probe temperature.
Relative Humidity Range: 0 to 90%
Calibration: Air or other standard of choice
Procedure: The probe, after air calibration, is lowered into the water sample which is stirred, or the probe is kept in motion. The DO and temperature are read directly in ppm and °C.
Unattended Period: Not Applicable
Maintenance: Battery service and probe service

Requirements

Power: 54 BP - Four 1.35 V mercury cells (ca 1000 hr)
54 RC - Four 1.25 V Ni-Cd cells (3 yr life; recharge every 100 hr)
Weight: 2.5 kg (5 lb)
Dimensions: Instrument - 25.5 cm x 9 cm x 16.5 cm (10" x 3-1/2" x 6-1/2")

Features

Output: Recorder 0 to 125 ± 15 mV
Training: Minimal - a few minutes of operator training are required
Options: Model 54 RC is powered by rechargeable batteries and contains a built-in charger operable on-line or on batteries.

Model 54 BP uses disposable Hg batteries (1000 hr life). It may be converted to a rechargeable model by means of a kit.

Model 51 A - similar to above, but has a salinity correction dial and can be read out in % saturation.

See also "Cost" under "Options"

YSI 5988 Carrying Case

YSI 5075 Calibration Chamber With
YSI 5739 Dissolved Oxygen Probe

YSI Model 51B Dissolved Oxygen Meter

YSI Model 54ARC Dissolved Oxygen
Meter with YSI 5492A Battery
Pack and YSI 5739 Dissolved
Oxygen Probe Mounted in YSI 5795
Submersible Stirrer

References

"YSI Dissolved Oxygen Meters," May 1972

Cost

Model 54A BP Oxygen Meter	$450.00
Model 54A RC Oxygen Meter (117 Vac 50-60 Hz Battery Charger)	480.00
Model 54A RC-230 Oxygen Meter (230 Vac 50-60 Hz Battery Charger)	510.00
Model 51B Oxygen Meter	355.00
Accessories:	
YSI 5775 Probe Service Kit, includes 0.5M KC1, membranes, replaceable o-rings	6.00
YSI 5075 Field Calibration Chamber	57.50
YSI 5776 High Sensitivity Membranes (15 pcs.)	6.00
YSI 5791 Submersible Stirrer, 50' lead (For longer leads place "X" after the part number, add $20.00 plus $0.35/ft. over standard length	201.00
YSI 5492A Battery Pack, including two 6 Vdc batteries	50.00
YSI 5988 Carrying Case	55.00
Probes:	
YSI 5739 Oxygen Temperature Probe	110.00
Order leads separately; 6 std. lead lengths:	
5740-10	29.00
5740-25	46.00
5740-50	57.50
5740-100	69.00
5740-150	95.00
5740-200	103.00
YSI 5720 Self-Stirring BOD Bottle Probe (117 Vac 50-60 Hz Stirrer)	275.00
YSI 5720-230 Self-Stirring BOD Bottle Probe (230 Vac 50-60 Hz Stirrer)	310.00
YSI 5450 Non-Stirring BOD Bottle Probe	140.00

Remarks

Available only from YSI franchised dealers. List provided upon request.

Address

Yellow Springs Instrument Company
Box 279
Yellow Spring, OH 45387
(513) 767-7241
Attn: Dick Horn

CONTENTS
FOR
BIOCHEMICAL OXYGEN DEMAND

INTRODUCTION

The early recognition of a relationship between the presence of microorganisms and organic matter in waters and their utilization of oxygen provided the impetus for the development of the present standard analytical procedure known as the *Biochemical Oxygen Demand (BOD)* test. (See Section 1. for a quantitative definition of BOD.) For more than 60 years BOD has been used to measure the presence of growth-supporting organic substances in aqueous solutions. First recommended in 1912 by the British Royal Commission on Sewage Disposal (Ref. 1) as a standard test of the purity of river waters and sewage effluents, the *5-day BOD test* was ultimately adopted in preference to the then current chemical (4-hour permanganate) test as the most sensitive quantitative indicator of organic pollution. Of all laboratory processes the BOD test came closest to reflecting actual in-stream conditions of oxygen depletion (Ref. 2). For example, in its study the Commission found that while chemical oxidation of either filter or tank effluents with potassium permanganate ($KMnO_4$; Section 3.3.1) might yield similar oxygen demand (OD) values, BOD analyses invariably resulted in much higher OD values for tank effluents. Consequently, the 5-day BOD test was adopted as "the most trustworthy chemical index of the actual state of a stream". It was further observed that if the BOD analysis was ≤ 4 ppm*, the stream would not show any apparent signs of pollution. Based on this maximum value for BOD (4 ppm), rivers were classified by the Commission according to their degree of pollution:

Table 1
(from Ref. 2, p. 131)
Royal Commission classification of rivers

Approximate 5-day BOD (ppm)†	Classification
1	Very clean
2	Clean
3	Fairly clean
5	Doubtful
10	Bad

†The Royal Commission used an incubation temperature of 18.3°C (65°F). The standard temperature now used is 20°C.

*Currently, the c.g.s. system of units (mg/l) is preferred to ppm. The latter terminology is used here for reasons of historical accuracy.

For a clean stream (BOD 2 ppm) providing a minimum of 8-fold dilution with clean water, it was calculated that the maximum BOD of sewage effluent should not exceed 20 ppm (Ref. 1). This maximum permissible figure was derived from the following considerations and the application of the law of mixtures:

Assuming the maximum safe BOD value for a stream to be 4 ppm, if

x = 5-day BOD (ppm) of the sewage effluent,

y = 5-day BOD (ppm of the stream just above the outfall (2 ppm), and

z = dilution factor (8) = the ratio of stream water to effluent moving past the outfall; then, from the law of mixtures,

$$4\ (z + 1) = (x \times 1) + (y \times z)$$

$$4\ (8 + 1) = x + 16$$

$$\therefore x = 20$$

Hence, assuming the arbitrary criterion of 2 ppm BOD for the above "clean" stream, the BOD of the sewage effluent may not exceed 20 ppm.

Biochemical Oxygen Demand defines the respiratory needs of a biologic community over a specified period of time, usually five days, expressed as mg/l of oxygen consumed. Microorganisms obtain their energy for cellular synthesis by the oxidation of organic substances available to them in the aquatic environment. Equation 1 depicts a typical aerobic respiration process using a biodegradable carbonaceous substance, glucose, as the energy source:

$$C_6H_{12}O_6 + 6O_2 \rightarrow 6\ CO_2 + 6H_2O + \text{energy} \qquad \text{(Eq. 1)}$$

Other energy sources function similarly to produce energy and the corresponding oxidative degradation products of the material utilized in the process. In waters containing relatively large amounts of organic substances, bacteria will consume most of the available oxygen. Most natural waters also contain algae populations which contribute to the BOD via their cellular processes or by functioning as degradable organic matter. The presence of algae can result in misleadingly high BOD values because of their increased oxygen demand (OD) in the dark resulting from their respiration.

A plot of BOD vs. time (Fig. 1) for waters polluted with organic wastes typically has a steep initial slope which decreases gradually,

plateauing as the *ultimate oxygen demand* value is approached. The curve is best expressed by Equation 2 below:

$$y = L(1-10^{-k_1 t}), \qquad \text{(Eq. 2)}$$

where

y is the BOD at time t
L is the ultimate oxygen demand when organic oxidation is essentially complete
k_1 is a rate constant, and
t is the time elapsed from the onset of oxidation.

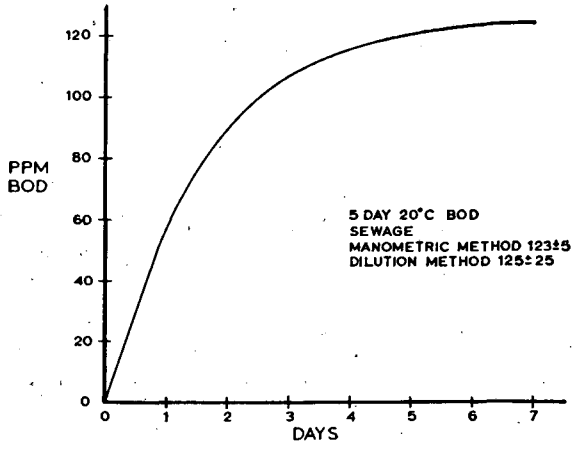


Figure 1. Rate curve, sewage (Ref. 52).

The *oxygen depletion curve* described in Equation 2 is related to the standard bacterial growth curve (Equation 3):

$$N_t = N_o e^{kt}, \qquad \text{(Eq. 3)}$$

where

N_o is the initial number of bacterial cells,
N_t is the number of cells at time t,
e is the natural logarithmic base, and
k is a growth constant.

The leveling off which occurs in the 5-day BOD curve (Fig. 1) parallels the exhaustion of initial biodegradable substrate in the sample.

1. Definition

Biochemical Oxygen Demand (BOD) is defined as "the quantity of oxygen required for biological and chemical* oxidation of water-borne substances under conditions of test" (Refs. 3, 4, 42). The BOD test (Section 7) is an empirical procedure used to determine the relative oxygen requirements of waters such as plant effluents, municipal waste waters, and receiving waters. It is widely used in the measurement of *waste loadings* in sewage treatment facilities. The *BOD removal* ability of a waste treatment facility is regarded as a measure of its functional efficiency.

Standard BOD test conditions include dark incubation of the sample at 20°C for a specified time -- frequently 5 days (Ref. 41). Since the complete *stabilization* of some wastes may entail impractically long incubation times, the 5-day incubation period has been universally adopted in the standard BOD procedure used by water analysis laboratories (Ref. 7). BOD measurements are usually reported in mg/l (preferred units) or ppm.

In the case of some industrial wastes, it is best to obtain an oxidation vs. time curve, particularly if one wishes to convert the data obtained from one incubation period to another. The assumption that all BOD rates follow simple exponential (first order) kinetics can lead to serious error (Ref. 7).

2. Factors Influencing BOD

Because the BOD determination is a biochemical test which depends on bacterial activity, it is not unexpectedly susceptible to error from a number of sources. Weston (Ref. 8) indicated that a minimum of 18 variables may influence the BOD test appreciably. In the following sections some of the most important of these factors will be discussed.

2.1 Temperature

The rate at which a biodegradable substrate is utilized by organisms in a biological system is temperature dependent. This stems from two factors:

1) The temperature dependence of chemical reaction rates in general, as described by the Arrhenius equation:

$$k = Ae^{-E/RT} \qquad \text{(Eq. 4)}$$

Here, k is the rate constant in reciprocal time units and

A = constant
E = energy of activation
R = gas constant, and
T = absolute temperature.

2) The effect of temperature on the rate of diffusion of substrate to the organisms in-

volved. This diffusion effect will not be considered here: for further information the reader may consult Refs. 9 and 10.

The Arrhenius equation was first proposed in 1889 to describe simple chemical reaction rates and was later extended by him to more complex biochemical systems. Here the activation energy E in Equation 4 denotes the overall activation energy for the organism(s) in a given system. The differential form of Equation 4 is also known as the van't Hoff equation:

$$\frac{d(\ln k)}{dT} = \Delta E/RT^2 \qquad \text{(Eq. 5)}$$

where k, E, R and T represent the values previously indicated for the Arrhenius equation (Eq. 4).

Temperature effects on the rate of substrate utilization have also been expressed in terms of *rate ratios* for substrate utilization -- the so-called Q_{10} *value*. This is simply the ratio of the substrate utilization rate for any temperature T to the corresponding rate at temperature T-10°. From the logarithmic form of Equation 5 one may infer the value $Q_{10} = 2$ in thermobiological reactions -- i.e., for every 10° rise in temperature the rate of reaction should double. This is known as the *van't Hoff rule* (Ref. 11). Thus, given the activation energy E of a biosystem, the Q_{10} value may be calculated. For example, using the E-value 14,200 cal/M for *E. Coli* (Ref. 12) and assuming that this value holds for the complex enzymatic reactions which occur in this system, the Q_{10} value obtained between 20 and 30°C is 2.23 (see Fig. 2(a).

It should be emphasized that the van't Hoff rule is a simple rule-of-thumb, to be applied cautiously. Used in this manner it generally furnishes a conservative estimate of the Q_{10} value (Ref. 13).

Streeter and Phelps (S-P) in their study of factors related to oxidation and re-aeration in the Ohio River (Ref. 14) developed the empirical expression below:

$$\frac{K'}{K} = \Theta^{(T'-T)} \qquad \text{(Eq. 6)}$$

where Θ is a thermal coefficient. K and K' are reaction velocities at temperatures T and T', respectively. For the average value of Θ=1.047 adopted by S-P, a Q_{10} value of 1.58 was obtained (Fig. 2(b)) is a comparison of rate-temperature curves obtained using the Arrhenius expression and the S-P formulation.

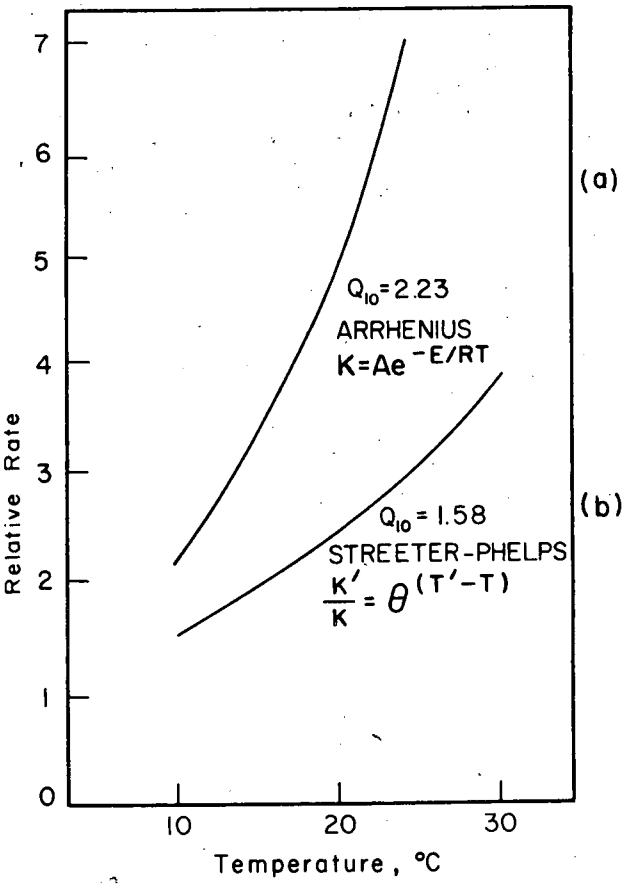


Figure 2. Rate temperature relationship (Ref. 9).

The S-P equation has been commonly employed to predict changes in reaction rate with temperature. However, as has been indicated (Section 11.1) the assumption of first order dependence of reaction rate on substrate is invalid. Busch concluded that the *soluble* component of substrate in a BOD bottle has been utilized within ca. 24 hours (Ref. 15). This reaction follows the bacterial growth curve, plateauing when the substrate has undergone complete conversion to energy and cellular materials. Respiration of the microbial population continues beyond this plateau stage, with cellular materials as substrates. Following the plateau, oxygen uptake is still partially contributed by the bacterial population, but it is attributed primarily to the growth of zooplankton which feed on the bacteria. Fig. 3 illustrates graphically the correlation suggested between utilization of substrate and microbial growth

in a BOD bottle. On the basis of this picture, the original substrate system is depleted when the plateau appears. Thus the rate of substrate utilization must be calculated on prior data. This explains the failure of the BOD curve to follow first order kinetics throughout. Phelps did in fact recognize the discrepancy and pointed out that it was indeed reasonable for the BOD curve to mimic the bacterial growth curve (Ref. 16).

Since the Arrhenius equation was originally developed for thermochemical reactions of the type occurring (enzymatically) within bacterial systems, Equation 4 is regarded as accurately descriptive of these biosystems. Starting with basic thermodynamic principles, Eyring also developed a slightly different relationship which agreed well in the moderate temperature range encountered in these biosystems.*

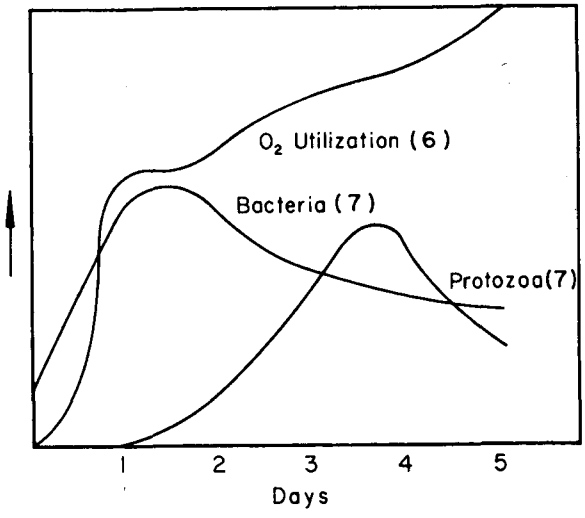


Figure 3. Changes in microbial-population with oxygen utilization (Ref. 9, p. 957).

For a system using sewage seed and glucose as the substrate, Busch (Ref. 9, p. 954) computed Q_{10} values on BOD progressions between 20° and 30°C to be about 1.35. This is well below the value predicted from the Arrhenius equation and from van't Hoff's rule for the system in question.

*Reference 11, Section 59c, "The Activated-Complex Theory of Reaction Rates" pp. 610-613 incl.; see also Sections 59a, b, pp. 606 ff, for a discussion of the Arrhenius equation and Collision Theory of Reaction Rates, respectively.

Only soluble substrate is utilized by bacteria; thus undissolved substrate must be solubilized before it can be converted either to energy or to new cellular materials. Once dissolved, the nutrient substrate must *diffuse* into the organism. Rate of diffusion of the substrate across the cell membrane is therefore an important temperature-dependent variable. Calculation of a Q_{10} value for glucose allowing for the effect of temperature on the diffusion coefficient of glucose in water results in a value of 1.3, which is in good agreement with the Q_{10} value calculated earlier on the basis of the experimental rate of substrate depletion (1.35). This is construed as evidence that the diffusion of substrate does actually constitute the rate-determining parameter related to the observed temperature dependencies (see Fig. 4).

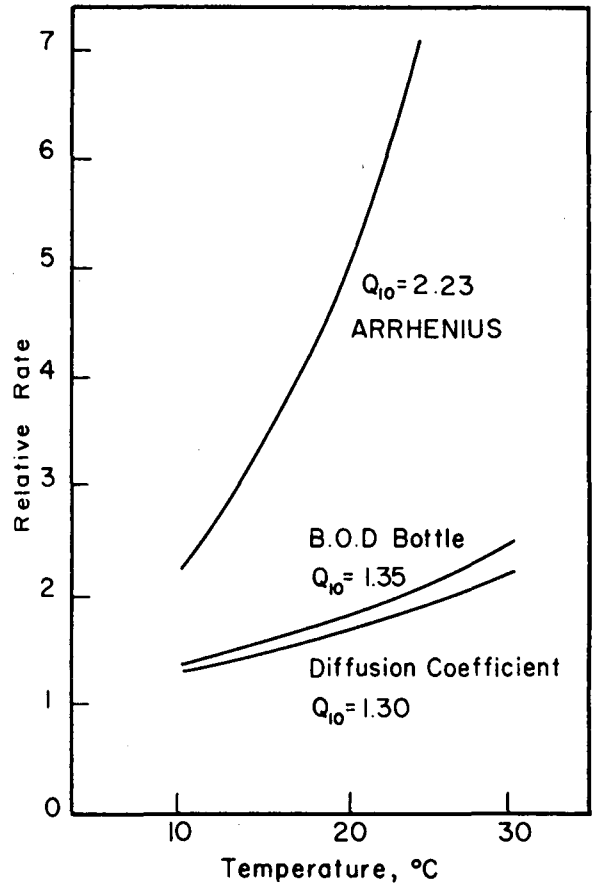


Figure 4. Rate temperature relationship (Ref. 9, p. 958).

Kehrberger et al have applied diffusion theory to a model bacterial substrate system and shown that:

1) The effect of temperature on substrate utilization in a quiescent BOD bottle is indeed diffusion dependent.
2) Agitation or stirring of the sample during incubation results in a higher Q_{10} value by favoring *reaction limiting* conditions -- i.e., conditions providing maximum nutrient at the bacterial membrane.

Since a temperature change of as little as 1°C can produce a significant change in the BOD value of an effluent because the growth rates of bacteria and algae are strongly influenced by temperature, this parameter must be carefully controlled and accurately measured.

The standard temperature for BOD determinations originally recommended by the British Royal Commission on Sewage Disposal was 65°F (18.3°C). Subsequently this was raised to 20°C in conformity with the practice on the Continent and in the United States.

2.1.1 Thermal Loading and BOD

The term *thermal loading*, sometimes called "thermal pollution" when it is associated with detrimental effects on an aquatic system, refers to the increase in temperature resulting from some plant discharges (e.g., power plants). Interest in thermal loading stems from the fact that a temperature change may alter the environment of resident fauna and flora, and thus the BOD, sufficiently to affect the propagation and even the survival of biotic species. This results from the increased rates of biological reactions with increasing temperature (Section 2.1). An increase in thermal loading which exceeds the rate of heat dissipation for the surface waters, may result in permanent increases in temperature (and changes in BOD) over large areas. For further treatment of this subject, the reader is referred to Ref. 17, p. 95. See also Ref. 10, Chapter 37, p. 17.

2.2 Dilution Factors

The variation in the composition of tap water with location, as well as the current practice of chlorination, makes it an undesirable diluent for BOD analysis. It has thus become a standard practice to use distilled water prepared and stored according to recommendations in Standard Methods, 13th edition (Ref. 7).*

Dilution water for BOD determinations should be prepared by the addition of essential mineral *nutrients* (see Section 2.5) to high quality water. The quality of the water may be checked by incubation with *seeded* (see Section 2.6) samples. Organic contaminants may be detected by means of a *total organic carbon analyzer* (OD Instrumentation, Section 3.2). Experiments by Wheatland and Smith have shown that dilution water should be freshly prepared, preferably, or, if this is not feasible, it may be stored no longer than one week in thoroughly cleaned containers (Ref. 18).

The requirements of acceptable BOD dilution water include: 1) pH limits within which biota will grow; 2) a reasonable buffer capacity; 3) proper salinity; 4) absence of toxic substances, such as metallic contaminants, chlorine, or other growth inhibitors; and, finally, 5) the presence of a balanced and viable seed. Since it is frequently difficult to be certain that all these fundamental requirements are satisfied, Sawyer et al (Ref. 19) recommended the use of two primary standards, to be employed in the standardization of the methods employed. One standard is pure glucose (300 mg/1; 5-day BOD @ 20°C = 224 mg/1); the other, pure glutamic acid (300 mg/1; 5-day BOD @ 20°C = 217 mg/1). Standard Methods also recommends a glucose-glutamic acid check of the viability of dilution water (pp. 492-493).

The degree of dilution may also be a factor influencing the BOD value obtained (Ref. 42, pp. 816-820). Klein (Ref. 2) therefore suggested the use of several dilutions in a BOD analysis. The value obtained for the dilution showing approximately 50% DO depletion is then assumed to most nearly reflect the BOD of the sample. For some industrial wastes BOD is so largely a function of dilution (because of the presence of inhibitors -- see Section 2.3 below) that it can no longer be employed as a reliable test. In such an instance it is best to turn to a chemical method such as the standard dichromate test for the presence of organic substances (Refs. 3, 4) or the 4-hour permanganate test (Ref. 2, pp. 124, 129-30).

2.3 Toxic Substances and Inhibitors

When either the sample or the dilution water contains substances such as chlorine or metals capable of inhibiting or preventing bacterial growth, the magnitude of the errors introduced in the BOD test may render it worthless.

The presence of mineral acids or alkalis can have a significant effect on bacterial activity, and strongly acid or alkaline samples should be brought within a pH range of 6.5-8.3 before *seeding* (Section 2.6).

Toxic metals such as Cu, Pb, or Hg inhibit bacterial growth even when present in low con-

*Ref. 7, inside front cover. See also Ref. 4, Section 1193. Hereafter Ref. 7 will be identified simply as Standard Methods.

centrations. Copper is the worst offender in this respect and should be limited to <0.01 mg/l to avoid marked depression of BOD. For this reason a glass still is recommended in the preparation of dilution water (Ref. 7, p. 4).

A "sliding BOD" value -- i.e., an apparent increase in BOD with sample dilution -- is diagnostic of toxicity in the sample.

According to one report on the toxicity of industrial wastes (Ref. 20) to the BOD dilution test, Hg toxicity increased only slowly for Hg values between 0.02-0.20 mg/l, but the curve rose steeply thereafter, and the BOD value was reduced to zero, for a Hg concentration of ∿2.0 mg/l.

As little as 0.1 mg/l of Cu or Zn was found to depress the BOD of sewage significantly, with copper the worse offender (when compared with zinc) for concentrations ranging all the way from 0.1-10 mg/l. For example, at 1 mg/l Zn lowers the BOD value by ca. 17%, but the effect of Cu at this concentration is nearly twice that of the Zn (33%) (Ref. 20). In a study on the effects of Cu and $CrO_4^=$, Placak et al (Ref. 21) reported that Cu and Cr ($CrO_4^=$) markedly inhibit BOD processes in concentrations as low at 0.01 mg/l Cu and ⩾ 0.3 mg/l Cr (as ($CrO_4^=$). For 0.01 mg/l Cu a 5% depression in the BOD value was observed; at 0.05 mg/l, Cu lowered the value as much as 23%.

The findings on chromium BOD toxicity as a function of valence state and form of the Cr are somewhat contradictory, with Coburn (Ref. 22) indicating that trivalent Cr does not function as an inhibitor in the BOD test, whereas the Research Committee Report cited previously (Ref. 20) implies that trivalent Cr has a greater toxic effect thatn $CrO_4^=$ in the range of 1.0-10.0 mg/l Cr as measured by the standard BOD dilution procedure. In the presence of 0.9 mg/l Cr ($CrO_4^=$) the BOD was lowered about 20%. More recently, the NTAC report has concluded that there is no appreciable difference in the toxicity of Cr^{+++} and Cr^{+6}, at least where fish are concerned (Ref. 40, p.86).

Biochemical oxidation of organics is retarded by as little as 0.1 mg/l Pb (Ref. 23). Similarly it has been shown that the oxygen uptake rate for activated sludge is inhibited by a large number of metal ions (Cd^{++}, Cr^{+++}, Cu^{++}, Ni^{++}, Zn^{++}) in concentrations ranging from 1-100 mg/l (Ref. 24). These findings are summarized in Table 2 below.

Table 3 illustrates the effect of Cu on a BOD analysis as shown by comparison of the value obtained with a 4-hour permanganate test of the same stream. Here the very low BOD/$KMnO_4$ ratio (see Section 3.3.1) is indicative of the toxic inhibition of BOD by Cu.

Table 2

Toxicity of Metal Ions as Measured by Inhibition of O_2-Uptake in the BOD Test

Ion	Conc. (mg/l)	% Reduction of BOD	Reported by or worker	Reference
Cr^{+++}	0.01	5	Placak, Ruchhoft, & Snapp	21
	0.05	23	"	21
	1.0	33	Research Committee on Toxic Industrial Wastes	20
Zn^{++}	1.0	17	"	20
Cr^{+6} ($CrO_4^=$)	0.9	20	"	20
Hg^{++}	0.02-0.2	Conc'n-dependent inhibition	"	20
	2.0	No O_2 uptake		
Pb^{++}	0.1	Inhibition	Kalabina	23
Ni^{++}	1.0	"	Dawson & Jenkins	24
Cd^{++}	1.0	"	"	24
Cr^{++}	1.0	"	"	24

Table 3

Analysis of Stream Water Containing Organic Matter and Copper

		Concentration, mg/l
pH value		7.1
3 min permanganate value		14.2
4 hr permanganate value		64.6
Nitrite nitrogen		nil
Nitrate nitrogen		4.0
Ammoniacal nitrogen		0.7
Albuminoid nitrogen		0.26
BOD (5 days, 20°C)		4.3
Copper (settled sample)		1.6
Copper (shaken sample)		5.8
Suspended solids	mineral	30.0
	volatile	81.0
	total	111.0
Total solids		437.0

Adapted from Ref. 2, p. 132.

Thus, waters containing industrial wastes may give very misleading results in the BOD test, and the previously mentioned chemical methods are best employed in their analysis.

Saline waters generally yield low BOD values. Gotaas (Ref. 25) has stated that the biochemical oxidation rate of sewage is greatest for low concentrations of sea water (up to 25%). Grindley and Wheatland (Ref. 26) account for the BOD changes with salinity by variation in activity and numbers of *nitrifying* (see Section 2.4) bacteria. Because of this variability, BOD is not the method of preference in the determination of the extent of organic pollution in saline waters. This parameter is best assessed by chemical methods.

2.4 Nitrification*

Sewage effluents which are undergoing an incipient nitrification process manifest abnormally high 5-day BOD values which may be misleading. This is brought about by the consumption of additional oxygen, over and above that which may be attributed to *carbonaceous OD*** in the nitrification process. Lockett has cited an instance in which the 5-day BOD of a sewage effluent analyzed at 31.4 mg/l contained only 9 mg/l from carbonaceous sources, and remaining 22.4 mg/l being utilized in the conversion of NH_3 to nitrate + nitrite (cited in Ref. 2, p. 125):

$$NH_4^+ + 3/2\ O_2 \xrightarrow[\text{bacteria}]{\text{nitrite-forming}} NO_2^- + H^+ + H_3O^+ \quad \text{(Eq. 7)}$$

$$NO_2^- + 1/2\ O_2 \xrightarrow[\text{bacteria}]{\text{nitrate-forming}} NO_3^- \quad \text{(Eq. 8)}$$

Figure 5 is an idealized illustration of the type of curve obtained

a) for the case of purely carbonaceous BOD, and

b) where nitrification is also involved.

Figure 6 illustrates the effect of temperature on the onset of the nitrification process in the BOD progression.

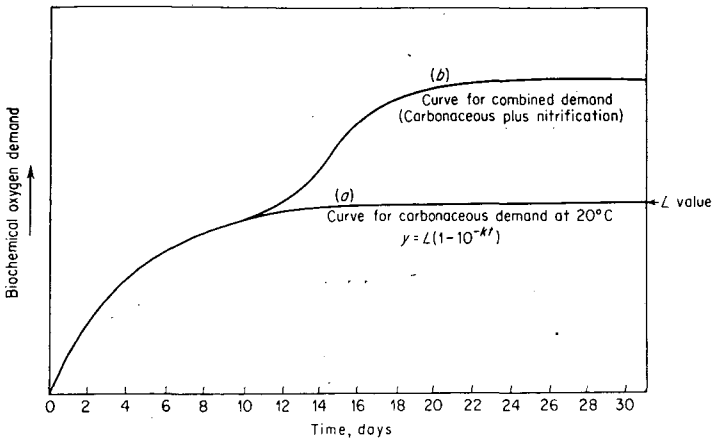


Figure 5. The BOD curve. a) Normal curve for oxidation of organic matter. b) The influence of nitrification. (Ref. 5).

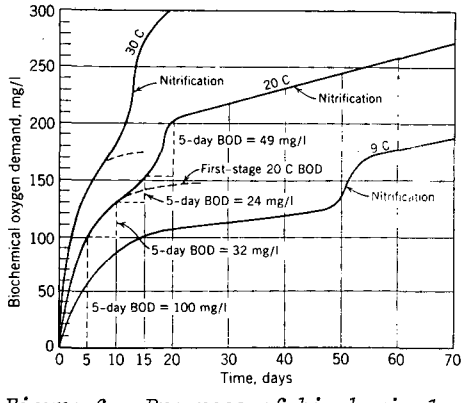


Figure 6. Progress of biochemical oxygen demand (BOD) at 9, 20, and 30 C. (Ref. 10)

*Bacterial oxidation of ammonia and organic nitrogen compounds to inorganic nitrites and nitrates

**OD of organic carbon constituents present in the sample.

A number of methods have been employed to prevent this early onset of nitrification:

1) Destruction of nitrifying bacteria at 60°-80°C by flash pasteurization.

2) Chlorination of the sample to remove nitrifying bacteria followed by a treatment with Na_2SO_3 to remove excess chlorine.

3) Acidification of the sample to pH 2 to 3: this suppresses the nitrification process in the sample which must now be neutralized prior to BOD analysis.

After one of these three procedures is used to destroy the nitrifying bacteria, the sample may be diluted with water which has been seeded with settled domestic sewage known to be free of nitrifying bacteria.

4) Another method which suppresses nitrification without affecting the oxidation rate of carbonaceous materials was originally reported by Abbott (Ref. 27). This entails treatment of the sample with methylene blue. The addition of 6 ml of the dye (.05% aq. solution) for each liter of dilution water used eliminated errors due to nitrification. Dissolved oxygen was then determined using the Rideal-Stewart modification (see H2O-DO, Section 2.23) before and after the 5-day incubation period.

Unfortunately, none of the methods of nitrification control listed is completely satisfactory.

Nitrification can be of appreciable importance when effluents from an *activated sludge (AS)* plant, which contains much ammonia but little nitrate, and those from a biological filtration plant (rich in nitrifying bacteria), are juxtaposed. Stones (Ref. 2, p. 126) has observed that such mixed effluents may have a greater BOD value than would be predicted from their individual contributions. Table 4 illustrates the BOD-enhancing effect of such mixtures. This increase in BOD in the mixture may be explained on the basis of nitrification in the AS effluent (oxidation of the NH_3) by nitrifying bacteria originating in the filter effluent. Since this increases DO depletion, it is quite conceivable that two effluents which have separate BOD values well within the allowable range will, when juxtaposed, result in excessive DO depletion to the detriment of resident biota in a stream.*

2.5 Nutrients

Bacterial growth is dependent on an adequate substrate supply of mineral nutrients. While C, N, P and S are the most important essential elements, traces of minerals containing Fe, Ca, Co, Cu, K, Mg, Mn, Mo and Zn also appear to be required by most bacteria (Ref. 28). Nearly 40 years ago Lea and Nichols (Ref. 29) determined BOD on sewage and industrial wastes with both plain and supplemented bicarbonate dilution water, and concluded from their experiments that low BOD values would be obtained with certain wastes unless sufficient mineral nutrients -- in particular N and P --

*Such an enhancement of BOD due to juxtaposition of effluents does not present a serious problem in the U.S. where both filter and AS plants are usually operated under non-nitrifying conditions.

Table 4

BOD of Mixtures of Activated Sludge Effluents and Filter Effluents from Plants Treating the Same Sewage

Activated sludge (Sheffield bio-aeration) effluent % by volume	Filtration plant effluent % by volume	BOD of mixture ppm
0	100	12.6
10	90	16.0
20	80	18.8
30	70	20.2
40	60	19.6
50	50	18.4
60	40	17.0
70	30	14.4
80	20	12.0
90	10	7.8
100	0	6.0

(Ref. 2, p. 126)

were available to satisfy the bacterial nutritional requirements. For example, they found that paper mill wastes diluted with water containing $Ca_3(PO_4)_2$, $MgSO_4$, KH_2PO_4, and $(NH_4)_2SO_4$ gave BOD values 2 to 5 times as high as those same wastes analyzed using unsupplemented dilution water.

In the case of pea canning wastes (high in N and P), the use of supplemented dilution water made no significant difference. Lea and Nichols' work indicated that the presence of a 0.2-0.5 mg/l of N and ca. 0.02 mg/l P would result in satisfactory BOD determinations. Sawyer and coworkers (Ref. 30) have demonstrated deficiencies in N or P or both in certain industrial wastes. Thus, cotton *kier* liquor is low in N, while brewery wastes are deficient in both N and P; tannery wastes are rich in N but P-deficient. In all cases where deficiencies exist, low BOD values may be expected unless these deficiencies are compensated in the dilution waters. For this reason, the standard dilution water now used contains essential supplementary nutrients. Although most natural stream waters probably contain sufficient mineral salts for the purposes of BOD analysis, those streams composed primarily of industrial effluent may pose analytical problems.

2.6 Seeding

For most sewage wastes and a few of the industrial wastes (e.g., those from the dairy industry) and for natural waters, the essential flora are already present and inoculation with bacteria will therefore not normally be required. However, chlorinated effluents require seeding after Cl_2 neutralization, and most industrial wastes, including strongly acid or alkaline effluents requiring neutralization before BOD analysis, will be deficient in the essential bacteria. To make up this deficiency, fresh settled sewage or sewage effluent is added to the dilution water. This type of seed has been shown by Sawyer et al (Ref. 19) to vary with the source of the seed when tested on pure organic compounds of known BOD. These variations in the character of the inoculum have been attributed to differences in the ratios of bacteria and protozoa in the seed source, and Zehnpfennig and Nichols (Ref. 31) demonstrated that, after filtration of the inoculum through a suitable sintered glass filter to remove the protozoa, reproducible BOD values can be obtained for the primary standards regardless of the source of the seed. High-BOD sulfite waste liquors from the digestion of wood chips with $Ca(HSO_3)_2$ solution (to produce pulp for paper) give unsatisfactory BOD results when standard seeding methods are employed (Tyler and Gunther, Ref. 32), but yield satisfactory results with a filtered soil extract as the inoculum.

Sewage effluents are not always a suitable inoculum for industrial wastes (Ref. 7, p. 490) -- in particular those which contain organic compounds resistant to oxidation by domestic sewage seed, or when the BOD is much less than

Table 5

Effect of Seed Type and Quality of BOD of Standard Glucose-Glutamic Acid Solution

Type of Seed	5-day Seed Correction *mg/l**	Mean 5-day BOD *mg/l*	Standard Deviation *mg/l*
Settled fresh sewage	>0.6	218	±11
Settled stale sewage	>0.6	207	±8
River water (4 sources)	0.05-0.22	224-242	±7-13
Activated-sludge effluent	0.07-0.68	221	±13
Trickling filter effluent	0.2-0.4	225	±8

*Section 1.6.1 (Ref. 7, p. 493)

2/3 of the *dichromate value* (see COD Section 2.1.1). In these circumstances the use of specially *adapted seed* is recommended, preferably obtained from the effluent from biological treatment of the waste itself, or from waters receiving it at a locus 2-5 miles below the discharge point. In the absence of these sources of adapted seed, it may be developed by continuous aeration of a large volume of water and by daily inoculation with small increments of the waste in question, along with domestic sewage or soil, until a suitable microbial population has been obtained (see Ref. 7, Section 219 3h).

The quality of the seed, dilution water and analytical technique employed (as well as the analyst!) should be checked periodically. The recommended procedure is described in Ref. 7, Section 4a-9. Table 5 illustrates the effect of seed type and quality on the BOD value obtained, using a standard glucose-glutamic acid test solution.

2.7 Anaerobic Organisms

In the presence of predominantly anaerobic bacteria from such sources as digested sludge, septic sewage or river muds, or the supernatent liquor from sludge digestion tanks, there is a lag of two or more days, so that the BOD values obtained are unusually low (see Fig. 7). This BOD-lag period results from the initially high concentration of the anaerobic species which do not require free (dissolved) oxygen for growth, but may utilize oxygen-containing compounds present for their metabolic processes. Ultimately as the concentration of anaerobic substrate decreases, the rates of the aerobic processes overtake and exceed the anaerobic rates, and the BOD curve "takes off".

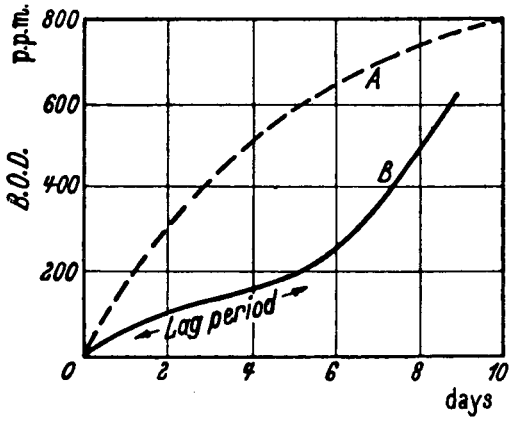


Figure 7. BOD curve of digested sludge supernatant liquid. A) BOD curve of normal sewage. B) BOD curve of supernatant liquor. (Ref. 2, p. 134)

2.8 Other Factors Influencing BOD

In addition to the sources of error and reasons for variability of BOD results reviewed in Sections 2.1 through 2.7 , many other variables appear as minor factors influencing this parameter. As an example, the presence of ferrous and ferric salts, nitrites and sulfites will interfere in the standard 5-day BOD test. Even a variation in bottle size, with its concomitant effect on the ratio of internal volume/surface may affect bacterial activity. A more complete discussion of the numerous minor errors appears in Ref. 33.

3. Relationship of BOD to Chemical OD Methods

Oxygen demand is also measured by a number of chemical procedures, each of which will be treated separately in later sections. However, a brief survey of the concepts involved should be helpful in clarifying such interrelationships between the chemical and biological measurements as do exist.

The BOD test has a biological basis in that it measures the amount of oxygen utilized during the oxidation of organic matter by aerobic bacteria under certain prescribed conditions (5 days @ 20°C). The difference between the initial and final concentrations of dissolved oxygen (DO, see H2O-DO Section of this Volume; also Ref. 7) in mg/1 is taken as a measure of the BOD of the sample.

*Chemical Oxygen Demand (COD)** tests, such as the dichromate test (Ref. 7, p. 495) and the 4-hour permanganate test (Ref. 2, p. 120) constitute rapid analytical methods of chemical oxidation occurring under test conditions; they are useful in the estimation of the OD of organic carbon present in a sample. A more detailed discussion of COD may be found in the following chapter of this volume.

Thus, both BOD and each of the chemical methods play a significant role in the assessment of organic pollution; each method is concerned either with oxygen utilization of organic constituents or, more directly, with the actual amount of organic carbon present. Each method in its own way thereby furnishes an independent approximation of the quantity of organic matter present. Here, however, the resemblance between BOD and COD ends, for it is

*Chemical oxygen demand (COD) is defined as "the amount of oxygen (in mg/1) consumed under specified conditions in the oxidation of organic and oxidizable inorganic matter in waste water, corrected for the influence of chloride." (Ref. 17, p. 214).

unreasonable to expect that the quantity of oxygen utilized in the course of metabolic processes of aerobic bacteria will correspond to that involved in a high-temperature chemical oxidation-reduction reaction. Factors which are operative in BOD (see Sections 2.3-2.7, inclusive) may have little or no influence on the chemical oxidation of organic constituents, and to some extent the converse is also true, as will be shown later in our discussion of chemical parameters.

3.1 Nitrogenous Wastes

In general BOD remains the most sensitive test for nitrogenous organic pollutants which resist complete chemical oxidation; these include dairy and food processing wastes, farm drainage and sewage. BOD constitutes the principle test of the *strength* of sewage and industrial wastes -- i.e., the oxygen required to stabilize these wastes. In Table 6 below the resistance of ammonia and organically bound

Table 6

Analyses of Nitrogenous Organic Waste Waters

	Farm drainage	River polluted by dairy wastes	River polluted by sewage*	Unsatisfactory ** sewage effluents			Unsatisfactory** dairy effluent
pH value	7.2	7.0	6.8	7.4	7.1	6.8	7.2
3 min permanganate test ppm	3.0	1.0	1.0	6.8	4.4	5.0	4.5
4 hr permanganate test ppm	10.0	4.6	3.8	18.0	14.2	10.0	10.9
Nitrite nitrogen ppm	nil	nil	nil	nil	trace	nil	nil
Nitrate nitrogen ppm	nil	nil	nil	nil	1.5	nil	nil
Methylene blue stability test	Failed	Failed	Failed	Failed	Failed	Failed	Failed
	4 hr	18 hr	18 he	4 hr	18 hr	18 hr	4 hr
	(H_2S)	(H_2S)	(H_2S)	(H_2S)	(H_2S)	(H_2S)	(H_2S)
BOD (5 days, 20°C) ppm	39.0	60.0	12.9	39.6	40.9	32.5	76.0
Ammoniacal nitrogen ppm	--	0.10	0.92	--	--	--	--
Albuminoid nitrogen ppm	--	0.86	0.24	--	--	--	--
Dissolved oxygen, % of saturation	--	37	9	--	--	--	--

* Stream bed showed signs of sewage pollution (e.g., sewage fungus).

** "Unsatisfactory" here denotes undiluted sewage with a BOD >20 ppm. (Data derived from Ref. 2, p. 130)

Table 7

BOD & COD Analyses of Citrus Wastes

Raw Citrus Waste				Citrus Activated Sludge Effluent			
5-Day B.O.D. (p.p.m.)	Standard Methods C.O.D. (p.p.m.)	Colorimetric C.O.D. (p.p.m.)	Visual Comparison C.O.D. (p.p.m.)	5-Day B.O.D. (p.p.m.)	Standard Methods C.O.D. (p.p.m.)	Colorimetric C.O.D. (p.p.m.)	Visual Comparison C.O.D. (p.p.m.)
1,295	2,290	2,450	2,375	4.0	45	55	—
1,330	2,310	2,500	2,375	6.7	55	70	—
1,400	2,295	2,350	2,250	5.0	66	70	50
1,630	2,330	2,475	2,355	6.1	52	70	50
1,705	2,285	2,500	2,355	5.7	42	65	50
1,565	2,240	2,375	2,375	6.6	51	70	50
1,385	2,300	2,490	2,375	3.4	34	30	50
1,410	2,270	2,375	2,375	3.6	26	60	50
1,220	2,175	2,350	2,250	5.8	20	60	25
1,680	2,300	2,350	2,375	3.0	31	40	25
AVERAGE							
1,462	2,280	2,422	2,346	5.0	42	59	44

Ref. 34, p. 898

N to oxidation is illustrated by the absence of nitrates and nitrites in the samples tested. It should be noted that the dye methylene blue was uniformly successful in suppressing the nitrification step in all wastes examined. Further experimental verification of the superiority of the 5-day BOD method for these wastes is obtained by a comparison of the 4-hour permanganate values with the 5-day BOD values. Thus, while the BOD analyses clearly indicate the presence of organic pollutants, the $KMnO_4$ test fails to reflect quantitatively the actual organic pollution in these streams. The divergence between BOD and the chemical method is particularly great in the case of stream pollution by dairy wastes.*

3.2 Non-nitrogenous Wastes

For non-nitrogenous wastes use of the COD method with acid dichromate oxidant generally yields higher values than BOD, since it is a measure of total oxidizable organic material present, without regard to its biological availability. Table 7 illustrates this point for the case of citrus wastes measured by the standard dichromate procedure which entails titration of excess reagent with ferrous ammonium sulfate in the presence of an o-phenanthroline indicator. In each case, the third and fourth columns represent rapid colorimetric variants of the standard COD method, with measurements made after only 10 minutes of refluxing (Ref. 34). Table 8 gives ratios and statistical correlations for BOD vis à vis the three COD procedures.

3.3 BOD-COD Ratios

Because of the time-consuming nature of the BOD test, attempts to correlate this biological parameter with the faster chemical methods are ongoing. Historically these led to the examination of BOD-permanganate ratios (see Section 3.3.1 below). More recently they have taken the form of BOD-dichromate ratios and the examination of the *Oxygen Demand Index (ODI)* as a rapid estimate of BOD.

3.3.1 BOD-Permanganate Ratios

For crude domestic sewage, the 5-day BOD-permanganate (4-hour, N/80 $KMnO_4$) ratios are of

* Standard Methods currently employs catalytic oxidation of organics with acid dichromate solutions as the chemical method of choice. This gives closer agreement with carbonaceous BOD in the absence of nitrogenous OD, but is subject to limitations which will be discussed in greater detail in the COD section.

Table 8

Ratios and Statistical Correlations of Analyses by Different Procedures (Ref. 34, p. 898).

C.O.D. Comparison	Raw Citrus Waste			Citrus Activated Sludge Effluent		
	Ratio	Correlation Coefficient	No. of Samples	Ratio	Correlation Coefficient	No. of Samples
Std. Methods C.O.D. *vs.* B.O.D.	1.56	0.4346*	23	8.40	0.4699*	20
Colorimetric C.O.D. *vs.* B.O.D.	1.66	0.4669*	23	11.80	0.4496†	17
Visual C.O.D. *vs.* B.O.D.	1.60	0.2639†	19	8.80	0.6780‡	15
Colorimetric *vs.* Std. Methods C.O.D.	1.06	0.3113†	31	1.40	0.4305*	24
Visual *vs.* Std. Methods C.O.D.	1.03	0.0973†	26	1.05	0.6255‡	21
Colorimetric *vs.* Visual C.O.D.	1.03	0.0325†	26	1.34	0.4218†	21

* Significant correlation at 5 per cent level.
† Correlation not significant at either 1 or 5 per cent levels.
‡ Significant correlation at 1 per cent level.

Table 9

Comparison of BOD and 4 hours permanganate figures for different types of sewage (Birmingham) (Ref. 2, p. 135).

Name of works	*Character of sewage*	*5-day B.O.D.* p.p.m.	*4 h permanganate value* p.p.m.	*Ratio B.O.D.: permanganate value*
Barston . .	Domestic	236	59	4
Coleshill. .	Domestic	228	76·5	3
Yardley . .	Industrial*	222	120	1·8
Saltley . .	Industrial*	264	159	1·66

* Contains large proportion of metallic trade wastes.

the order of 2 to 4 ($BOD/KMnO_4$). With carbohydrate-rich or nitrogen-rich wastes (dairy and food processing) the ratio may exceed these values. This ratio may be adversely affected by industrial chemical effluents containing non-nitrogenous organics, metals, etc. In Table 9 above the $BOD-KMnO_4$ data for four different sewage effluents are compared. The corresponding ratios for sewage containing industrial effluents are consistently lower than for domestic sewage. The significance of this divergence is that the $KMnO_4$ figure indicates the *amount of organic pollution* requiring treatment, whereas the BOD value is a measure of the *ease of biological oxidation*. A low $BOD/KMnO_4$ ratio (e.g., <1) therefore indicates that the effluent is more resistant to biochemical oxidation (Ref. 35).

Inhibition effects on BOD of industrial wastes were further shown by Goldthorpe and Nixon (Ref. 36) who mixed chemical wastes containing Fe, organics and dyestuffs with sewage in varying ratios. They obtained $BOD/KMnO_4$ ratios which varied all the way from 0.2 for chemical wastes alone to over 3.0 for sewage alone.

In the absence of industrial wastes, sewage and tank effluents give relatively high $BOD/KMnO_4$ ratios (>1). However, a properly purified sewage effluent or effluent of good quality containing industrial organic nitrogenous wastes, will generally have ratios of <1, indicating a BOD value which is lower than the corresponding permanganate value.

Table 10

Winter T_bOD of Davis Municipal Sewage (Test Series 1) (Ref. 38).

1 Test Date	2 Theoretical Initial COD_m	3 Mixture Initial COD_m	4 Measured Cell COD	5 Initial COD_s	6 Endpoint COD_f	7 ΔCOD	8 Sewage Dilution Factor	9 T_bOD	10 Measured Sewage COD
2/17	585	584	293	287	36	251		279	318
2/24	618	598	367	251	33	218	0.9^{-1}	242	279
3/5	791	746	681	110	62	48		53	122
3/25	372	363	188	184	49	133	0.918^{-1}	145	200
3/26	534	524	296	238	60	178	0.9^{-1}	198	264
4/2	658	626	330	328	38	290		322	364

Table 11

Summer T_bOD of Davis Municipal Sewage (Test Series 2) (Ref. 38).

1 Test Date		2 Theoretical Initial COD_m	3 Mixture Initial COD_m	4 Measured Cell COD	5 Initial COD_s	6 Endpoint COD_f	7 ΔCOD	8 Sewage Dilution Factor	8a T_bOD	9 Average T_bOD	10 Average Measured Sewage COD
6/26	1	333	316	144	189	34	155		172	173	210
	2	461	437	272	189	32	157		174		
6/28	1	-	417	292	125	23	102		113	117	147
	2	-	703	564	139	30	109		121		
7/2	1	527	520	291	236	27	209	0.9^{-1}	232	235	266
	2	813	817	570	243	28	215		239		
7/9	1	256	258	141	115	20	95		105	105	128
	2	399	358	285	114	20	94		105		
7/16	1	353	357	147	206	37	169		188	188	229
	2	505	433	299	206	37	169		188		

3.3.2 BOD-Dichromate Ratios

In a recent investigation of a rapid BOD method based on a differential COD technique (Ref. 37, see Section 11.3.2) Schroeder and co-workers (Ref. 38) calculated the TBOD (Total Biological Oxygen Demand) for municipal sewage from COD data. Tables 10 and 11 above list their TBOD and COD values for winter and summer months, respectively. As in the case of citrus wastes cited previously (Table 7, p. 1), BOD/p. 11 dichromate ratios are <1, i.e., COD values are consistently higher than BOD, since they reflect organic (and inorganic) oxygen demand without regard to biological activity or toxicity factors.

Similarly, OD analyses on primary effluent from Midland, Michigan, show a COD/BOD ratio $\gg 1$ (Fig. 8).

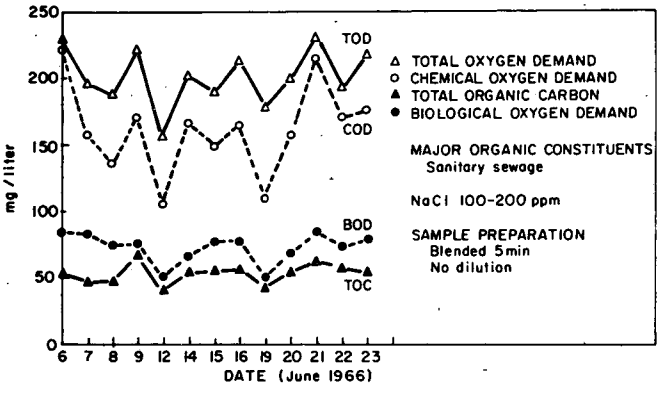


Figure 8. City of Midland primary effluent. Reprinted from Ref. 39, Vol. 4, p. 1470.

4. Limitations of the BOD Method

Some disadvantages of BOD as an indicator of organic pollution have already been noted under Section 2 in dealing with factors which influence BOD values obtained. In this section these limitations will be summarized briefly.

4.1 Time Factor

The standard BOD procedure is time-consuming at best. At worst, as in the case of nitrogenous compounds and inhibitors, the 5-day incubation period may yield misleading (low) results due to a lag or induction period before the biochemical oxidation process begins. Conversely, nitrification may lead to excessively high BOD values.

4.2 Validity

The test is of limited value when used to obtain OD values for surface waters, since it does not reproduce actual stream conditions. BOD is a *batch* or *discrete* measurement, executed under static aerobic conditions. Thus such continuous variables as stream velocity, temperature and the existence of anaerobic as well as aerobic areas in a dynamic stream situation are not accurately reflected by the BOD measurement.

4.3 Reproducibility

Because of the large number of variables which may influence the BOD test (see Sections 2 and ff), comparisons of BOD data are valid only for identical test conditions.

4.4 Metals and Toxic Inhibitors

Even in low concentrations the following metals are toxic to bacteria: Cu, Cr, Hg, Pb. Because of its dependence on bacterial growth, BOD is very vulnerable to the toxic effects of metals, whereas chemical methods are relatively insensitive to them.

4.4.1 Other BOD Inhibitors

Other *bacteriocidic** and/or *bacteriostatic** substances which may inhibit bacterial activity, and thereby result in low BOD values in the presence of organic pollution, include free chlorine, cyanides, formaldehyde (CH_2O), and phenols. Numbered among the important industrial wastes which may give low BOD results because of the presence of such inhibitors are those from gas, petroleum and chemical (phenols, formaldehyde, TNT, etc.) and plating industry wastes. In these instances, the BOD analysis is best replaced by a more suitable COD method such as the dichromate test (Refs. 3, 7).

4.4.2 Evidence for BOD Inhibition

When an apparent increase of BOD is observed within a series of increasing dilutions of a sample, the presence of a toxic substance or inhibitor is indicated.

*See glossary

4.5 BOD-resistant Organic Materials

The assumption that BOD is directly proportional in magnitude to the organic pollutants present is only approximately correct since there exist organic substances and partial degradation products, such as lignins, oils, and alkybenzenesulfonate type detergents which are strongly resistant to further biochemical oxidative degradation. These substances are not detectable via the standard BOD procedures, but their build-up in a stream may be nonetheless objectionable, either by virtue of their imparting undesirable physical characteristics (taste, odor, frothing, etc.) or because they are toxic.

Analysis of the supernatants from sewage sludge, septic sewage, or any liquor which has undergone initial *anaerobic* fermentation will invariably give a low 5-day BOD value. However, this is probably due to an initial lag period during which the changeover to aerobic fermentation occurs, and further fermentation of such samples beyond the 5-day limit is likely to show a rapid increase in OD. This phenomenon is illustrated in Fig. 7, and was discussed under Section 2.7.

5. Criteria

The report of the National Technical Advisory Committee (NTAC) (Ref. 40) does not specify allowable BOD values for various kinds of effluent. Clearly, BOD limits will vary with the intended use of the water. For public water supplies, "permissible criteria" are stated in terms of dissolved oxygen ($\geq$ 4 ppm, monthly mean value); "desirable" criteria: near saturation (i.e., negligible OD present). The allowable BOD values for undiluted waste waters will vary with the nature of the waste treatment prior to discharge and stream dilution of the discharged effluent.

For further discussion of BOD in relation to the following subjects the reader should consult Ref. 40: aquatic life, p. 57; farm wastes, p. 132; irrigation water, pp. 118, 166; pulp wastes, p. 90; *Sphearotilus*, p. 51; supplemental irrigation, p. 175.

6. Summary and Conclusions

In summary, it may be stated that while BOD is still regarded by most sanitary engineers as the method of choice for determining organic pollution of waters, it is subject to a number or limitations and errors discussed under Section 4 as well as to additional parametric limitations (Section 2). Briefly, these are as follows:

1) BOD is temperature-sensitive and limited by the viable temperature range for the biota involved.
2) BOD measurement to be meaningful requires a mutually compatible substrate and bacterial population. In the case of a resistant substrate, a suitable seed may be developed (Section 2.6).
3) The BOD test must be conducted under non-nitrifying conditions.
4) The sensitivity of BOD to a large number of metal ions and other inhibitors serves as an indicator of the presence of toxic substances by virtue of the "sliding scale" of BOD -- e.g., the apparent increase in BOD with sample dilution.

These factors must be considered in any reasonable interpretation of BOD data.

Where BOD results are ambiguous, the data from this bioanalytical method should be compared with data obtained using chemical methods. Thus, when the 5-day BOD appears too low compared with the dichromate or permanganate analysis, each of the following possibilities may need to be considered:

1) A bacteriostat or toxic substance may be present.
2) Unsuitable seed, or seed requiring acclimatization may be the problem.
3) Biochemically oxidation-resistant substances may be resulting in low BOD values vis à vis the chemical ones.
4) Or, the presence of anaerobic bacteria may be causing a BOD lag. In any of these instances, examination of long-term BOD-rate curves can be illuminating (see for example, Figs. 7 and 8).

Despite its limitations, the BOD test by its very nature remains the most sensitive criterion of organic pollution and continues to serve as the principal pollution *indicator* for sewage and industrial wastes.

7. Five-day BOD: The Method

The BOD test is identified primarily with the standard laboratory procedure developed to measure water quality (Refs. 2, 3, 7). The sample of waste water and appropriate dilutions are incubated in the dark for five days @ 20°C. Reduction of DO content during the incubation

period is taken as the measure of BOD of the sample (see Refs. 3, p. 117; 7, p. 489; 41). EPA recommends the BOD procedure described in the 13th edition of Standard Methods. The exact procedure used will depend on the nature of the sample and involves one of three methods:

1) Direct Method: For samples whose DO is <7 mg/l*, the sample is first aerated to near saturation (Ref. 3) and the DO** determined initially and after the 5-day dark incubation period at 20°C.
2) Unseeded Dilution Method: For waters with DO ≥ 7 mg/l, the following procedures are recommended:
   a) Appropriate dilutions are prepared with O_2-saturated standard dilution water (Ref. 7a); or,
   b) Appropriately diluted samples are saturated with O_2 (Ref. 3).
3) Seeded Dilution Method: When the sample contains microorganisms capable of oxidizing the organic substrate present (as would be the case for domestic sewage or unchlorinated effluents), it is not seeded. However for samples likely to be deficient in microorganisms -- i.e., chlorinated effluents or those subjected to extremes of pH or temperature, a standard seed material is employed. This consists of settled domestic sewage stored at 20°C for 24-36 hours. Standard dilution water (Ref. 7a) containing 1 to 2 ml of this standard seed per liter is used as diluent for microorganism-deficient samples (Ref. 7, Section 219-3h). The preparation of adapted seed for organism-resistant industrial wastes has already been described (Section 2.6).

Dilution water which has been seeded should be used the day it is prepared.

7.1 Procedure†

If the pH of the waste sample is not between 6-8, it is first neutralized to pH 7 with the help of a pH meter (see this volume H2O-pH) or the use of bromothymol blue as an external indicator. It is then diluted as required (see below) with buffered distilled water containing 1 ml each of the following reagent solutions per liter of distilled water: phosphate buffer, $MgSO_4$, $CaCl_2$ and $FeCl_3$ solutions. It is essential that the dilution water be sufficiently buffered that the pH will remain constant throughout the dilution range.

For dilution water which is stored in the refrigerator prior to use, the phosphate buffer is not added until immediately before its use.

For diluting samples the dilution water, seeded if necessary, is carefully siphoned into a graduated cylinder to 1 to 2-liter volume avoiding entrainment of air. The desired amount of sample is then added, again avoiding aeration, and the solution is further diluted as required. Mixing is done with a plunger to avoid air entrainment. Two aliquots of the solution are then siphoned into separate BOD bottles. One is incubated in the dark at 20°C, the other analyzed for initial DO content. Incubation and analysis of blank dilution water is carried out simultaneously. Oxygen depletion on the unseeded dilution water should not amount to more than 0.1-0.2 mg/l. Dissolved oxygen analysis may be chemical (azide method; H2O:DO, Section 2.2.2) or by means of a membrane electrode (H2O-DO, Section 3.6).

Incubated samples are sealed tightly against air and should be water sealed, either by the use of a special water-seal bottle, or by inversion in a tray of water.

An alternate technique simplifies water sealing: it consists of measuring known aliquots into volumetric bottles or flasks which are then filled with sufficient dilution water that air bubbles are excluded on sealing.

The viability of the seed, when used, and/or the presence of toxic materials which act as growth inhibitors are detected by means of the glucose-glutamic acid check (Ref. 7, Sec. 219-4a7). A mixture containing 150 mg/l each of reagent grade glucose and glutamic acid provides a stabilized oxidation rate comparable to that obtained from municipal wastes.

7.2 Glucose-Glutamic Acid Check Procedure

All three variables (analyst, dilution water, and seed) may be checked as follows: 5 ml of the glucose-glutamic acid solution are diluted with seeded dilution water and incubated with a seed control @ 20°C for five days. The variation of glucose-glutamic acid BOD with seed type is illustrated in Table 5 of Section 2.6 (p. 9).

*i.e., below the saturation value of DO @ 20°C.

** *Dissolved Oxygen*: see this volume H2O:DO, section 1.0 for factors influencing oxygen solubility.

†For preparation of standard solutions, dilution techniques, and other procedural details, the reader is referred to Ref. 7, Sec. 219, p. 489 ff.

Results obtained from sample dilutions with a residual DO content of ≥ 1 mg/l after the 5-day incubation, and a depletion of ≥ 2 mg/l are most likely to be reliable.

7.3 Seeding

The seeding of dilution water is described in greater detail in Standard Methods, 13th edition (Ref. 7), and in Traversy (Ref. 3). A general discussion is also included in Section 2.6 of this chapter. The seeding errors incurred in BOD measurements are considered in detail by Stack (Ref. 42).

7.4 Chlorinated Waters

Waste samples containing residual chlorine are allowed to stand 1 to 2 hours to dissipate the chlorine. For higher chlorine residuals*, the chlorine is destroyed by reduction with sodium sulfite solution (Na_2SO_3). The quantity of Na_2SO_3 required is determined as follows: a 0.1-1.0 liter aliquot of the sample is treated with 1:1 acetic acid or 1:50 H_2SO_4-H_2O solution and 10 ml KI solution containing 10 gm KI/100 ml solution. It is then titrated to the starch-iodine endpoint with Na_2SO_3 solution (0.025 N). The required volume of sulfite solution as determined above is then added to another waste aliquot and tested for residual Cl after 10 to 20 minutes. The necessary BOD dilutions are then prepared using seeded standard dilution water.

Several dilutions of the treated sample should be prepared to bracket the BOD value of the waste sample. The following dilution ranges have been recommended (Ref. 7): 1) high level industrial wastes, 0.1-1%; 2) raw or settled sewage, 1-5%; 3) oxidized effluent, 5-25%; and 4) polluted streams, 25-100%. For further discussion of samples requiring special treatment, the reader is again referred to Section 219 of Standard Methods, 13th edition.

8. BOD Versus IDOD

A number of substances are rapidly oxidizable by molecular O_2 and will therefore also deplete the water of DO. These include aldehydes, ferrous salts, sulfides and sulfites. Waste waters polluted with such reducing agents will show an *Immediate Dissolved Oxygen Demand (IDOD)*; the total OD is then the sum of this initial OD value plus the 5-day BOD. IDOD does not necessarily indicate that the oxidation by DO will be immediate; rather, these substances may merely react with the liberated iodine in the iodometric (Winkler) DO analysis (H2O:DO, Section 2.2):

$$2Fe^{++} + I_2 \xrightarrow{H^+} 2Fe^{+++} + 2I^-$$

Thus, they add to the apparent OD of the sample. IDOD is arbitrarily measured at 15 minutes. This is done by determination of the initial OD (usually zero) for the sample and the dilution water, and the OD for an appropriate dilution of the sample after 15 minutes. The difference between the initial DO and the DO after 15 minutes of an appropriate dilution is termed the IDOD of the sample.

*i.e., residuals which persist beyond two hours; where this is suspected, the sulfite titration is done on an initial aliquot.

9. Calculations of BOD

A. For the unseeded system,

$$\text{BOD (mg/l)} = \frac{D_1 - D_2}{P}, \text{ where} \qquad \text{(Eq. 9)}$$

D_1 = IDOD (i.e., DO after 15 minutes)

D_2 = DO of incubated sample, and

P = sample dilution, expressed as a decimal fraction.

B. For the seeded system,

$$\text{BOD (mg/l)} = \frac{(D_1 - D_2) - (B_1 - B_2)f}{P} \text{ where,} \qquad \text{(Eq. 10)}$$

D_1, D_2 and P are as defined under A, and

B_1 = DO of dilution of seed control prior to incubation,

B_2 = DO of dilution of seed control after incubation, and

f = ratio of seed in sample to seed in control

$$= \frac{\% \text{ seed in } D_1}{\% \text{ seed in } B_1}$$

$(B_1 - B_2)f$ = seed correction.

C. For the seeded system, if IDOD = 0 or not determined,

$$\text{BOD (mg/l)} = \frac{D_C - D_2}{P}, \text{ where} \qquad \text{(Eq. 11)}$$

$D_C = (DO)_O = D_O p + SP$ (time = 0)

D_2 and P are as defined under A.

S = DO of undiluted sample, and

p = fraction of dilution water used (expressed as a decimal).

D. For IDOD $\neq 0$,

$$\text{IDOD (mg/l)} = \frac{D_C - D_1}{P}, \text{ where} \qquad \text{(Eq. 12)}$$

D_C, D_1, and P are as defined previously.

10. Precision and Accuracy

Precision was determined by analysis of a glucose-glutamic acid mixture in 34 laboratories, each with its own seed material. The geometric mean value obtained was 184 mg/l; the standard deviation, ±31 mg/l or 17%. A single analyst working in his own laboratory obtained a 5% precision (±11 mg/l for a BOD of 218 mg/l).

It is not possible to determine the accuracy of the BOD test, since there is no suitable standard for this purpose.

11. Alternatives to the 5-day BOD Test

The standardized laboratory procedure for determination of the oxygen requirements of effluents, polluted waters and waste waters as described in Standard Methods, 13th edition, is used primarily to assess the waste loads imposed on treatment facilities and their efficacy in coping with these imposed burdens, measured in terms of "BOD removal". Biochemical oxygen demand is widely used in the evaluation of sewage strength, process efficiency and effluent quality. However, in order to have any validity, the BOD test must be executed under carefully controlled conditions. It is extremely limited as a measure of the oxygen demand (OD) of surface waters and extrapolation of the results obtained to in-stream oxygen demands is not without hazard, since clearly the environment of the aliquot contained in a sample bottle has totally different biotal, oxygen, sunlight, temperature, and kinetic conditions. The information supplied by the test provides a "historical" record which is related to the organic components present at the beginning of the test, but it is seriously limited as a parameter of ongoing water quality control (Refs. 7 and 42).

A number of alternatives have been suggested in an attempt to overcome the uncertainties and shorten the duration of the BOD test (Refs. 37, 38, 42-45 inclusive). These will be discussed briefly in the following sections.

11.1 Energy Oxygen: Definition

As Stack (Ref. 42) has so aptly remarked, the "bottled" 5-day BOD system is "100% accurate in representing itself, but unreliable as a representation of the (dynamic) system from which the sample was taken." He has suggested an alternative approach to the problem of obtaining more current, and therefore, in his opinion, more useful BOD-*related* information based on the fundamental reactions involving *energy oxygen (EO)*.

Energy oxygen is defined as that part of the required oxygen which is utilized by biota in the synthesis of new cellular products or biologically stable organic substances. "Thus at the point where the original organic material no longer exists, oxygen consumption corresponds to energy oxygen and is equivalent to 10-40% of the *chemical oxygen demand (COD)* of the original organic material" (Stack, Ref. 42, p. 804). Incubation time for this process is of the order of one to two days. Long-term first stage *carbonaceous BOD* utilizes 60 to 80% of the total *Chemical Oxygen Demand (COD)* leaving behind relatively inert materials such as polysaccharides (Ref. 46) which are not readily susceptible to further breakdown. This takes 10 to 20 days. During this *cell stabilization* period ammonia is released via degradation of N compounds such as amino acids.

Bacterial *nitrification* (oxidation to nitrites and nitrates) may or may not occur at this stage. If incubation is continued beyond this stage, the ultimate value of BOD developed will represent essentially total oxidation of all C, H, and N *(ultimate OD)* (Ref. 47).

11.1.1 Energy Oxygen as a Biological Parameter

Early theoretical treatments of BOD have been based on the assumption of the occurrence of first order kinetics (see Introduction, p.2) within the BOD bottle, an assumption which has not withstood the test of everyday sanitary engineering practice (Refs. 6, 15, 48, 49). Stack (Ref. 42) therefore recommends discarding the questionable first order assumption and substituting the "actual occurrences in the BOD bottle." These are:

a) oxygen utilized in the energy reactions previously discussed (*energy oxygen - EO*), and
b) oxygen consumed in subsequent *endogenous reactions* which result in relatively stable organic end products.

Assuming that a method can be developed to determine EO rapidly, simply, and reliably, then biological cell production during that time may provide the basis for a calculated endogenous oxygen value. The sum of these two values (i.e., EO + endogenous oxygen) is the *stabilization oxygen demand* (Ref. 42).

Figs. 10 and 11 illustrate BOD curves for glucose and sodium acetate, respectively. *Ultimate carbonaceous BOD* is differentiated from the *stabilization OD* values in that the former value is defined as the oxygen required for complete conversion of organic carbon and hydrogen to CO_2 and water. This value is reached

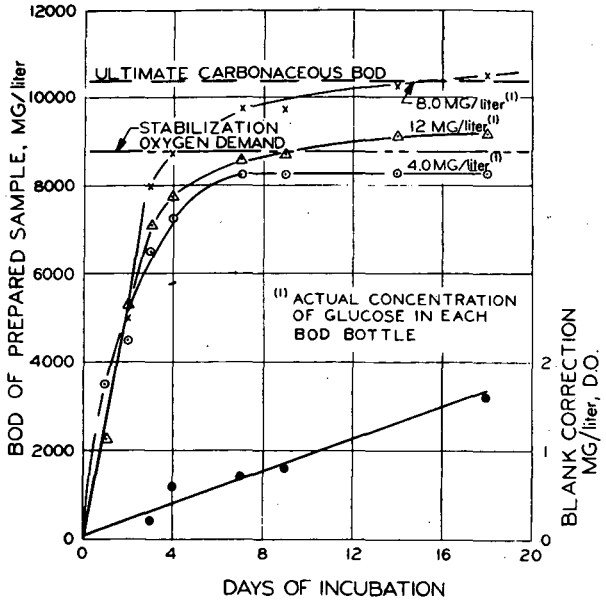


Figure 9. Biochemical oxygen demand, glucose. 10,000 mg/liter prepared sample.

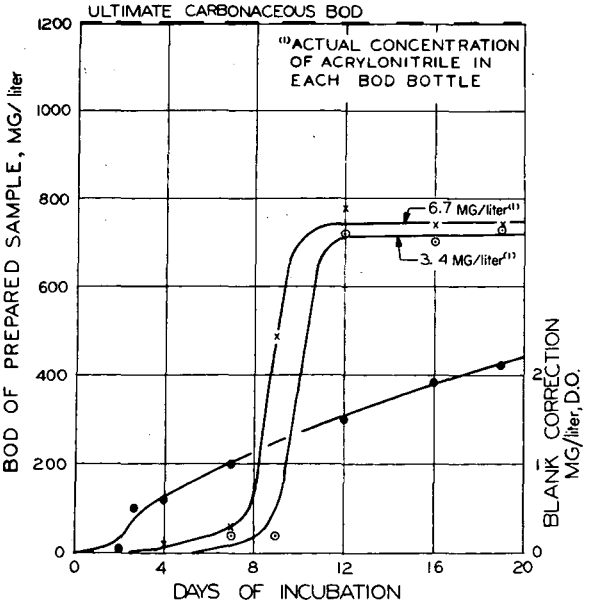


Figure 11. Biochemical oxygen demand, acrylonitrile. 670 mg/liter prepared sample.

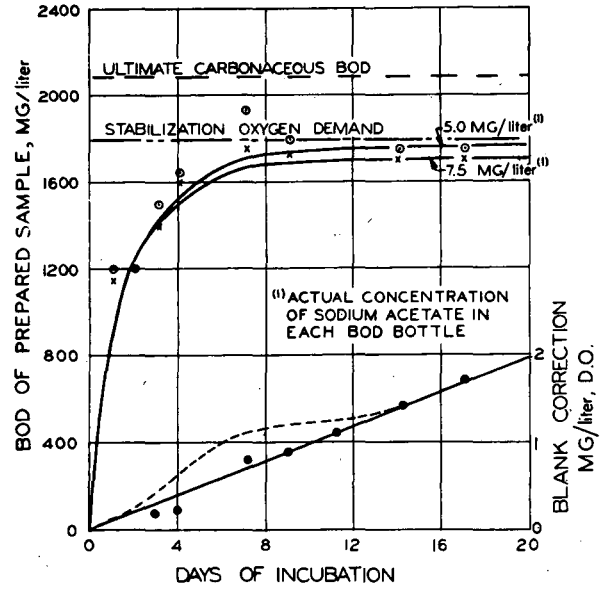


Figure 10. Biochemical oxygen demand, sodium acetate. 2,500 mg/liter prepared sample.

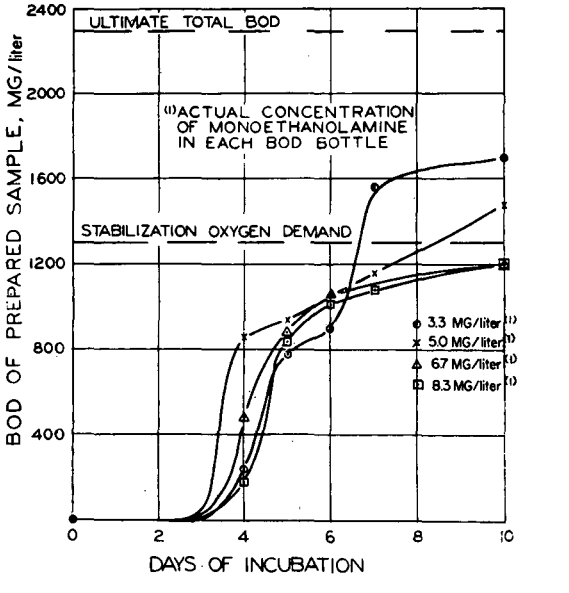


Figure 12. Biochemical oxygen demand, monoethanolamine. 1000 mg/liter prepared sample.

asymptotically whereas the stabilization OD is attained in a finite time (approximately 8 days for glucose, and 7 days for NaAc). For these simple (non-nitrogenous) examples the BOD curves appear to fit roughly first order kinetic expressions. However nitrogen-containing compounds (see Figs. 11 and 12) such as acryonitrile and monoethanolamine show poor correlation in the 5-day BOD test, exhibiting induction periods (*lag*) and concentration-dependent nitrification.

11.1.2 Measurement of EO

For the measurement of energy oxygen, the Warburg Respirometer (Fig. 13) is frequently employed (Ref. 43). In the respirometric method, oxygen consumption is measured as the difference between the values obtained for seed alone and for seed and sample. Net oxygen consumption at the endogenous stage (corrected for seed O_2 consumption) represents *energy oxygen*.

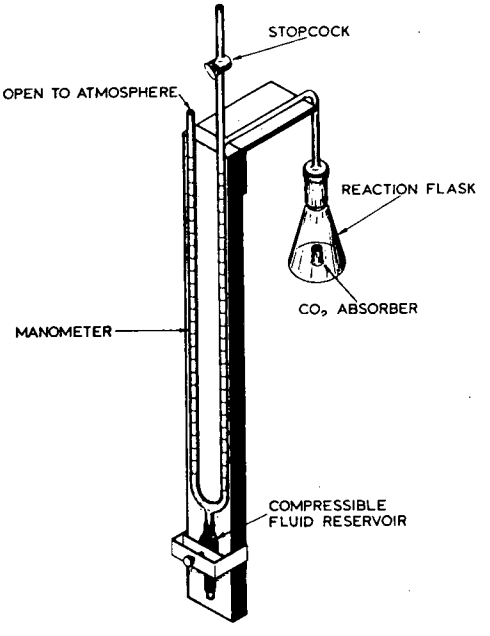


Figure 13. Diagram of Warburg apparatus.

Energy oxygen measurement has also been used as a parameter in biological activity studies (Refs. 43 and 50). It is an important concept in the clarification of bio-oxidation processes. An attempt to correlate EO values obtained from turbidity data (related to cell synthesis) with those gleaned from Warburg measurements has not been satisfactory (Ref. 51.)

11.2 STOD

Another approach is that of Vernimmen and coworkers (Ref. 44) who used the following procedure for *short term oxygen demand (STOD)* measurement. The O_2-uptake in a stirred, sealed system, seeded with a culture, was measured under endogenous conditions using a DO probe (see H2O-DO, Sec. 3.6). Introduction of the wastewater sample resulted in an increase in O_2-uptake, followed by a return to the endogenous state when the energy OD of the organic wastes had been removed. The net consumption of oxygen between initial and final endogenous states reflected the EO utilized by the waste (Fig. 14).

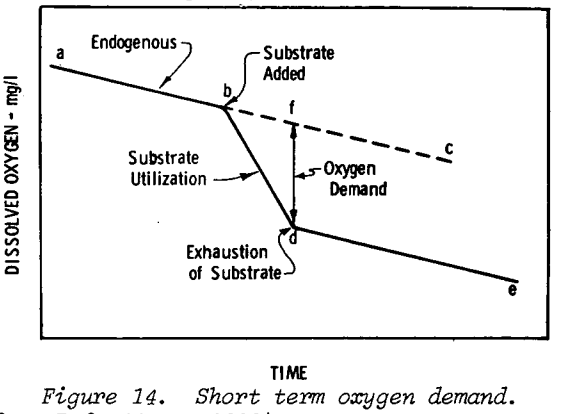


Figure 14. Short term oxygen demand. (from Ref. 44, p. 1006)

11.3 TBOD

Mullis and Schroeder (Ref. 38) applied the *mass culture aeration* technique of Hiser and Busch (Ref. 37) to the determination of the *TBOD (total biological oxygen demand)* of insoluble wastes. In a mass culture, the bacterial concentrations are much greater than in the usual BOD test, being of the order of several hundreds or thousands of milligrams of organisms per liter of the culture. The procedure involves separate chemical oxygen demand (COD) (Sec. 1.2) determination of the soluble substrate and of a washed mass culture of aerobic microbial organisms suspended in tap water. A mixture containing a known volume of each component is then aerated. Substrate utilization is traced by first analyzing *filtered* samples withdrawn periodically, employing the COD test. The point at which filtrate COD becomes constant is termed the *end-point filtrate COD (ef-COD)*. From it, TBOD is obtained using the following equation:

$$TBOD = D.F. \times \Delta\ COD\ (mg/l), \qquad (Eq.\ 13)$$

where D.F. = dilution factor = volume of mixture/volume of substrate, and
ΔCOD = difference between initial COD and ef-COD.

Fig. 15 shows a typical curve: examination of the diagram reveals that a suitably selected substrate-culture ratio (*loading*) can insure a short completion time for the test.

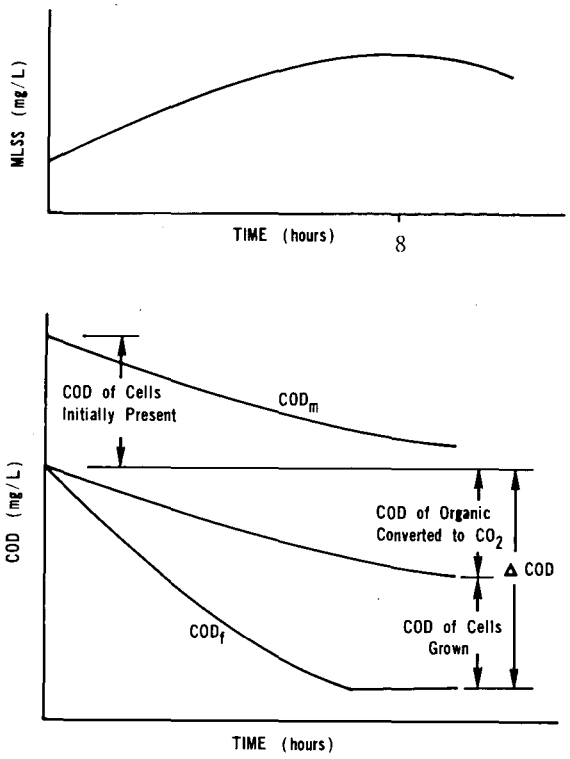


Figure 15. TBOD

The experiments of Hiser and Busch (Ref. 37) indicate that the TBOD test is accurate within ±10%. This is greater accuracy than afforded by the 5-day BOD test and therefore acceptable for use in process control.

11.3.1 Mass Culture Aeration Methods: General Considerations

In the mass culture TBOD test, it is the remaining soluble* carbon (food) present at any given time that is measured -- not oxygen uptake. Consequently, and unlike its importance in the 5-day BOD test, the fraction of food converted to cellular matter, i.e., the ratio of cellular material formed/CO_2 produced, is irrelevant here. The use of a 0.45 μ filter excludes new cellular material formed from the filtrate, since bacterial dimensions are generally >1 μ. Consequently there is no danger of confusing new organic carbon formed with that originally available. Only the chromate-oxidizable fraction of the *soluble* organic carbon is measured; and only that total amount of soluble organic carbon that is biodegradable by the culture used. Thus TBOD, unlike the 5-day BOD test, is a measure of the ultimate OD of the substrate.

When the TBOD test is applied to a mixed solid and soluble substrate, difficulties arise due to the difference in COD for the *MLSS (mixed liquor suspended solids)* and the filtrate moieties. The modified test described above takes this difficulty into account in that the difference between the initial and final COD in the filtrate reflects the OD of the insoluble organics, and new cell synthesis, rather than TBOD. Substitution of this difference (Δ (COD)) in Equation 13 will then yield the TBOD value.

11.3.2 Δ COD**

Since most of the rapid procedures suggested as alternates to the 5-day BOD method are based on certain similar assumptions, a brief analysis of the salient points will be presented in this section. For simplicity the treatment will exclude from consideration any nitrification or non-bacterial processes.

Denote initial and final COD values as $(COD)_o$ and $(COD)_\phi$, respectively. Then

$$\Delta COD = (COD)_o - (COD)_\phi \quad \text{(Eq. 14)}$$

$(COD)_o$ = Σ soluble carbon + seed + insoluble carbon

$$= \Sigma\, SC_o + B_o + IC_o \quad \text{(Eq. 15)}$$

$(COD)_\phi$ = Σ soluble carbon + seed + new cells + insoluble C

$$= \Sigma\, SC_\phi + B_o + B_n + IC_\phi \quad \text{(Eq. 16)}$$

$$\Delta COD = (COD)_o - (COD)_\phi$$
$$= SC_o + B_o + IC_o - [SC_\phi + B_o + B_n + IC_\phi] \quad \text{(Eq. 17)}$$

For $IC_o = 0$, and COD determinations carried out on *filtrates* only, $B_o + B_n$ are eliminated, and ΔCOD reduces to:

$$\Delta COD = SC_o - SC_\phi \quad \text{(Eq. 18)}$$

For $IC_o \neq 0$, and $B_o \approx$ constant,

$$\Delta COD = SC_o + IC_o - [SC_\phi + IC_\phi + B_n] \quad \text{(Eq. 19)}$$

*Soluble material is defined as that which will pass through a .45 μ filter.

**This section is based on an analysis by J.J. Connors of the assumptions of the Mass Culture Aeration technique (private communication).

At time t,

$(COD)_t = SC_t + IC_t + B_t$ (where $B_t = B_o + B_n$)

For t = 0, $(COD)_o = SC_o + IC_o + B_o$

From Mullis et al (Ref. 38), the COD for substrate plus new cells is:

$$(COD)_s = [SC + IC + B_o + B_n] - B_o \quad \text{(Eq. 20)}$$

For t = 0, $B_n = 0$, and Equation 20 reduces to

$$(COD)_{s,o} = SC_o + IC_o \quad \text{(Eq. 21)}$$

From Equation 19 above, $\overbrace{SC_\phi + IC_\phi + B_n}^{A}$

$$\Delta COD = SC_o + IC_o - [SC_\phi + IC_\phi + B_n]$$

$$\Delta COD = (COD)_{s,o} - A \quad \text{(Eq. 22)}$$

At this point, Mullis et al make the following two assumptions:

1) All insoluble carbon is converted either to CO_2 or to new cells. Thus,

$$IC_\phi = 0, \text{ and} \quad \text{(Eq. 23)}$$

2) B_n (new cells formed) may be ignored, analytically, since they are not filterable, so that

$$\Delta COD = (COD)_{s,o} - SC_\phi, \text{ and} \quad \text{(Eq. 24)}$$

$TBOD = [(COD)_{s,o} - SC_\phi] \times D.F.$ = total biological oxygen demand.

This is identical with Equation 13.

In a recent article Gaudy and Gaudy (Ref. 45) argued that the use of the BOD test as a measure of "purification efficiency" was not defensible and recommended ΔCOD for this purpose. They pointed out that the purpose of biological treatment was the removal of biologically available organic matter, and that any method which measured this removal was acceptable. They further cited two measurement criteria: 1) the method must reflect the *% metabolizable* organic matter removed during treatment, and 2) it must be fast enough to be useful in dealing with any malfunction which results in a lower quality effluent in a treatment facility. Examination of the plot of a hypothetical system (Fig. 16) reveals the changes which would be observed when a system containing a biologically available organic substrate, S, is seeded with appropriate (i.e., *acclimated*) microorganisms. Microbial growth is shown as an increase in biological solids. The accumulated oxygen uptake, y, is a measure of the BOD of the system, and ΔCOD measures the amount of substrate removed. Dichromate digestion of organic matter to $CO_2 + H_2O$ measures total oxidizable organic matter in solution (COD). By a plot of the results of periodic analyses for solids (x), collected using the membrane filter technique, and a corresponding plot of COD determined on the filtrates,

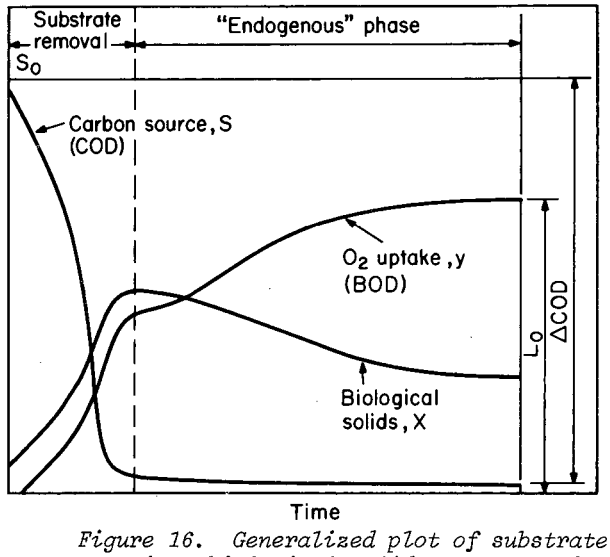


Figure 16. Generalized plot of substrate concentration, biological solids concentration, and oxygen utilization during exertion of biochemical oxygen demand. This figure shows the course of microbial growth (increases in biological solids, X) which would be observed if one placed a small inoculum (seed) of microorganisms in a vessel in the presence of a biologically available source of carbon (substrate, S) to which the microorganisms were acclimated. Also shown are plots of the accumulated oxygen uptake (BOD, y) and the total amount of organic matter remaining in solution measured by a general chemical test involving the digestion of organic matter to carbon dioxide and water in the presence of potassium dichromate under acid conditions, i.e., the chemical oxygen demand test. The total amount of substrate removed is ΔCOD. L_o represents so-called ultimate BOD; at this point the oxygen uptake has ceased. (From Ref. 45, p. 32.)

equivalent diagrams may be obtained experimentally. Oxygen uptake *(BOD exertion, y)* may be determined manometrically or by means of a sensor in the case of dilute solutions. This yields three vital parameters of the system: (a) the amount of solids present at a given time t, (b) the organic substrate (COD) present at time t, and (c) the oxygen uptake (BOD exertion) for the time in question. For the simplest system which contains *aerobic organotrophs* only (e.g., no nitrifying bacteria, etc.) oxygen uptake will measure carbonaceous BOD only. Where the slope of the curve y approaches zero, the *ultimate BOD* value, L_o, has been attained. As is clear from the diagram, O_2 uptake continues at the expense of the biological solids produced, long after BOD removal of the original substrate. The familiar "plateau" in

the BOD curve occurs when substrate removal is essentially complete and is often used as an indicator that this condition has been achieved.

If the curves in Fig. 16 are viewed from the standpoint of waste purification such as occurs in an *activated sludge (AS)* aerator, essentially similar reasoning may be applied: i.e., the carbon source is removed, biological solids build up, and O_2 is utilized in the process. The difference is that during the normal operation of an AS process, the *endogenous* phase reactions of the right hand side of Fig. 16 are not allowed to occur, since the solids are generally separated in the clarifier before the treated waste is discharged as effluent. The latter, depending on flocculation and settling efficiencies, will contain more or less of the non-metabolized organics (COD), but the biologically-produced solids will have been largely retained as sludge. The difference between influent and effluent COD is a measure of the organic matter removed in the aerator:

$$COD_{influent} - COD_{effluent} = \Delta COD \qquad \text{(Eq. 25)}$$

When ΔCOD is at a maximum value -- i.e., cannot be reduced further by biological means -- then ΔCOD becomes a measure of the amount of organic wastes available to the microorganisms in the system. This is often confused with BOD, but as may be seen from the diagram, L_o (the *ultimate BOD* of the waste) is different from ΔCOD. Because a significant fraction of L_o is exerted after original carbon removal has occurred, the oxygen-uptake of this fraction depends on the degree of aerobic digestion of the solids produced, and may be considerably more variable than ΔCOD. Thus, it would appear that ΔCOD is a more reliable test than the 5-hr BOD test or L_o. Since ΔCOD (as opposed to COD) is a measure of only that fraction of the waste which is *biologically available*, it may be used to estimate the organic BOD present, even in the presence of non-biodegradable COD. Thus, a waste may be high in lignins which are relatively inert biologically, but which are oxidized chemically in the COD test. Such a waste would have a high COD, but the effluent would not present any serious challenge, at least so far as DO depletion is concerned.

11.4 Parameters Related to Cell Synthesis

Since the synthesis of new cellular substances is the direct result of energy consumption, quantitative measurement of all syntheses is essential to ascertain the degree of biological activity. The suggestions of Busch and Myrick (Refs. 15, 48, 49) for the gravimetric determination of *suspended solids (SS)*, or the measurement of increased COD for the SS, presents difficulties where precipitates are already present, or where there is a low degree of synthetic activity by bacteria utilizing organic substances in dilute solution.

Production of new *deoxyribonucleic acids (DNA)* may also be used as a measure of new cell production. The method involves a differential technique and is unfortunately a slow and laborious one (Ref. 53).

Two other methods which have been used in cell synthesis measurements take advantage of biochemical oxidation-reduction processes. When 2,3,5-triphenyltetrazolium chloride (TPTZ-oxidized form) is reduced by diphosphopyridine nucleotide (DPN-reduced form), it forms the red-colored formazan. This reaction was used by Kun and Abood (Ref. 54) as an indicator of the viability of cells. Brodie reported that the reaction is a stoichiometric one under aerobic conditions (Ref. 55) and it has been used to measure biological activity in activated sludges (Ref. 56).

The production of ATP *(adenosine triphosphate)* has been related directly to bacterial growth, and is the intermediate in energy transfer for this process (Ref. 57). Thus ATP production and the reduction of TPTZ both offer promise in the measurement of cell synthesis reactions.

11.5 Utility of Alternatives

In the last analysis, biological activity can be quantitatively ascertained only through parameters which relate directly to such activity, i.e., cell production and/or O_2 consumption. However, the *indirect* relationship to biological activity of such parameters as COD and TOC *(total organic carbon)* often provide useful and rapid indicators for ongoing monitoring operations when used in conjunction with BOD measurements.

12. General Analytical Considerations

A BOD analysis may be concerned with 1) establishing the biosynthetic and oxidation reactions of a naturally existing population of microorganisms such as might occur in domestic sewage, or in a surface stream, or 2) the detection of organic substances which may provide the substrate for an *acclimated** culture of microorganisms.

*See p. 9 and below; see also Standard Methods 13th edition.

Where a natural culture is employed, it should be checked for BOD activity with the standard glucose-glutamic acid substrate, as described in Ref. 7. Since a domestic source of sewage may contain inhibiting industrial wastes at times, the glucose-glutamic test is necessary to establish the viability of the seed source. In the case of the so-called *acclimated cultures*, the organisms are exposed to the organic substances which are not a normal food source (Refs. 2 and 7) and natural adaptation is allowed to occur.

12.1 Toxicity

When BOD fails to develop in the presence of an inoculum, it may be due to one of two factors; 1) materials resistant to bio-oxidation and/or 2) the presence of toxic substances in the sample.*

The procedure recommended for determining toxicity consists of a series of BOD tests over a wide dilution range. It is assumed that, where acute toxicity exists, bio-oxidation reactions are inhibited. However, masking chemical reactions which utilize DO may also be involved. It is therefore advisable to perform an *IDOD (immediate dissolved oxygen demand)* test. In addition, if organically polluted wastewaters fail to show an OD, an internal control in the form of a readily oxidized organic substance should be added to each dilution in the series (Ref. 58). For a further discussion of toxicity tests and interpretation of results, see Ref. 42, pp. 814-16.

12.2 Dilution

The procedure for preparing high quality dilution water is described in Ref. 7. Toxic inorganic cations are removed in the distillation process, or by the use of an appropriate ion exchange procedure. Organics, in particular the lower boiling ones, pose more of a problem. BOD dilution water may be checked by incubation with seed or by analysis using a *total organic carbon (TOC)* analyzer, which can detect as low as 0.2% (mg/l) of organic C (Ref. 59). In any event, dilution water is best checked for organic contamination prior to use.

As has already been indicated, low concentrations of organics are not easily removed from dilution waters. Among the methods used to accomplish this end are 1) pre-seeding and long (>1 week) incubation of dilution water prior to use; and 2) re-distillation with rejection of the first cut to eliminate low-boiling organics. Fig. 17 illustrates a still recommended for the latter procedure. The use of a blank correction may sometimes be essential for the meaningful interpretation of BOD data, according to Stack (ref. 42).

*For acute toxicity tests see Ref. 4: 1973 Book of ASTM Standards, Vol. 23.

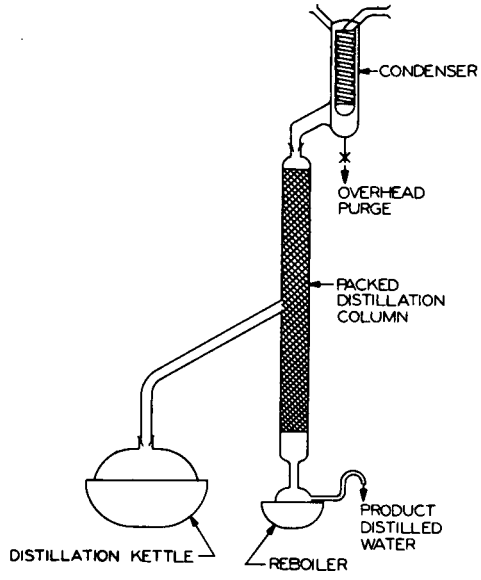


Figure 17. Water distillation apparatus (from Ref. 42, p. 817).

Interpretation of oxygen depletion results must consider at least the following factors: 1) "blank" oxygen consumption related to organic contaminants present in the dilution water; 2) the oxygen consumed by the seed itself plus any organic substances present in the seed inoculum; and 3) nitrification processes. In addition to these considerations, oxygen may be consumed in the (auto-oxidative) reactions of free radicals (Ref. 60) in solutions which are otherwise sterile.

12.3 Nitrification

Samples which have not been *biologically stabilized* may undergo long periods of carbonaceous BOD development without concomitant oxidation of nitrogenous materials to nitrates *(nitrification)*. However, where partial biological stabilization has occurred, nitrification (Sec. 2.4) may take place within the 5-day BOD test period, yielding confusing oxygen-consumption data. Such unadjusted data, if applied to problems such as the organic loading of a stream, or the efficiency of a bio-oxidation process, can be very misleading.

As the emphasis on water quality becomes greater, it will become more essential to determine the ultimate OD's of systems, isolating the carbonaceous and nitrogenous moieties. A number of techniques have been employed to deal with this problem; they have been discussed briefly in section 2.4 of this chapter. For a more complete discussion of these alternatives and additional references, the reader is referred to Ref. 42, Chapter 15 (pp. 820 ff).

In Figs. 9-12 (p. 19), the effect of concentration of substrate on nitrification indicates a correlation between sample dilution and the initiation of nitrification. Stack (Ref. 42) recommends that one approach to the problem would be to substitute re-aeration for sample dilution where nitrification is a problem. By the use of oxygen probes, the DO content can be monitored non-destructively, and the sample re-aerated at intervals as necessary (Ref. 42, p. 822).

12.4 Sampling

"...The prime requirement of all samples, regardless of the method of collection, is that they be representative....For in all cases, the quality of any investigation of an aquatic eco-system is no better than the sampling program used." (Ref. 61)

In general, the sampling methods and precautions employed for DO (H2O:DO, Sec. 2.1) analysis apply to BOD. See Ref. 4, Sec. D-510, for a discussion of sampling techniques.

12.4.1 Samplers and Sampling Locations

Samples for BOD determination are generally collected in narrow-necked glass-stoppered (G.S.) flasks of 200 to 300 ml capacity, with flared rims. Great care must be exercised in the collection of samples for BOD analysis to avoid agitation or post-sampling contact with air, in order to minimize the risk of oxygen exchange. The method of sampling is influenced by the source of the sample, the depth from which it is to be aliquoted, and even the method of analysis to be used. King (Ref. 61) suggests the use of special samplers such as the Kemmerer water sampler or the Nansen water bottle for the collection of all water samples to be used in the determination of DO, in order to avoid oxygen exchange between the sample and the atmosphere. Standard Methods (Ref. 7) recommends a Kemmerer-type sampler (Fig. 18) for all samples collected from depths of more than five feet. In the latter instance the sample is bled from the bottom of the sampler through a tube reaching to the bottom of a 250-300 ml BOD bottle. The bottle is filled to overflowing, then allowed to overflow for about 10 seconds, great care being exercised to avoid turbulence and bubble formation during the bottle-filling operation. Water temperature is recorded with the desired precision.

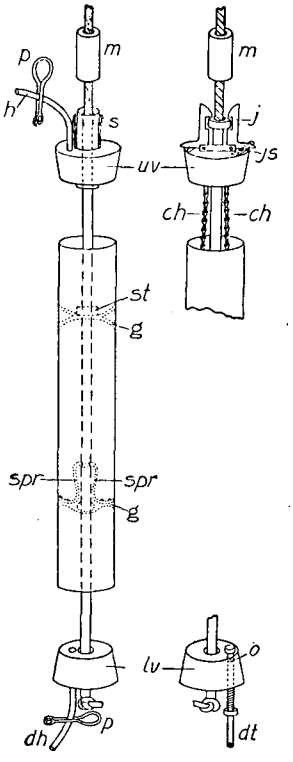


Figure 18. Modified Kemmerer sampler. Left: view of complete sampler with valves open. Top right: another type of construction of upper valve and tripping device. Bottom right: another type of construction of lower valve and drain tube. Key: ch--chain which anchors upper valve to upper interior guide; dh--rubber drain tube; dt--brass drain tube; g--interior guide fastened to inner surface of body of sampler; h--rubber tube; j--jaw of release; js--jaw spring; lv--lower valve; m--messenger; o-opening into interior of drain tube; p--pinchcock; s-upper release spring operating on horizontal pin, one end of which fits into groove on central rod; spr--spring fastened to lower internal guide and operating in groove on central rod to provide lower release; st--stop on central rod; uv--upper valve (from Ref. 7, p. 728).

The locations of sampling points for waste waters are best situated where homogeneous mixing is most likely (e.g., the downstream side of a hydraulic jump or weir). When a narrow, deep channel or a sewer is sampled, a grab sample, to be representative, should originate at approximately 1/3 the depth of the sample source. For wide channels sample collection points should be rotated across the channel width, and the flow velocity should be sufficiently great to avoid the deposition of solids. The creation of turbulence during sampling must be avoided, since this can result in a misrepresentative sample due to the loss of dissolved gases. It is very difficult to obtain a truly "representative" sample of such a heterogeneous mixture as, say, oil-polluted wastewater. Nevertheless the collection of a composite sample can result in analytical data which do give a reasonable profile of the waste waters sampled.

Figs. 19 and 20 are a sketch and a schematic diagram of an automatic sampler (Ref. 17, pp. 124-5) used in sewer sampling.

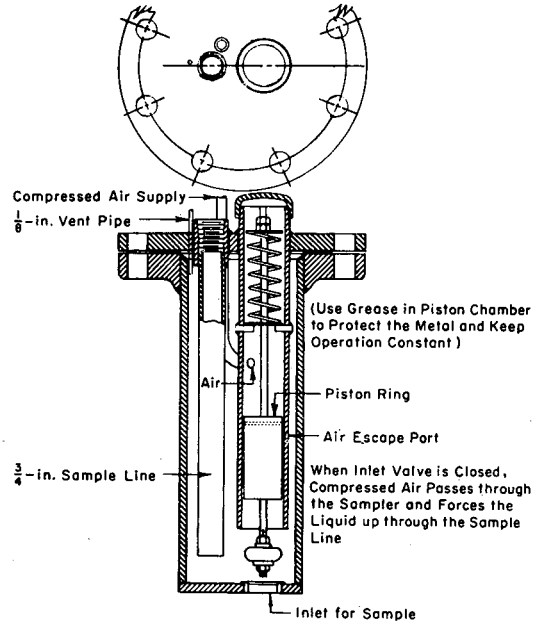


Figure 19. Automatic sampler. This air-lift automatic sampler takes samples from a sewer when a pump cannot be used. (From Ref. 17, p. 124.)

Depth sampling requires special precautions to eliminate effects of pressure and temperature changes. Techniques of sampling waters under

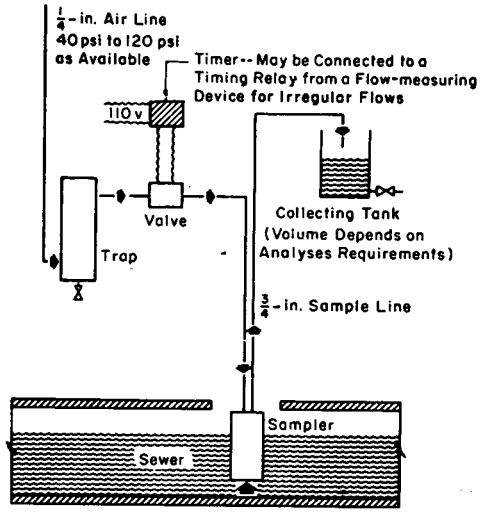


Figure 20. Schematic arrangement of automatic sampler shown in Fig. 20. (From Ref. 17, p. 125.)

pressure, as well as surface waters, are described in detail in Refs. 17, Chapter VIII, and 4 (D-510-68). Fig. 21 illustrates an APHA type sampler used for sampling at moderate depths.

Selection of a sampling site is determined primarily by two factors: a) the type of investigation, and b) the degree of mixing in the body of water to be analyzed. Rainwater and Thatcher (Ref. 62) recommend the use of a 3-dimensional grid intersection method of sampling, with samples taken at various depths as necessary to provide a representative sampling. If only a single sample is to be taken, it should derive from the center of the water mass.

Sampling frequency is determined by the variability of the source sampled. No important change in quality of the water should go unnoticed in an adequately planned sampling procedure. The U.S. Geological Survey follows the arbitrary rule for sampling once per day.

12.4.2 Sampling Apparatus: Materials and Handling

Sampling equipment is made from a variety of materials. Containers of hard rubber, polyethylene, and a few other plastics have been found satisfactory. No appreciable difference

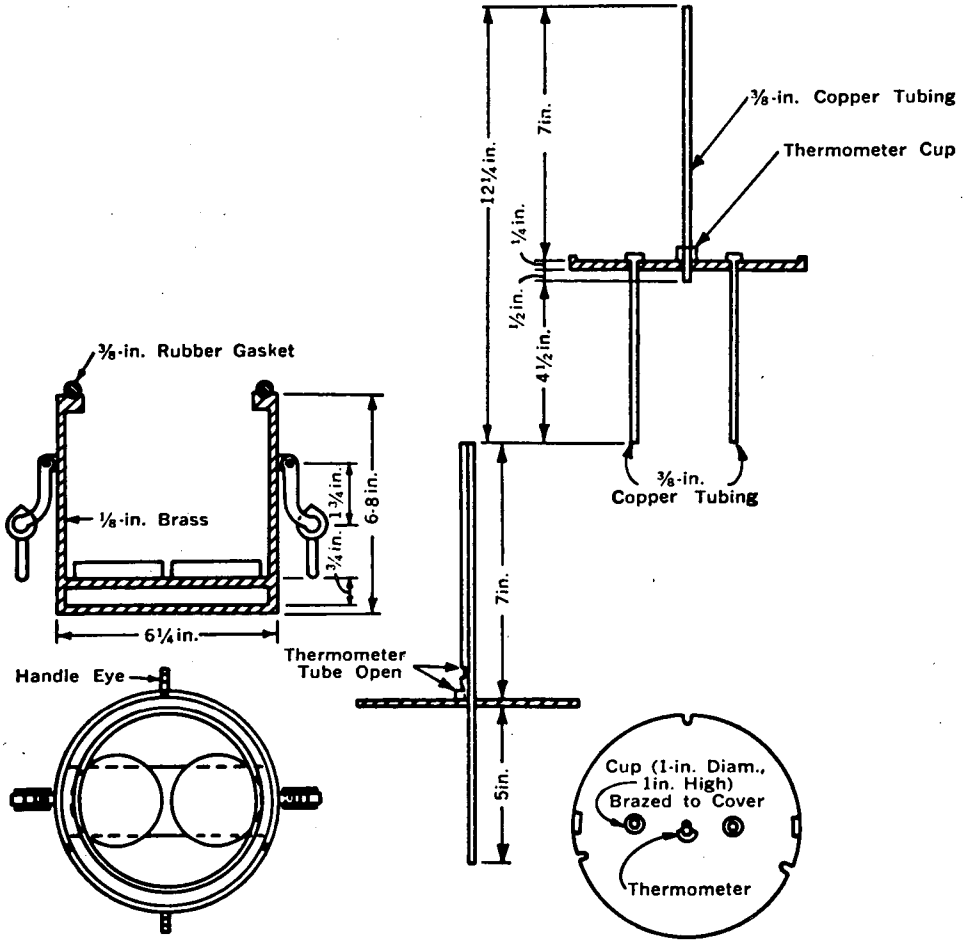


Figure 21. DO and BOD sampler assembly. (From Ref. 7, p. 476.)

in the following characteristics was detected for pyrex vs. polyethylene containers: silica content, Na^+, alkalinity, Cl^-, boron, specific conductance or pH, when water samples were stored for about five months.

Soda lime glass sampling bottles are, of course, not recommended because of the risk of sample contamination through leaching of ions from the glass and/or ion exchange between the glass and the water sample.

The use of stainless steel tubing for sampling lines used in the acquisition of industrial water samples for DO testing is recommended by the ASTM Committee on Water (D-19). "The sample line shall contain a cooling coil (C.C.) if the water being sampled is above R.T., in which case, cool the water to 60-65°F (16-18°C). Where a C.C is used, the valve shall be at the inlet to the C.C. and the overflow shall be to a point of lower elevation." (Ref. 4, p. 93).

Standard BOD bottles have a capacity of 250-300 ml and are fitted with ground glass stoppers. They should be routinely cleaned with a good detergent and rinsed and drained thoroughly prior to use. The use of a water seal is recommended as a precaution against introducing air into the bottle during the incubation period. Inversion in a water bath of the BOD bottle containing the sample or the addition of water to the flared mouth of the (sealed) BOD bottle may be employed as the means of preventing air (O_2) diffusion into the sample.

Incubated samples should be placed in a thermostated bath at 20 ±1°C, and all light excluded during incubation to prevent additional oxygen production by algae.

12.4.3 Sample Preservation

For biochemically active samples it is best to analyze immediately after sampling. Where this is not possible the aliquot should be refrigerated at 4°C.

The matter of sampling precautions, volumes, and equipment is further discussed in ASTM Standards, Vol. 23 (Methods D-510 and D-596) and in this volume under H2O-DO, Section 2.1.

12.4.4 Procedures

ASTM procedures for the determination of dissolved oxygen in industrial wastewaters are described under methods D-888 and D-1589 (Ref. 4). For further discussion of reagents and procedures, pre-seeding of BOD samples, etc., see this chapter, Sec. 2.6 and Refs. 7, Sec. 219; 4, under methods D-888 and D-1589; see also Ref. 3, pp. 114-16. In addition, procedures are briefly discussed in this chapter under Sec. 7. See also this volume, chapter H2O-DO. Results are expressed in mg/l.

For a more detailed description of the standard method for reporting the results of water analyses the reader is referred to Refs. 4, D-596-69; and 17, p. 224.

13. BOD in Natural Waters: *In Situ* Environmental Factors

The development of OD below the point of discharge of an organic pollutant into a moving stream depends on a number of physical factors, of which stream geometry ranks as one of the most important (Refs. 63-64).

For a relatively deep body of water, the biological activity of soluble organic pollutants and/or those in colloidal suspension may be dispersed in a homogeneous manner. With the synthesis of microorganisms, some flocculation is likely to occur, followed by settling of flocculent material and *anaerobic stabilization*. Under dynamic stream conditions, if the organic discharge is continuous, aerobic biosynthesis depends on the food/organism ratio. Thus, the stabilization rate for organics discharged to a stream is strongly dependent on whether or not a population of appropriate microorganisms is already present. If this is indeed the case, then a rapid increase in oxygen consumption and biosynthesis will occur.

In the case of a shallow stream, there is generally a favorable food/organism ratio. Because of the shallow depth, the area/volume ratio of bottom surface to stream is large. Generally shallow streams have relatively high velocities, providing turbulent flow conditions. These conditions favor rapid reaeration and microorganism growth. Just below the organic discharge, attached organisms may luxuriate. The stream here behaves as a *trickling filter* with a BOD removal rate considerably greater than for comparable pollution conditions in a deeper stream. The OD in the active zone (i.e., where attached organisms are feeding on the discharge) may be more closely correlated with EO than with BOD removal. Ultimately, the attached organisms may grow large enough to be detached by the stream current and be deposited down stream in a more quiescent section of the stream. In addition, *anaerobic stabilization* of settled materials will tend to reduce the oxygen consumption over that theoretically required to stabilize the organics and remove the initial BOD.

Resuspension of sediment during short periods of high stream velocity can have a profound effect on a column of water. It is well known that the short term BOD value of relatively stable organic matter of low (short term) BOD will be enhanced after a period of anaerobic decomposition in the stream sediment (Ref. 65). Resuspension of such sediments can suddenly impose an appreciable additional BOD burden on the stream. Jansa and Akerlindh (Ref. 66) studied the relationship between the amount of settleable solids found and the distance which the suspended solids were carried before settling out, as a function of stream velocity. They found that there is a sedimentation equilibrium point which exists downstream from a sewage outfall -- that is, a point where BOD deposition/day equals the amount oxidized/day. This is a reasonable assumption to make for those situations where only the oxidizable fraction of the suspension is a consideration, but may be applied with confidence only for those cases of stream pollution in which resuspension of the sediment is negligible. Under these (non-turbulent) conditions the following expression for oxygen depletion due to sedimentary BOD may be used to improve the fit of the Streeter Phelps (S-P) equation:*

*The Streeter-Phelps equation takes the form: $dD/dt = K_1B - K_2D$, where D is the oxygen deficit at time t, B is the organic oxygen demand, and K_1 and K_2 are depletion and reaeration rate constants, respectively.

$\frac{dI_S}{dt} = k_S L_S e^{-k_S t}$, where (Eq. 26)

I_S is settled sludge BOD at time t

L_S is the total quantity of settleable sludge BOD, and

k_S is the sedimentation rate constant.

This was found to be a useful relationship in describing the DO status of one sewage-polluted Swedish stream, where k_S was found to be 40 day^{-1}. It was further indicated by these workers that the settling of BOD-containing solids was negligible when stream velocities were >50 cm/sec.

Sludge-carrying capacity may be assumed to have a first-order dependence on stream velocity at low velocities, as a first approximation (Ref. 67). However, for stream velocities >12 cm/sec the capacity varies as the square of the velocity. The BOD of suspended solids may of course be experimentally determined. Similarly, their settleability under simulated flow conditions or at v = 0 is empirically verifiable. However, the trend toward adequate settling of BOD solids should render the sedimentation term of the S-P expression superfluous and merely a matter of academic interest in the treatment plants of the future.

For the description of a general design model for sedimentation basins showing the effects of such parameters as geometry, flow velocity, and particle size, density and quality, see Refs. 68a to 68c inclusive.

It should be noted that "physiologically inert"* brines such as NaCl or Na_2SO_4 may, by virtue of competition of their anions with phosphate for sorption sites, favor the release of $PO_4^{\equiv}$ from sediment, and thereby promote eutrophication. For this reason increase in the ionic strength of a site due to the desorption of salts may be expected to increase the eutrophication rate.

14. Some BOD-Related Phenomena in Natural Waters

There are two principal aspects of biological processes: one involves the *self-purification* activity of plants and animals which transforms potentially harmful substances into innocuous metabolic products, generally forfeiting DO in the process and frequently utilizing some of the species normally present in the unpolluted waters.

*The term "physiologically inert" is here used in the eutrophication sense only.

The second aspect involves biotal changes in response to pollutants. Thus biota may be used as quality criteria and as means of assessing environmental impact of pollution. For comprehensive treatments of the biological aspects of wastewater management see Refs. 69a, b, c, d, and e. The latter reference (69e) is a collection of classical papers, including the pioneering contributions of Kolkwitz and Marsson (Refs. 70a and b).

14.1 Self-purification

Self-purification, as the name implies, is the process whereby a stream rids itself of pollutants (impurities). Waste materials introduced into a body of water affect the biota directly and indirectly. The effect of waste may be lethal, or it may be more subtle, affecting behavior of biota, or reproduction, adversely.

The toxicity of substances or mixed wastes is determined by means of bioassays using fish, larvae and other invertebrates or microbes. A variety of laboratory procedures are used, but the methods of Doudoroff et al have become standard (Ref. 71). See also Standard Methods, 13th edition. For toxicity and bioassay methods, see Chapters 13 and 14 of Ref. 39, Vol. 2 (Refs. 72a and b).

14.2 pH and BOD

Photosynthetic and respiratory activities of biota have a direct effect on the CO_2 content of streams, and the diurnal variation in pH as a result of these processes is usually of the order of ±0.5 pH unit. However, in the presence of intense algal growth, it is possible for the pH to approach the upper physiological limit by the end of the day. This may be illustrated by the simplified equation below which considers only the calcium bicarbonate in fresh waters:

$$Ca(HCO_3)_2 - 2CO_2 \text{ (photosynthesis)} \rightarrow Ca(OH)_2$$
$$\downarrow \qquad\qquad\qquad\qquad \downarrow$$
$$\left[Ca^{++} + 2(HCO_3^-)\right] \qquad \left[Ca^{++} + 2(OH)^-\right]$$

(Eq. 27)

This reaction clearly favors increase in pH. The relationship of the various carbonic chemical species of the pH range 4-10 is shown in Table 12. However, in soils (particularly when water-logged), and in deep waters of lakes, the total content of carbonic species may go far beyond the level implied by solubility equilibria due to anaerobic metabolic processes (Benoit, *Op. cit.*, Ref. 67).

Table 12

Dependence of Carbon Dioxide, Bicarbonate, and Carbonate Ratios on pH Values[a]

pH	CO_2	HCO_3^-	$CO_3^=$
4	0.996	0.004	$\sim 10^{-9}$
7	0.21	0.79	$\sim 10^{-4}$
9	0.003	0.966	0.03
10	10^{-4}	0.76	0.24 .

[a] *Adapted from Ref. 73.*

14.3 Organic Matter

Natural waters contain organic matter in the form of living animals and plants, their nonliving particulate remains (*detritus*) as well as their soluble organic residues and excretions. It has been estimated by Parsons (Ref. 74) that the surface waters of the North Atlantic contain approximately 2 mg/l of soluble organic matter, 0.2 detritus, 0.04 phytoplankton, 0.004 zooplankton and 0.00004 fish. Fresh waters contain perhaps 10 times as much organic material. The differences are related to the more direct organic contribution which fresh waters receive from the land rather than to any great difference in productivity.

14.4 Dissolved Oxygen Relations

Dissolved oxygen (DO) is a very commonly used water quality criterion (see this volume, H2O-BIO, DO). Loucks (Ref. 75) and coworkers give the following description of DO relations in a stream polluted with oxygen-consuming waters:

$$\frac{dB}{dt} = (K_1 + K_3)B + R, \text{ where} \qquad \text{(Eq. 28)}$$

$\frac{dB}{dt}$ is the rate of change of BOD with time,

B is the BOD present at time t, and

R is the rate of BOD addition from run-off and scour.

K_1 and K_3 are rate constants for deoxygenation and sedimentation, respectively.

A related expression in terms of the DO deficit, D, is:

$$\frac{dD}{dt} = K_1B - k_2D - A, \text{ where} \qquad \text{(Eq. 29)}$$

$\frac{dD}{dt}$ is the change in DO deficit with time,

D is the difference between existing [DO] at time t and the saturation value,

A is the net rate of oxygen production from the photosynthesis-respiration cycle, and

K_2 is the reaeration rate constant.

Integration of equations 28 and 29 above results in:

$$B_t = (B_o - \frac{R}{K_1-K_3})e^{-(k_1 + k_3)t} + \frac{R}{K_1+K_3}, \qquad \text{(Eq. 30)}$$

and

$$D_t = \frac{K}{K_2-K_1-K_3}\left[(B_o-\frac{R}{K_1+K_3})e^{-(K_1+K_2)t} - e^{K_2t}\right]$$

$$+ \frac{K_1}{K_2}\left[(\frac{R}{K_2+K_3} - \frac{A}{K_1})(1-e^{-K_2t})\right] + D_o\, e^{-K_2t} \qquad \text{(Eq. 31)}$$

In Table 13 the reaeration coefficient K_2 was calculated from experimental data obtained under actual stream conditions. Typical values of the parameters involved are shown in columns 2 through 6; of K_1 (the deoxygenation coefficient), in column 7.

The data for K_2 are summarized in Table 14 on page 31 (Ref. 14).

Equation 30 is that of a typical oxygen sag curve (Fig. 22). The minimum t_c in the figure reflects the time of minimum DO value. Prior to t_c, reaeration dominates. From velocity information for a stream one can determine the location of the critical point. The oxygen sag equation is applicable only on the assumption that K's, A and R all remain essentially constant throughout the time element for which the calculation is made and that values for these constants are either obtainable or may be reasonably estimated. For (A, K_3, R) = 0, equation 31 reduces the classic equation of Streeter and Phelps (Ref. 14).

The minimum cost of meeting any given set of DO standards for the river reaches of a basic system may be determined using the model of Loucks and coworkers (Ref. 75).

14.5 Temperature

While temperature is not included as a variable in the DO model, it certainly has a profound effect on oxygen solubility, reaeration, sedimentation and animal and microbial functions (see also this volume, H2O-BIO: DO, Sec. 1.2). Bradshaw and Davidson (Ref. 76) discuss both negative and positive effects of increased temperature on pollution and develop

Table 13

Factors in resultant oxygen formula (1) obtained from data in Table No. 1, Ref. 14, P. 18*

Notation:
D_A = Observed dissolved oxygen content of the river at the upper station, in terms of parts per million of deficit below the oxygen saturation value at the mean river water temperature between the two stations.
D_B = Observed dissolved oxygen content of the river at the lower station, in the same terms as (D_A).
L_a = Corrected initial oxygen demand at the upper station, in terms of parts per million of oxygen.
t = Mean time of flow from the upper to the lower station, in days.
T = Observed mean temperature of the river water, in degrees Centigrade.
K_1 = Coefficient of deoxygenation at the observed mean river water temperature. (Calculated from a value, 0.1 at 20° C.)
K_2 = Coefficient of reaeration, calculated from the other terms.

Month	At temperature of river water							K_2 (at 20° C.)	Mean velocity of flow (feet per second)
	D_A (parts per million)	D_B (parts per million)	L_a (parts per million)	t (days)	T (° C.)	K_1	K_2		
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)
Station 3 to station 11:									
May 1914	0.89	0.63	2.54	0.21	15.9	0.083	0.990	1.38	2.48
June	3.13	1.09	1.91	1.07	24.5	.123	.544	.35	.50
July	4.00	1.32	2.73	1.81	24.6	.124	.380	.25	.29
August	5.53	1.95	4.22	2.73	24.8	.125	.276	.17	.19
September	6.28	2.49	3.59	3.06	20.8	.104	.197	.18	.18
Oct. 1-15	8.63	3.11	3.30	6.23	18.7	.094	.105	.12	.09
Station 11 to station 19:									
May, 1914	.63	.72	4.89	.18	15.9	.083	.245	.34	2.50
June	1.09	1.14	2.20	.77	24.5	.123	.192	.12	.59
July	1.32	1.04	2.54	1.36	24.1	.121	.289	.20	.32
August	1.95	1.60	3.44	1.98	24.4	.122	.217	.14	.22
September	2.49	1.09	3.14	2.30	20.5	.102	.144	.14	.19
Oct. 1-15	3.11	2.60	1.74	4.37	18.6	.092	.052	.06	.10
Station 23 to station 65:									
May, 1914	.85	1.22	5.16	.62	16.3	.084	.200	.30	4.20
June	1.33	.93	2.94	1.90	22.9	.115	.330	.25	1.36
July	1.24	.94	2.65	3.00	24.8	.124	.230	.15	.86
August	1.88	.75	3.69	4.90	24.4	.121	.260	.17	.53
September	3.77	.76	2.56	6.14	20.0	.100	.190	.19	.43
Oct. 1-15	2.83	.50	15.74	11.35	18.0	.091	.353	.43	.23
Station 65 to station 77:									
May, 1914	1.22	.72	4.89	.18	15.9	.083	.245	1.11	3.64
June	.93	.46	3.08	1.02	23.2	.116	.801	.59	.71
July	.94	.54	2.14	1.73	24.8	.125	.436	.28	.44
August	.75	.49	1.26	2.47	24.4	.122	.253	.17	.31
September	.76	.44	1.92	2.54	20.0	.100	.334	.33	.31
Oct. 1-15	.50	.80	3.34	5.02	18.0	.091	.189	.23	.15

*Integrated form of the S-P equation, see footnote, p. 28)

Table 14

Derived values of (K_2) at 20° C. (from Table No. 13)
(from Ref. 14, p. 38)

Stretch	May (1914)	June	July	August	September	Oct. 1-15	October	November	December	January (1915)	February	March	April
3-11	1.38	0.35	0.25	0.17	0.18	0.12	------	------	------	------	------	------	------
11-19	.34	.12	.20	.14	.14	.06	------	------	------	------	------	------	------
23-65	.30	.25	.15	.17	.19	.43	------	------	------	------	------	------	------
65-77	1.11	.59	.28	.17	.33	.23	------	------	------	------	------	------	------
77-88	1.07	.71	.33	.16	.70	.16	------	------	------	------	------	------	------
104-349	.24	.18	.12	.14	.15	.22	------	------	------	------	------	------	------
349-461	.16	.65	.28	.15	.13	.33	------	------	------	------	------	------	------
475-482	.29	.32	.33	.26	.40	------	0.73	3.98	0.96	1.14	0.61	1.43	1.09
482-488	.05	------	.13	.07	.05	------	.35	.81	.39	.10	.78	.71	.14
492-598	.27	.32	.57	.46	.61	------	.31	------	1.05	.99	.59	.65	1.88
598-611	.21	.36	.47	.43	.87	------	.54	------	.75	.58	2.44	.82	------

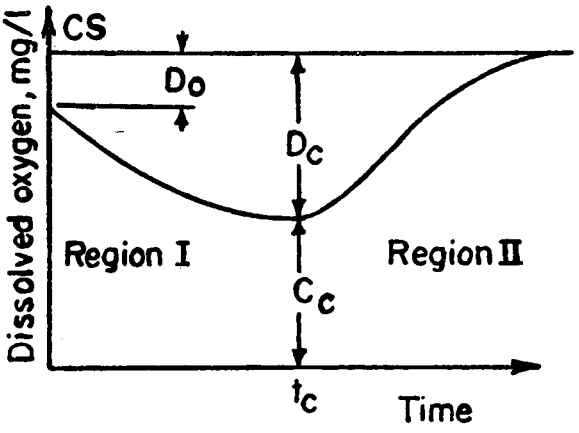


Figure 22. Oxygen sag curve. C is dissolved oxygen (DO) saturation; D_o is initial DO deficit; D_c is critical DO deficit; C_c is critical DO level (from Ref. 75).

a mathematical expression for the temperature effect on the DO of streams carrying a BOD load. Their mathematical model indicates that, theoretically, at least, there exists an optimum temperature profile at a location downstream from a (BOD) pollution point source. This is illustrated with specific examples studied by the authors.

14.6 The BOD Plateau

In two papers (Refs. 77 and 78) Torpey has given valuable empirical data which help evaluate mathematical models. He examined the pattern of the long-term summer DO levels vis à vis BOD loads. Such studies should be most helpful in the planning of long range programs for the monitoring of water quality. Torpey's data are interpreted as evidence for the existence of a "homeostatic"* DO plateau (Fig. 23) in the range of 30% to 50% oxygen saturation. BOD loading rates ranged between 20-135 lb/day/acre in these estuaries with depths which averaged ∿30 ft. Oxidation to NO_3^- of the nitrogenous materials present was not evident during the plateauing, and Torpey interpreted the plateau phenomenon as resulting from symbiosis between the algae present which provided photosynthetic oxygen and bacteria which synthesized essential mineral nutrients for the algae.

*Homeostasis - Homeo (same); statis (condition)
Homeostatic Plateau - relative OD equilibrium exists in this range.

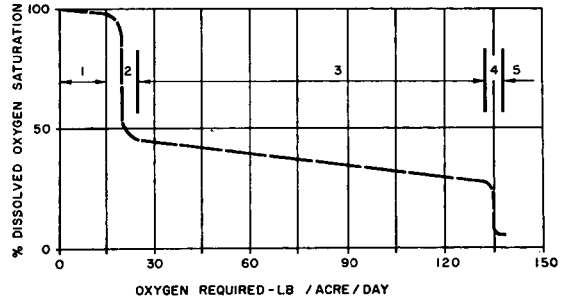


Figure 23. Response of New York Harbor and Thames Estuary. (Ref. 78)

14.6.1 The BOD Plateau and Zoning

Torpey divided the plot into three *ecological zones*, the first of which supported biota such as mollusks, crustacea, and fish (higher forms in the food chain). The "homeostatic plateau" (zone 3) has a primarily microbial biotal composition. He concluded that for loading rates exceeding the plateau region of oxygen requirements, the introduction of sewage treatment by no means guarantees the DO content will undergo any marked increase. For such systems as the Thames and New York harbor, oxygen sag considerations alone will not be indicative of the degree of treatment required for these waters to be restored to a condition enabling them to support large fish populations. To achieve this goal generally demands much more intensive treatment than implied by these indications.

Stream sediments make an important contribution to *total oxygen demand (TOD)*. Oldaker, Burgum and Pahren (Ref. 79) studied the OD of both aged and young river sediments related to sewage outfall. The effects of sediment depths on OD under quiescent conditions were examined in 20 liter carboys. Coincidentally, information was obtained as to the burden incurred where a system is subjected to severe scouring conditions, such as the resuspension of solids during a period of turbulent flow. In-field conditions which normally obtain (i.e., where benthic animals disturb the bottom muds somewhat) are usually intermediate between the extremes of complete quiescence and total resuspension.

Fair and coworkers (Ref. 80) had earlier observed that it took more than a year for attainment of the ultimate OD by bottom muds.

14.7 Reaeration

The absorption rate of oxygen in natural waters is given by the following equation:

$dc/dt = k_2 (C_S - C)$, where (Eq. 32)

C is the measured [DO],

C_S is the saturation value at the temperature of dissolution, and

k_2 is the coefficient of aeration.

Durum and Langbein (Ref. 81) demonstrated the effects on the aeration coefficient of velocity, v, and depth, H (hydraulic effects). In their study of the Kansas-Mississippi-Missouri River system they demonstrated that k_2 decreases as the square root of the mean discharge rate in the downstream direction. This is in the same direction as the variation in stream height and velocity with discharge (depth increases as the 0.4 power, velocity as the 0.1 power of discharge). These same workers also demonstrated regional differences in the square root relationship, k_2 varying as $15\sqrt{Q}$ for coastal plain rivers, and as $80\sqrt{Q}$ in the (northern) Rocky Mountain region, where Q is the mean discharge rate in cubic feet per second. This difference has been related to the slopes of the respective stream beds, since the regions represented are extremes with regard to slope.

There is a general downward trend in reaeration coefficient with increasing height or 'stage' of a river, but shallow reaches *(riffles)* behave differently from deeps or pools. Fig. 25 illustrates a rapid decrease in k_2 with increase in discharge rate; conversely, for pools k_2 increases (more moderately) with increase in discharge. Ultimately the distinction between these stream features disappears at some high stage.

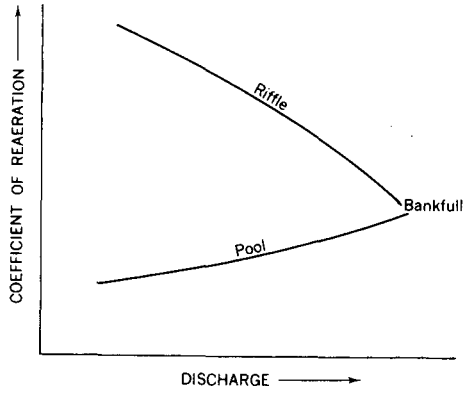


Figure 24. Effect of discharge on aeration (from Ref. 81, p. 4).

Langbein and Durum also estimated nationally the total assimilation capacities for a variety of streams in eight size categories. With their data it is possible to estimate the BOD capacity in tons of oxygen-consuming substances which can be assimilated/mile under conditions which would reduce DO (in mg/l) by one unit. Table 15 lists the assimilatory capacities for three classes of stream: small (I); medium (II); and large (III).

Table 15

Relation of Assimilatory Capacity and Stream Size[a]

Stream class	Assimilatory capacity[b]	Average depth, ft	Assimilatory capacity per ft of depth	k_2 day^{-1}
I	0.04	0.55	0.07	9.5
II	1.0	5.0	0.2	—
III	5.2	45.0	0.12	0.1

[a] *From Ref. 84.*

[b] *Tons of BOD per mile per unit O_2 deficiency.*

15. Waste Assimilation

There are two classes of biological processes which predominate in waste assimilation. They are (1) the photosynthetic and respiratory processes of plants and (2) the ingestive (feeding), digestive and respiratory processes of animals. The latter group includes microscopic multicellular animals and protozoans; the former includes microscopic algae, bacteria and fungi. Although bacteria and fungi can absorb organic matter from solution and digest the absorbed materials, they are commonly found adsorbed onto the surfaces of organic particulate matter. In this case extracellular enzymes are believed to function as mediators in the feeding cycles of the bacteria and fungi. They are, furthermore, known to thrive under conditions unfavorable to the higher plant and animal species, and are therefore the dominating biotal population where stream pollution is most severe.

Bacteria and microalgae constitute the chief food of most protozoan species. In addition they constitute an important food source of the so-called filter-feeding (micro- and macroscopic) invertebrate species. The Chinese adage which may be translated as "big fish eat little fish; little fish eat shrimp, and shrimp eat mud" is a succinct description of the food chain (or web) concept. However, the signifi-

cance of the "mud" in question is overlooked in the ancient adage. It is, in fact, at the base of the food chain, consisting of the partially decomposed remains of plants and animals, and/or the products of the photosynthetic cycle.

Stream oxygenation is effected by two (often simultaneous) processes: (1) the diffusion of atmospheric O_2 in the water and (2) the provision of a net excess of oxygen in the photosynthetic cycle:

$$CO_2 + H_2O \underset{\text{respiration}}{\overset{\text{photosynthesis}}{\rightleftharpoons}} CH_2O + O_2 \quad \text{(Eq. 33)}$$

The photosynthetic component may be further identified according to sources of the contribution as benthic flora -- *epiphyton*, *periphyton* and/or the free floating microscopic plant species known as *phytoplankton*.

Theoretically, the net O_2 production in the cycle represented by Equation 33 above is zero. The formaldehyde polymer $(CH_2O)x$ of the equation schematically represents the carbohydrate production in plant photosynthesis. However, proteins and fats are also synthesized. For nitrogenous compounds such as the proteins or nucleic acids, a source of nitrogen is clearly required, as well as sources of sulfur and phosphorus.

The energy required is supplied by the carbohydrate respiration in the photosynthetic process. Thus, one would not expect a positive net yield of oxygen where anabolic activity is high. However, the removal of plant matter downstream from the active water zone, or the settling of plant tissue to the stream bottom where decomposition may either stop or proceed by an anaerobic mechanism, disturbs the equilibrium situation represented in Equation 33 and results in available oxygen at the water zone in question.

Oxygenation components in streams were measured directly by Stay and coworkers (Ref. 83). These included such parameters as diffusion rates, the photosynthesis of periphyton and phytoplankton, and respiration. The standard practice of using light and dark bottles (Ref. 7, Sec. 601 E)* to exclude or permit photosynthesis, has a number of serious disadvantages: a) it obviates the important contribution of benthos in shallow streams; b) since bottle conditions are stagnant they do not reflect the normal states of interchange between nutrients and the wastes produced in streams; and c) the ratios of surface-to-volume which obtain are excessively high and do not reflect natural conditions, either.

In order to reflect more accurately stream conditions in their field studies, Stay and coworkers used three types of large plastic chambers; the first was sealed to the atmosphere and transparent; the second, also sealed but opaque; and the third chamber was both open and transparent. The chambers were designed for use with either artificial or natural substrates and natural flow velocities were simulated by paddle wheels which were driven either by artificial means or by the use of external water-wheels. Sampling and analysis for gases in the vapor phase as well as those in aqueous solution (i.e., O_2, CO_2, etc.) were possible. The Type 1 chamber (i.e., sealed but transparent) permitted photosynthesis and respiration to go on as simultaneous events or processes, but the atmospheric exchange or diffusion of CO_2 or O_2

*For a detailed description of biological sampling and analysis, see Ref. 7, Sec. 600 ff.

Table 16

Component Processes in Stream Metabolism from Chamber-Dissolved Gas Measurements

Chamber type	Configuration	Process occurring	Change in dissolved gases
1	Transparent, closed to atmosphere	Photosynthesis, respiration	$O_2\uparrow:CO_2\downarrow$ $O_2\downarrow:CO_2\uparrow$
2	Opaque, closed to atmosphere	Respiration	$O_2\downarrow:CO_2\uparrow$
3	Transparent, open to atmosphere	Photosynthesis, respiration, diffusion	$O_2\uparrow:CO_2\downarrow$ $O_2\downarrow:CO_2\uparrow$ $O_2\updownarrow:CO_2\updownarrow$

(Ref. 83)

was not possible. Chambers of Type 2 (opaque) permitted only respiration. Only in Type 3 -- the open, transparent chamber -- do all three processes (i.e., respiration, photosynthesis and diffusion) occur. Thus, it was possible to measure net photosynthesis (i.e., excess of photosynthesis over respiration) using a Type 1 chamber. Similarly the sum of data from Types 1 and 2 chambers is a measure of the gross photosynthetic process. Subtraction of Type 3 data from Type 1 yields the gas exchange between air and water, etc. The processes involved are enumerated in Table 16. Contributions of benthos vs. phytoplankton were measurable by simply damming off the upper chamber substrates. The predominant effects of the former (benthos) was thus clearly shown by these workers in their studies of the Blue River (Oklahoma). The photosynthetic effects of diurnal variations in light intensity were also apparent.

Gaseous exchange phenomena in river ecosystems represent one of a large number of biotal processes occurring in streams. It is not possible to measure dynamic relationships between biota by the relatively simple physiochemical techniques available for the measurement of non-living variables (trace metals, for example). It therefore becomes essential to provide as complete a description of biota as feasible, subsequently providing a suitable theoretical model of the ecodynamics involved in the system.

16. Bio-oxidation Processes in Waste Treatment

Biological waste treatment systems are generally recognized as the most efficient means of removing organics from wastewaters. A discussion of these systems is outside the scope of this chapter, and the reader is referred to Genetelli's excellent description of the three basic systems most often employed in waste removal: a) *activated sludge* (AS), b) *trickling filters* (TF), and c) *aerobic oxidation* (AerOx) lagoons (Ref. 84).

Treatment units for organic wastes may 1) convert the waste to CO_2 and other decomposition products or 2) convert the organics to some settleable form. While the system characteristics may differ as to, say, oxygen requirements, the manner in which biological slimes are utilized, or the waste detention time required to complete treatment, the basic biochemical processes involved are alike.

The production of CO_2, water, and NH_3 during an aerobic waste treatment process is, of course, oxygen-dependent. The energy liberated from the H-transfer process is both consumed in the cellular synthesis and utilized by the cellular products to fulfill their energy needs. The quantity of O_2 required to oxidize the organic pollutants will depend largely on *biological oxygen demand (BOD)** satisfied during the biological treatment process (Ref. 84 above). Treatment methods vary somewhat in the percentage capability of satisfying applied BOD, with the converted activated sludge method ranking first (90-95%), low rate trickling filters in second place (80-90%), and high rate trickling filters third (65-85%) (Ref. 85).

The disappearance of organic material during bio-oxidation results in new cell synthesis. The amount of new cellular material produced per pound of BOD load is a function of the chemical composition of the substrate (Ref. 86). Helmers and coworkers reported that solids production varied with BOD removal and Okun (Ref. 87) also found that the total

*Normally BOD is the notation for *biochemical oxygen demand.*

Table 17

Division of Substrate between Oxidation and Synthesis[a]

Class of compound	Per cent		
	Range present	Oxidized mean	Converted to sludge
Carbohydrates	5-25	13	65-85
Alcohols	25-38	30	52-66
Amino Acids	22-58	42	32-68
Organic acids	30-80	50	10-60

[a] 24-hr, batch-fed activated sludge system. Units lbs/1000 ft.^{3} (from Ref. 88)

quantity of new cell materials formed was a function of BOD loading. With high load ratios high growth rates were obtained, whereas low loadings resulted in sludge destruction. Table 17 shows the influence of substrate type on the proportion of oxidation and synthesis obtained in 24-hour, batch-fed AS systems (Ref. 88). The variation in conversion yields may be rationalized on the basis of different utilization rates or efficiencies for different substrates given a specific set of organisms.

16.1 BOD-Related Parameters

The "nutrient substrate" or food value of wastewater is defined in terms of *BOD (biochemical oxygen demand)* of the constituents present. So-called "Loading Parameters" have been variously defined (Ref. 84, pp. 420-26), but invariably relate to the efficiency of BOD removal from a substrate. However, since BOD removal efficiencies of the order of 90% may be achieved for loadings ranging from 30 to 120 lb/1000 ft^3, it is clear that such relationships are of little value. Similarly, parameters based on the volume of treatment tanks fail to consider the solids aerated or the aeration time. These considerations led the Water Pollution Control Federation to recommend that *sludge loading ratio (SLR)* be used as the loading parameter for AS systems. This parameter is expressed in terms of lbs BOD/day/lb MLVSS and thus reflects the ratio of food to organisms. This parameter (SLR) is synonymous with the symbol *F* often encountered in mathematical formulations used to describe waste treatment systems.

Another, more recently suggested parameter utilizes lbs of BOD/day/unit weight of *deoxyribonucleic acid (DNA)*. As a reflection of cell material available in the system, DNA would appear to offer a reasonably accurate means of determining the food/organisms ratio (Ref. 90). The DNA parameter has proved the one most useful in predicting specific operational upsets (Ref. 91).

16.2 Bio-oxidation Summary and Conclusions

Technology is presently available for effecting up to 95% removal of organics (BOD) in waste waters. Conventional waste water treatment is capable of removing only about 25% of the total solids which may be present in domestic waters (more than 750 mg/1). In recent years the excessive enrichment (eutrophication) of receiving waters by nutrient-rich wastes has also emerged as a major problem for which conventional treatment methods are inadequate. These difficulties along with our diminishing supply of potable waters have led to a more intensive examination of the area of advanced waste treatment (AWT) methods (Ref. 84).

Advanced waste treatment requires a) the concentration and disposal of impurities present in municipal waste waters and b) the establishment of markets for the relatively pure waters which can be produced by such advanced treatment systems. An inherent requirement of these advanced systems is the concomitant development of effective methods of disposal of recovered concentrated pollutants so that they will not re-enter the water cycle. Thus, water *pollution* and *supply* problems may both be solved simultaneously by the development of advanced treatment systems.

17. BOD: Future Trends

In 1971 the BOD Task Group of Committee D-19 in Water (ASTM) withdrew the 5-day BOD test (BOD_5) D2329-68 for industrial and industrial waste waters. At the time this decision was made it was hotly contested and it remains a highly controversial one today. The reasons for the Committee's decision to discontinue BOD_5 as an ASTM standard procedure are evident from a consideration of the limitations of the method as discussed under Sec. 4, and under Sec. 11 we have attempted to explore some viable alternatives to the standard BOD_5 procedure which would have the advantages of greater reproducibility and shorter analysis times (1-8 hours) whilst still utilizing those features of bio-oxidation which are uniquely suited to dealing with municipal wastewater analysis.

The use of the mass culture aeration analytical technique coupled with the ΔCOD concept (Sec. 11.3.2) appears to offer considerable promise. The concept of energy oxygen, determined by means of the Warburg Respirometer which measures O_2 uptake (p. 20), offers yet another promising alternative. Differential oxygen uptake has also been measured by an oxygen probe in one STOD procedure (Ref. 44).

The use of BOD-COD or BOD-TOC ratios has gained favor in recent years (see Sec. 3). Often BOD_5 is used in conjunction with a more rapid chemical method, since it is quite possible to correlate the two for a particular kind of waste. Thus, the best features of both methods are utilized -- BOD giving the longer term picture, with a rapid COD method furnishing the necessary short-term interim information.

Finally, the BOD_5 test has a long and respectible tradition of useful application behind it, is presently still in wide use in certain industrial and essentially all sewage treatment plants -- and particularly in the latter instance -- will probably survive in its present form for some time to come.

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[2]Trans: "Relationship between Nature, Load Capacity, and Biological Composition of Activated Sludge Floors as Exemplified by a Multistage Pilot Plant".

CONTENTS

FOR

CHEMICAL OXYGEN DEMAND

INTRODUCTION

The ecosystems of natural streams, as well as systems such as municipal sewage facilities, are essentially biological reducing agents, and the *Biochemical Oxygen Demand (BOD)* test which has been so extensively employed in their monitoring is based on the biochemical oxygen requirements of these systems. Because of the inherent difficulties of the 5-day BOD test discussed in the BOD Section 4 of this volume, (length of time required for analysis, seed variability, and the need for acclimatization, toxicity, etc.) chemical methods have been developed. Although extreme care must be exercised in correlating BOD with *Chemical Oxygen Demand (COD)*, the potential for automation of the latter measurement and its relative rapidity and reliability have recently catapulted it into favor (Ref. 1).

1. Historical

The removal of organic matter from effluents usually involves oxidative processes, particularly in secondary treatment. Although there has been extensive quantitative investigation of the amount of oxygen necessary for the removal of a variety of organics, no universal procedure has been found to cover the wide variety of effluents analyzed (Ref. 2). Of the many methods suggested over a span of more than 100 years*, only three have gained prominence. Two of these are chemical, the third involving a biochemical procedure (see this volume, H2O-BOD).

The two chemical methods are: (1) oxidation by boiling acid potassium dichromate (i.e., the *dichromate value*) and (2) the *permanganate value* (no longer used in the United States) obtained by oxidation of the effluent with acid potassium permanganate ($KMnO_4$). Both methods will be described in greater detail in later sections. However, the salient points related to their applicability and limitations will be discussed below. Both methods determine an oxygen equivalent value, oxygen playing no direct role in the oxidations.

1.1 Dichromate Value

Adeney and Dawson (Ref. 4) introduced the use of potassium dichromate ($K_2Cr_2O_7$) in boiling acid solution in the determination of *oxygen absorbed (OA)* by effluents. This procedure in modified form has since come to be known as *chemical oxygen demand* or *COD* in the United States. A more detailed description of the method is given in section 5ff of this chapter and in the 13th edition of Standard Methods (Ref. 5). As is the case in the permanganate procedure, only a portion of the organic matter (depending on structure) is oxidized by the dichromate, and nitrogenous organics generally resist oxidation by this reagent. The method does not differentiate between biochemically stable and/or unstable organics. Thus, COD does not normally correlate strictly with the BOD of the effluent. Nonetheless the (silver sulfate-catalyzed) dichromate oxidation method is generally preferred over the acid $KMnO_4$ oxidation because of its greater reproducibility and wider applicability (Ref. 2).

1.2 Permanganate Value

The determination of oxygen equivalent from acid permanganate solutions is the oldest of the oxygen demand tests now in use, deriving its great popularity from its simplicity and rapidity. Since this is one of the earliest procedures used to assess pollution, the permanganate oxidation method provides a continuing basis for comparison with data obtained in prior determinations. Usually this method is a feasible one for use in routine control analyses. It has also been used where toxicity precludes the use of the 5-day BOD analysis.

The *permanganate oxygen consumed test*, as it was originally (and incorrectly) termed, has serious disadvantages. It is not always effective as an oxidant for many of the organic compounds found in sewage and particularly in industrial waste. Secondly, results depend strongly on both the size of the sample and the strength of $KMnO_4$ used. This latter problem was circumvented in part by adjusting the amount of permanganate so that not less than 25% of the reagent -- and no more than 50% -- was consumed at the end of the test. The method is both time- and temperature-sensitive. Time was standardized to 1/2 hour, and fluctuations in temperature over the period influenced the reproducibility of the results obtained. Moore (Ref. 18) compared four tests with the standard permanganate procedure (Ref. 6). Three of the tests used potassium dichromate, the fourth, iodic acid as the oxidizing agent. The iodic acid procedure is long and rather complicated, but the reagent has excellent oxidizing power and the test has good reproducibility.

In Great Britain the permanganate value is usually determined at 3 minutes and 4 hours (Ref. 7). The 3-minute test measures immediate

*For further historical references see the end of this chapter, including Ref. 2 and Moore, Kroner and Ruchhoft (Ref. 3).

oxygen demand of the sample from both inorganic and any *easily oxidizable* organic sources. The presence of ferrous salts, nitrites, phenols, sulfites, sulfides, thiocyanates and/or thiosulfates results in high 3-minute permanganate values.

When the 3-minute permanganate value is low, the 4-hr value provides a relatively rapid and simple method of measuring total oxidizable organic (and inorganic) constituents of sewage and plant effluents as well as river waters. Here (i.e., when the 3-minute $KMnO_4$ test yields a low value) a high 4-hr value generally indicates pollution.

The ratio: 4 hr:3 min permanganate value can be significant, frequently providing a clue as to the cause of the pollution. Thus, effluents from domestic sewage sources, rivers, etc., containing untreated sewage normally yield a ratio of ∿3. However, certain industrial wastes disturb this ratio, gas liquor tending to lower the value to ca. 2. On the other hand, waters polluted with vegetable wastes usually have a high 4 hr:3 min ratio which may lie between 4-10. This is illustrated in Tables 1, 2, and 3.

Table 1
Ratio 4 h:3 min permanganate value for a final effluent from domestic sewage (Bolton, Longworth) (Ref. 7, p. 121).

Date	*Permanganate value* p.p.m.		*Ratio* 4 h:3 min
	3 min	4 h	
2.2.49	2·8	8·6	3·1
11.1.50	3·6	10·2	2·8
3.12.50	1·4	4·2	3·0
30.5.51	2·6	7·6	2·9
10.10.51	4·0	10·8	2·7
5.2.52	1·6	5·6	3·5
24.6.52	2·0	6·8	3·4
3.2.53	2·4	7·2	3·0
13.5.53	3·2	9·6	3·0
3.9.53	2·4	7·2	3·0
		Average =	3·0

Table 1 shows typical 4 hr:3 min ratio of ca. 3 for a domestic sewage source; table 2, the ratio for a sewage effluent carrying about 20% by volume of gas liquors. In the last table, a comparison of the 4 hr:3 min ratios above and below a gasworks discharge shows the marked effect of the effluent on this value.

As with the dichromate oxidation, the permanganate method is used as an empirical measure of chemically oxidizable matter, and nitrogen compounds are similarly resistant to oxidation.

Table 2
Ratio 4 h:3 min permanganate value for a final effluent from sewage containing about 2 per cent by volume of gas liquor (Ref. 7, p. 121).

Date	*Permanganate value* p.p.m.		*Ratio* 4 h:3 min
	3 min	4 h	
6.8.47	20·8	42·2	2·0
16.12.47	25·4	54·0	2·1
11.2.48	20·4	44·4	2·1
24.6.48	12·4	27·6	2·2
28.4.49	25·2	51·4	2·0
13.10.49	15·6	31·8	2·0
18.5.50	30·8	62·8	2·0
19.10.50	14·0	30·8	2·2
18.4.51	19·0	42·6	2·2
9.1.52	13·2	29·6	2·2
		Average =	2·1

Table 3
Ratio 4 h:3 min permanganate value for rivers above and below gasworks discharges of gas liquor (Ref. 7, p. 122).

River	*Date*	*Permanganate value* p.p.m.		*Ratio* 4 h:3 min
		3 min	4 h	
R. Douglas { above gasworks discharge	3.7.53	6·0	18·0	3·0
R. Douglas { below gasworks discharge	3.7.53	59·8	93·0	1·6
R. Irwell { above gasworks discharge	6.5.53	3·6	12·0	3·3
R. Irwell { below gasworks discharge	6.5.53	19·0	40·0	2·1
R. Medlock { above gasworks discharge	15.4.53	1·6	5·2	3·3
R. Medlock { below gasworks discharge	15.4.53	320	530	1·7

Thus, the scope of this analysis is limited and results obtained from it have only a rather ill-defined relevance to the ultimate chemical or biochemical OD of a system, depending on the chemical nature of the constituents present in the system. Because of this limitation, instructions in the use of the permanganate method generally stress the importance of rigorous adherence to specified conditions if valid comparisons are to be made.

Of the extensive research carried out on variants of the permanganate oxidation, none led to a completely satisfactory method (Refs. 8-14).

Stamm (Ref. 8) carried out the $KMnO_4$ oxidation in alkaline solution preventing the precipitation of MnO_2 by addition of a barium salt, thus preventing interference of the brown MnO_2 precipitate with the endpoint. Benson and Hicks

(Ref. 9), in their study of pollution in seawater, used the Zimmerman Reinhardt procedure to obtain more reproducibile results in their titration of the excess permanganate. Haupt (Ref. 10) examined the wastes from paper pulp factories using acid permanganate, attempting to correlate them with BOD results. Not surprisingly, the chemical results were much higher than those obtained from the BOD test, since cellulose resists attack from both bacteria and dissolved oxygen.

Matsubara (Ref. 11) reported dependence of permanganate values on a variety of factors, including length of boiling, permanganate concentration, and state of hydrolysis (*saponification*) of fats or oils analyzed. Lovett (Ref. 12) confirmed the dependence of permanganate analyses on concentration. Koshkin and Karasik (Ref. 13) determined excess permanganate titrating with oxalic acid at boiling bath temperature, and Shutkovskaya (Ref. 14) compared the permanganate color of heated solutions with standard colored glass plates, after 5 minutes.

1.3 Other Oxidants

Of the numerous oxidizing agents available, only four have been used to any appreciable extent in the determination of the oxygen-consuming power of wastes; they are: ceric sulfate, $Ce(SO_4)_2$; iodic acid, HIO_3; potassium dichromate; and potassium permanganate. The latter appeared as the recommended method in earlier editions of Standard Methods (Ref. 6, p. 122) but is no longer recommended for use in the United States.

1.3.1 Iodic Acid Oxidation

In the iodic acid oxidation the sample is digested in a Kjeldahl flask with standard iodic acid in H_2SO_4 heated to 190°C in a wax bath for 35 minutes after the mixture has stopped boiling. For wastes containing volatile acids the mixture is refluxed for an hour in lieu of the digestion process. The flask is then cooled and the liberated iodine steam distilled. Potassium iodide is added to reduce the unused iodate in the flask and the free iodine formed titrated with sodium thiosulfate ($Na_2S_2O_3$) solution in the presence of a starch indicator.

While the iodic acid method was the most time-consuming of those studied, agreement between replicate samples was good and approached more nearly the theoretical values obtained in the oxidation of pure organic standards.

1.3.2 Sodium Hypochlorite/Permanganate Ratio

Sodium hypochlorite (NaOCl) determined at 3 min and 4 hrs, has proved useful in the differentiation between animal and vegetable pollution when compared with permanganate (Ref. 15). This can be extremely useful in identifying a discharge and locating the source of pollution. Gibson has shown that when the 4 hr ratio hypochlorite/$KMnO_4$ is less than 1.0, the pollutant is largely of vegetable origin. Conversely, for ($NaOCl/KMnO_4$) > 1.0, animal matter is the chief pollutant. Table 4 below lists examples of wastes from animal and vegetable sources which may be differentiated on the basis of their $NaOCl/KMnO_4$ ratios.

Table 4
The $NaOCl:KMnO_4$ ratio for various wastes and polluted waters (Ref. 7, p. 115).

Wastes, etc., of vegetable origin ($NaOCl:KMnO_4$ *ratio* <1·0)	*Wastes, etc., of animal origin* ($NaOCl:KMnO_4$ *ratio* >1·0)
Paper making wastes	Sewage and Sewage effluents
Calico printing wastes	Farm drainage
Cotton bleaching wastes	Piggery wastes
Brewery wastes	Dairy wastes
Vegetable canning wastes	Tannery wastes
Vegetable pickling wastes	Rivers polluted by any of the above wastes
Pea vining wastes	
Coal washing effluents*	—
River waters polluted by any of the above wastes	—
Peaty river waters	—

* Coal-dust can be regarded as well-decomposed vegetable matter.

It is often possible to shorten the Gibson hypochlorite procedure using 3-min instead of 4-hr ratios, but less reliable conclusions result.

Gibson's generalization does not hold for certain sewage sludges (e.g., activated sludge, digested sludge, and Imhoff tank sludge) which gives ratios of less than 1.0, thus behaving as though they were of "vegetable" origin.

2. Theory of COD Measurement

As with all *oxygen demand (OD)* parameters, COD measurement is based on the reduction of the oxidant by the sample and this, in turn, is interpreted as reflecting sample carbon content. However, this assumption is a valid one only in the absence of other reducing substances (see section 4).

Whatever the nature of the OD test, at its conclusion the system will be stabilized in a

lower (final) energy state as compared thermodynamically with its initial state. For a chemical system, less carbonaceous material will remain in the final state than for a biochemical test system, thus providing a better approximation to the total carbonaceous matter *initially* present. By contrast, the biochemical system measures only the *biodegradable* portion of the organic material initially present.

It should further be noted that, given a detailed knowledge of the oxidizable organic constituents present in an effluent, it is possible to calculate its total oxygen requirement theoretically. This quantity, known as the *ultimate oxygen demand (UOD)*, has been determined from the equation (1) below:

$$UOD = .2.67C + 4.57N, \text{ where} \qquad \text{(Eq. 1)}$$

C = the organic carbon content of the effluent, and

N = the sum of ammoniacal and organic nitrogen.

In the presence of other elements contributing to the OD of the system (e.g., H, S, and/or P), this equation must be modified for greater accuracy. Similarly, organically bound oxygen must also be considered in the equation (Refs. 2, 16).

2.1 Chemical Oxidation of Carbon Compounds: Oxidation-Reduction Equations

While it is not possible to write a simple numerical expression for the oxidation of all organic compounds using either acid dichromate or acid permanganate reagents, the illustrative examples below should provide a basic explanation of the chemistry involved in the dichromate (and permanganate) methods of COD determination of organic (*carbonaceous*) pollutants.

2.1.1 Acid Dichromate Oxidation

One of the classical tests for *ethanol* (ethyl alcohol)† consists of warming the alcohol with a solution of *sodium dichromate* ($Na_2Cr_2O_7$) in sulfuric acid (Ref. 17). Under these conditions, ethanol is oxidized to *ethanal** (acetaldehyde†), the yellow dichromate solution is reduced to a green solution (chromic ion, Cr^{+++}), and the aldehyde may be recognized (a) by its fruity odor or (b) alternately by its reducing action on filter paper impregnated with an ammoniacal silver nitrate solution. In the latter instance silver ion is reduced to free silver producing a dark stain on the paper: $Ag^{+} + e \rightarrow Ag^{\circ}$.

The oxidation of the ethanol to ethanal may be expressed by the following equation:

$$\underset{\text{ethanol}}{3C_2H_5OH} + \underset{\substack{\text{sodium}\\\text{dichromate}}}{Na_2Cr_2O_7} + \underset{\substack{\text{sulfuric}\\\text{acid}}}{4H_2SO_4} \rightarrow$$

$$\underset{\text{ethanal}}{3CH_3CHO} + \underset{\substack{\text{chromic}\\\text{sulfate}}}{Cr_2(SO_4)_3} + \underset{\substack{\text{sodium}\\\text{sulfate}}}{NA_2SO_4} + 7H_2O \qquad \text{(Eq. 2)}$$

The addition of silver sulfate (Ag_2SO_4) under reflux conditions in the presence of concentrated H_2SO_4 catalyzes the further oxidation of the alcohol (probably through the acetic acid stage) to carbon dioxide and water (Ref. 18).

$$C_2H_5OH \xrightarrow[Ag_2SO_4 \text{ catalyst, } \Delta]{H_2CrO_4,2[O] \text{ (chromic acid)}} [CH_3CHO \rightarrow CH_3COOH] \rightarrow 2CO_2 + 3H_2O \qquad \text{(Eq. 3)}$$

Table 5 (Ref. 19) compares the efficiency of oxidation of typical organic compounds in the absence or presence of Ag_2SO_4. It is clear that straight chain acids (including amino acids) and alcohols are oxidized more completely in the presence of the catalyst. Particularly striking is the case of the highly oxidation-resistant acetic acid which may be oxidized to near completion in the presence of Ag_2SO_4. Oxidation-resistant aromatics such as benzene and toluene, as well as the *heterocyclic* aromatic compounds such as pyridine, are not significantly affected by the catalyst (Ref. 19).

2.1.2 Permanganate Oxidation

In acid solutions permanganate ion (MnO_4^-) is reduced to the manganous state (Mn^{++}). This is the basis of a standardization method for $KMnO_4$ solutions involving oxalic acid or sodium oxalate in acid solution:

$$\underset{\substack{\uparrow\text{(gain)}\\ 5\varepsilon}}{2MnO_4^-} + \underset{\substack{\downarrow\text{(loss)}\\ 2 \times 1\varepsilon}}{5C_2O_4^{=}} + 16H^{+} \rightarrow 2Mn^{++} + 10CO_2 + 8H_2O \qquad \text{(Eq. 4)}$$

In equation 4 a formal charge of +3 on each carbon may be assumed for the oxalate ion, $C_2O_4^{=}$. This is more apparent if the ion is

†Classical nomenclature

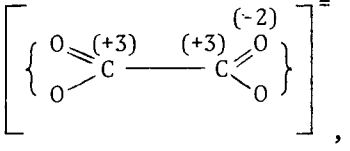
*IUC nomenclature. The root name is derived from the parent hydrocarbon -- in this instance *ethane*, with substitution of the appropriate ending (e.g., *ol* for the alcohol and *al* for the *al*dehyde).

Table 5

Effect of Addition of Silver Sulfate on Dichromate Oxygen Consumed (Ref. 19, p. 795)

Compound	Per Cent of Theoretical Oxidized Without Ag_2SO_4	With Ag_2SO_4
Acetic acid	2.4	95.1
o-cresol	83.2	95.8
Ethyl alcohol	29.7	80.1
Glutamic acid	63.9	100
Lactic acid	45.4	82.7
Sodium stearate	74.2	91.7
Benzene	7.8	8.1
Pyridine	1.3	0.8
Toluene	21.4	22.5

pictured as



wherein the electron pairs are visualized as in closer proximity to the more *electronegative* (i.e., electron-attracting) oxygen atoms. If the oxygens are assumed to bear their usual charge (-2), then each carbon must be assigned a formal charge of +3 in order for the oxalate ion to be divalent (-2). Thus in equation 4 above, each carbon will lose one electron in going to CO_2, while the Mn (+7) in the permanganate radical will gain 5 electrons. This is indicated by the up (↑, gain) or down (↓, loss) direction of the arrows in the equation.

As with the acid dichromate reaction discussed earlier, the acid permanganate reagent oxidizes straight chain alcohols such as ethanol imcompletely to the aldehyde stage rather than all the way to CO_2 and water.

3. Definition

Chemical oxygen demand (COD) is defined as the amount of oxygen in mg/l consumed under specified conditions in the oxidation of organic and oxidizable inorganic substances in wastewater, corrected for the influence of chlorides (Refs. 20, 21).

3.1 Dichromate Oxygen Demand

Dichromate value (British : Ref. 2, p. 687) is essentially synonymous with *Dichromate Oxygen Demand* (American) and this latter term is in turn now used interchangeably with COD in the U.S. (Ref. 22).

Dichromate value is defined as "the number of milligrams of oxygen absorbed from standard dichromate/liter of sample" (Ref. 2)[a]. Dichromate oxygen demand has already been defined above (as COD).

3.1.1 Conditions of the Dichromate OD Method

The analysis is carried out under acid conditions (50% by volume H_2SO_4), employing 0.25 N $K_2Cr_2O_7$. Mercuric sulfate (0.4 gm $HgSO_4$/40 mg Cl^-) is added to complex the chlorides, and Ag_2SO_4 previously dissolved in concentrated H_2SO_4 (reagent grade) is used to catalyze the oxidation of the more resistant organics. Since the oxidation is carried out at reflux temperature, no temperature control is required (Ref. 2, 5- section 220).

a) In the *absence* of chlorides, samples with DOC values of 50 mg/l or more may be analyzed with the concentrated dichromate solution (0.25N). For more dilute samples an alternate procedure using 0.025 N dichromate solution is recommended (Ref. 5, p. 498).

b) When chloride is *present* this method is applicable to samples with an oxygen absorption at least 1/4 as great as the [Cl^-] in mg/l.

The method is broadly applicable. Certain nitrogen compounds (e.g., urea) interfere, as will large amounts of chloride ion (i.e., [Cl^-] $\geq$ 4xCOD value). The dichromate procedure is described in greater detail in section 5 of this chapter and in Ref. 2, p. 687, and 5, Sec. 220-4a.

4. Factors Influencing the Dichromate Value

A number of factors influence the dichromate value obtained. Thus the presence of chloride ion, which is oxidized by acid dichromate, enhances the dichromate value. On the other hand, certain aromatic organic structures (benzene, pyridine, toluene) resist dichromate oxidation, even in the presence of a silver sulfate (Ag_2SO_4) catalyst.

[a] see footnote, p. 9

4.1 Chloride

Chloride, a common constituent of natural waters, is oxidized by dichromate. Moore and coworkers at first recommended a correction based on 100% oxidation of the chloride (Ref. 3). However, at high chloride concentrations, AgCl precipitates in a form which dissolves slowly, requiring prolonged reflux periods. Filtration of the precipitate results in the loss of colloidal organic matter thus reducing oxygen absorption (Ref. 23). Table 6 lists OA data for substances typically found in industrial effluents, showing the effects of chloride addition, correction for chloride and removal of chloride by precipitation. The reduction in OA value in the latter instance is evident.

In the absence of Ag^+, sodium chloride (NaCl) solution showed maximum, albeit incomplete, oxidation in 1/2 hr. when solutions of various NaCl concentrations were refluxed with acid dichromate solution and then back-titrated with ferrous ammonium sulfate solution. Table 7 shows the results of these experiments.

The findings of Cameron and Moore clearly indicated that incomplete oxidation of chloride at high concentrations will lead to low OA values. Thus, if the true oxygen equivalent of Cl^- in solution is C and S the OA value of the organic pollutant, then

$\frac{C}{S} \times P$ = the error in observed OA for % error P incurred by assuming 100% oxidation of Cl^-.

For N/8 dichromate Cameron and Moore (Ref. 23) recommend that the [Cl^-] should not exceed 4 times the OA values of the organic pollutants, if the latter are between 250 and 500 mg/l and total OA is to be within 5% of the true value. When [Cl^-] is 10,000-20,000 mg/l (OA equivalents 112-224 mg/l), the errors incurred might constitute a significant fraction of the OA values for the organic pollutants, leading to low results (see expression above). Thus, alanine and lactic acid both showed severe depression of OA at high Cl^- concentration (~12,000 mg/l).

4.2 Oxidation of Nitrogenous Pollutants in the Presence of Cl^-

In a preliminary experiment with urea, Cameron and Moore found that oxidation of this natural constituent of domestic sewage underwent direct oxidation by dichromate in the absence of Cl^-:

$$NH_2CONH_2 \xrightarrow{3[O]} CO_2 + 2H_2O + N_2 \qquad \text{(Eq. 5)}$$

However, the reaction was enhanced by the presence of chloride in contrast to the inhib-

Table 6

Results for Oxygen Absorbed with Added Chloride (Ref. 23)

Compound	O.A. value, p.p.m.	Chloride added, p.p.m. of oxygen absorbed	Oxygen absorbed with correction for chloride, p.p.m.	Oxygen absorbed with precipitation of chloride, p.p.m.
Cresylic acid	400	400	400	405
Soap	360	800	356	140
Soap	740	800	732	350
Soap	300	400	296	160
Glue	190	500	182	137

Table 7

Oxidation of Chloride in Absence of Silver (Ref. 23)

Chloride taken, ppm	Equivalent volume of N/8 $AgNO_3$, ml	Volume of N/8 $K_2Cr_2O_7$ added, ml	Volume of N/80 $Fe(NH_4)_2(SO_4)_2$ required, ml	Oxidation %
225	1.25	2.0	6.3	109.7
558	3.15	5.0	18.75	99.2
1058	6.10	10.0	40.10	98.1
2112	11.90	15.0	34.40	97.4
4224	23.80	30.0	67.90	97.4
5310	29.90	40.0	118.75	94.0

iting effect of Cl^- on lactic acid and alanine. The authors postulated a possible intermediary role in which Cl^- was itself oxidized to free chlorine by the dichromate, the free Cl_2 formed in turn oxidizing urea, etc. By this mechanism it was possible to explain the dependence of urea oxidation on the presence of Cl^- in the absence of any Cl^- concentration dependency (Table 8).

Table 8

Oxidation of Urea in Presence of Chloride
25 ml of N/8 $K_2Cr_2O_7$ ≡ 5.2 mg of urea
(Ref. 23, p. 681)

Chloride present, p.p.m.	Total volume of N/8 $K_2Cr_2O_7$, ml	Absorption as volume of N/8 $FeSO_4$, ml	Oxidation of urea, %
266	26·5	6·5	52
639	28·6	8·5	68
1278	32·2	9·7	77
6327	60·7	7·14	57
Nil	25·0	4·2	33·6

Although there are a number of possible routes for the oxidation of organic nitrogen by Cl_2, it is assumed that in each case a trivalent N atom is involved. Thus the correction is based on:

$$1 \text{ ml } \frac{N}{8} K_2Cr_2O_7 \equiv 0.5833 \text{ mg } N^{\ddagger} \qquad \text{(Eq. 6)}$$

This correction is only approximate, since not all of the nitrogen will be oxidized by this route, some of it being oxidized directly by the reagent (see Eq. 5, above).

4.3 Oxidation of Organically Bound Chlorine Compounds

In the case of ring and chain compounds containing organically bound chlorine, the percent oxidation obtained varied with structure. Table 9 illustrates the negligible effect of Ag^+ as an oxidation catalyst in all but one (chlorobenzene) of five compounds studied.

‡At wt. of N = 14.008/3 = 4.669 equivalent wt. X 0.125 = 0.5836 mg N/ml reagent

5. Procedure: COD Test

5.1 Dichromate Method: Summary

The test is based on the susceptibility of most organic compounds to a boiling mixture of chromic and sulfuric acids. An excess of potassium dichromate ($K_2Cr_2O_7$) in sulfuric acid (H_2SO_4) is employed to oxidize the sample at reflux temperature. Residual dichromate is titrated with ferrous ammonium sulfate [$Fe(NH_4)_2(SO_4)_2$] in the presence of ferroin indicator and the oxidized organic matter calculated in terms of *oxygen equivalents (OE)*. The potassium dichromate consumed and the OE of the sample are related by a proportionality factor. Chemical Oxygen Demand is calculated using the following equation:

$$\text{COD (mg/l)} = \frac{(a-b)N \times 8{,}000}{\text{ml sample}}, \text{ where} \qquad \text{(Eq. 7)}$$

COD = Dichromate Oxygen Consumed

(a-b) = the difference in $Fe(NH_4)_2(SO_4)_2$ *titre* of blank and sample

N = normality of $Fe(NH_4)_2(SO_4)_2$ used.

Mercuric sulfate (0.4 gm) is placed in a 250 ml Erlenmyer flask provided with a ground glass (24/40) neck. The sample (20 ml or a suitably diluted aliquot of the same volume) is mixed with the mercuric sulfate ($HgSO_4$). Ten ml of the standard $K_2Cr_2O_7$ (0.250 N) solution and pumice granules (or glass beads) previously heated to 600°C for an hour are added and the flask fitted with a condenser. Sulfuric acid (30 ml) containing Ag_2SO_4 (22g/9 lb bottle) is gradually introduced through top of the condenser. During addition of the acid the assembly is swirled for *thorough mixing before heating*. This is to avoid *local superheating* of the unmixed H_2SO_4-Ag_2SO_4 solution which is of sufficient density to collect at the bottom of the flask -- in which case it may build up a high enough local vapor pressure to be blown out of the condenser. The mixture is then refluxed for 2 hours.

Table 9
Oxidation in the Presence of Organically Combined Chloride
(Ref. 23, p. 681)

Compound	Oxidation with silver absent, %	Oxidation with silver present, %
Carbon tetrachloride	6·4	6·4
Trichloroethylene	20·0	20·0
Benzoyl chloride*	94·3	94·5
Benzyl chloride	65·2	62·4
Chlorobenzene	12·0	25·6

* Owing to hydrolysis this test becomes in effect a test of benzoic acid and hydrochloric acid.

After the reflux period the mixture is diluted to ∿150 ml with distilled water, cooled to room temperature, and the excess dichromate present titrated with a standard ferrous ammonium sulfate solution (Ref. 5, Sec. 220-3 Reagents), after the addition of 2 to 3 drops of ferroin indicator solution. For best results the same quantity of indicator should be maintained from sample to sample. The color change at the endpoint is a sharp transformation from blue-green to reddish brown.

A blank is treated in an identical manner and the COD calculated from equation 7.

Notes:

1) The quantity of $HgSO_4$ recommended will complex 40 mg of Cl^- (2000 mg/l) when the volume of sample is 20 ml. In the presence of a greater [Cl^-] than the above, sufficient $HgSO_4$ is added to maintain a 10:1 ratio, $HgSO_4$:Cl^-. Appearance of a small precipitate for the larger quantities does not interfere in the dichromate method.

2) The standard reflux time of 2 hr may be reduced for wastes which develop their maximum COD values sooner.

3) Table 10 (Ref. 5, p. 498) lists recommended ratios of reagent quantities and normalities with size of sample. For larger samples, a 500 ml erlenmeyer flask is used for refluxing the sample, so that it may be titrated *in situ*.

4) An alternate procedure employing 0.025 N dichromate reagent and 0.01 N ferrous ammonium sulfate reagent is given in Ref. 5, section 220-4C, p. 498. Some hard-to-digest volatiles may be lost in this procedure, and the increased volumes used may reduce effectiveness of $HgSO_4$ as a complexing agent for Cl^-.

5.1.1 DOC Method Precision and Accuracy

In a test by 74 laboratories of unknowns containing potassium acid phthalate ($KHC_8H_4O_4$) the following precisions were obtained (Table 10).

Table 10 (Ref. 5, p. 498)

COD (mg/l)	Chloride (mg/l)	Standard Deviation	Coefficient of Variation (%)
200	0.0	±13	6.5
160	100.0	±10	6.5
150	1,000.0	±14	10.8

Moore and coworkers have found 95 to 100% of the theoretical oxidation values for a large number of organic compounds. This excludes the stable aromatics such as benzene and toluene and the nitrogen heterocyclic, pyridine, which are not oxidized in the standard dichromate procedure.

A more complete discussion of the dichromate oxygen demand method is found in Standard Methods, 13th ed. (section 220, pp. 495-9, inclusive).

5.1.2 Dichromate Oxidation: Advantages and Disadvantages

A. Advantages

1) Results obtained with the dichromate method are generally closer to theoretical than the permanganate test (Ref. 2).

2) The dichromate method requires considerably less time (2 hrs max) than the permanganate test.

3) Since the DOC test is carried out at boiling temperature, there is no error due to temperature difference and no need for temperature control.

4) The apparatus required, while slightly more complicated than for the permanganate test, is readily available in any routine laboratory (Ref. 2).

5) For a given effluent, the BOD/COD ratio may be sufficiently correlated so that the chemical data may be used in process and treatment-plant control.

B. Disadvantages

1) Chloride may introduce error not readily corrected if the Ag_2SO_4 is added initially. This may be circumvented by dichromate oxidation of the chloride prior to addition of the Ag_2SO_4 oxidation catalyst.

2) When chloride and nitrogenous compounds are present simultaneously the error correction becomes more difficult, since the nitrogen may be oxidized by two different paths: directly and via liberated Cl_2.

3) Not all organics are oxidized by dichromate reagent, even in the presence of Ag_2SO_4 catalyst. Aromatic compounds such as benzene and the nitrogen heterocyclics related to pyridine resist oxidation in the standard procedure (Ref. 5).

4) The method does not differentiate between biochemically stable and/or unstable organic pollutants.

5.2 COD: Sampling

In general, COD sampling recommendations are similar to those for BOD; namely,

a) Unstable samples should be tested immediately.

b) Care should be taken to insure representative sampling as outlined in the BOD section. Settleable solids should be dispersed throughout the aliquots taken by prior homogenization of the sample.

c) In case of unavoidable delay in analysis, the sample should be preserved by the addition of sulfuric acid.

d) For samples with a high COD, volumetric dilutions should be made to avoid the inherent analytical errors in the measurement of small volumes.

e) Samples should be collected in accordance with ASTM methods D 1496: Sampling Homogeneous Industrial Waste Water (Ref. 24).

For more detailed discussions of OD sampling procedures in this volume, the reader is referred to the DO and BOD chapters' sections on Sampling.

5.3 Permanganate Value: "Oxygen Absorbed"[a] from Acid $KMnO_4$ Solution

The usual concentration of $KMnO_4$ reagent is N/80. However, in the case of some trade wastes N/8 reagent is recommended (Ref. 2, p. 691). The standard time for the $KMnO_4$ test is 4 hr, with the 3-minute $KMnO_4$ test used as a guide to the nature of the waste.

The volumes of samples are adjusted so that the same amounts of reagent permanganate and H_2SO_4 may be used throughout, with the volume (~50 ml) of $KMnO_4$ solution adjusted so that ca. 50% unused reagent remains at the end of the test.

Where small sample volumes (e.g., high COD) are indicated, it is recommended that a larger volume of a suitable dilution be used in order to be certain that the suspended solids are uniformly distributed.

5.3.1 Reagents

For a detailed description of reagent preparation, the reader should consult Ref. 2, pp 689-90. In addition to the N/80 permanganate solution, the following reagents are used in this method:

a) Potassium iodide (KI) solution (10% w/v). This must remain colorless (i.e., free of iodine). It is stored in an amber bottle.

b) Potassium iodate (KIO_3) solution (N/40), pre-dried at 120°C.

c) Sodium thiosulfate ($Na_2S_2O_3$, ~N/4), prepared from the pentahydrate, $Na_2S_2O_3 \cdot 5H_2O$ and copper-free, freshly-boiled distilled H_2O. The solution is stabilized by the addition of $CHCl_3$ (1 ml), or alternately, 10 mg of mercuric iodide (HgI_2). Kept in the dark, this reagent is reasonably stable but requires frequent standardization against the iodate solution.

d) Sulfuric acid (1:4 dilution).

e) Starch indicator: may be freshly prepared or stabilized with HgI_2 (10 mg/gm of soluble starch) or thymol (0.1 gm/gm of soluble starch).

5.3.2 "Permanganate Oxygen Absorbed"[a]: Procedure

A. 4-hour test

Ten ml of 1:4 sulfuric acid and 50 ml of N/80 $KMnO_4$ are measured into a 12 oz glass stoppered (G.S.) bottle. Distilled water is added so that the combined volumes of the water and effluent when added will add up to 100 ml and the mixture is incubated at 27°C. The effluent, also at 27°C, is then added to the above mixture containing the acidified, diluted oxidant, and the whole is mixed by a gentle rotation of the bottle. The solution (or suspension) is incubated at 27°C for 4 hours. (If solids are present, the sample is re-mixed at least every hour.)

At the end of 4 hours, 5 ml of KI solution, or approximately 0.5 gm KI, are added, mixed or dissolved, and the solution titrated with N/80 $Na_2S_2O_3$. As the endpoint is approached, 2-3 drops of the starch indicator solution are added and the titration continued to the first disappearance of blue color, ignoring the reappearance of any blue color on standing.

A blank determination is put through the same procedure.

Calculation of the 4-hr permanganate value is made using expression below:

$$\frac{[(\text{Vol. N/80 } Na_2S_2O_3, \text{ blank}) - (\text{Vol. N/80 } Na_2S_2O_3, \text{ sample})] \text{ ml} \times 100}{\text{Total vol. sampled (ml)}} = \text{4-hr. } KMnO_4 \text{ value, mg/liter} \qquad \text{(Eq. 8)}$$

[a] This terminology is misleading, since the sample does not absorb oxygen from the reagent. See Sections 1.2 and 2.1.2.

B. 3-minute test

This procedure is essentially the same as in A above: the sample and reagents are prewarmed to 27°C, mixed and maintained at 27°C for exactly 3 minutes, and titrated.

5.3.3 Permanganate OA: Interferences

a) *Nitrite* will reduce permanganate. A correction may be made for its interference by subtracting the factor nitrite N x 1·4.* For significant amounts of nitrite, the latter is best destroyed prior to analysis by the addition of 1 gm of urea to the acidified sample (and blank). The treated sample is allowed to stand for 5 min before proceeding with the $KMnO_4$ addition.

b) *Chromates* are reduced by KI in acid solution, and will therefore decrease the $KMnO_4$ value. A correction for this error may be made by carrying out a preliminary titration with thiosulfate reagent prior to addition of the permanganate solution and adding the equivalent OA value to the observed permanganate obtained (Ref. 2).

6. Oxygen Demand Index (ODI)

The COD method was developed as a relatively rapid OD technique for use in conjunction with the time-consuming BOD method (see Introduction to this chapter and Section 3, BOD). However, the standard COD procedure is still a relatively lengthy one for effective monitoring of the frequently rapidly changing OD conditions of receiving and effluent wastewaters. To cope with this problem, the Oxygen Demand Index was introduced by Westerhold (Ref. 25). This is a rapid COD test based on the Standard Methods procedure. However, instead of refluxing for two hours, the sample and reagent mixture are heated in a test tube (T.T.) at boiling water temperature for only twenty minutes and titration is replaced by the more rapid colorimetric measurement of green chromic ion at 600 mμ (Ref. 26). The ODI is then read off a calibration curve based on glucose. The latter curve is obtained by comparing the percent transmission of the oxidized standard glucose solution with its known 5-day BOD value. Sample readings are made with reference to a similarly treated distilled water blank.

*For method of determining low (i.e., <2 mg/l) and high concentrations of nitrite N in solution, see Ref. 7, pp. 38-9.

Shriver and Young (Ref. 26) concluded from their examination of wastewater samples collected from a number of sources that

1) the ODI test furnishes an approximate BOD value of wastewater simply and rapidly provided that sufficient data are collected at each sampling point.
2) Precision for the ODI test is comparable with that reported by a number of workers for COD.
3) Correlation of BOD-ODI values is poorer than for other BOD-COD tests, but better than BOD-TOC correlations obtained.

Reynolds and Goellner (Ref. 27) concluded from their statistical evaluation of the ODI method that it did indeed give higher values than BOD_5 as had been reported previously. They further expressed the opinion that the "use of elaborate instrumentation or gadgetry being marketed today" should not be recommended to "the less well informed operational personnel."

7. Correlation of COD with Other Parameters

The literature abounds with attempts to correlate COD with BOD, TOC (Total Organic Carbon), TOD (Total Oxygen Demand), and variants of these parameters. Section 3 of the BOD chapter dealt with the significance and limited validity of BOD-COD comparisons. Since TOC and TOD-related parameters involve instrumentation, these comparisons will be discussed in the appropriate sections of the following chapter on Instrumentation of Oxygen Demand Parameters.

8. Criteria

There are as yet no separately promulgated COD standards. Recommended criteria vary with the use for which the water is intended (BOD, section 5, DO, section 4). Thus, the following limits "Oxygen Consumed" values were suggested for boiler feed waters:

Table 11

Recommended Oxygen Consumed Limits for Boiler Feedwaters (Ref. 28, p. 233)

Pressure in Psi	*Oxygen consumed, mg/l*
0-150	15
150-250	10
250-400	4
400 and over	3

For potable waters the 1962 USPHS standards based on the *Carbon Chloroform Extract (CCE)* procedure is still in effect, with the recommended limit set at 200 μg (or 0.2 mg) per liter. The re-

cent development of a new minisampler and a micro-extraction technique is expected to result in a lowering of the recommended CCE limit to 100 µg/l.* It is reasonable to expect that COD methodology will result in attempts to correlate the more rapid COD techniques with the CCE method.

9. COD: Summary and Conclusions

The COD test has been applied to problems of industrial waste treatment. It has also found use in the areas of process control (Refs. 3, 18, 25, 26, 27).

Chemical oxygen demand has been used in the detection of toxic conditions interfering with the normal BOD test, and for the detection of biologically resistant organic pollutants. Used as an adjunct to the BOD test, COD can assess the biological stability of an aquatic system, often providing a rapid estimate of its BOD. Measurement of COD provides an estimate of the total organic content of the sample -- not just the carbon portion of it. Thus, compounds containing organically-bound nitrogen, phosphorus or sulfur may also be measured using the COD method.

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*Private communication, J. J. Connors

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INSTRUMENTAL MONITORING OF OXYGEN DEMAND AND RELATED PARAMETERS

INTRODUCTION

A successful water quality management program frequently requires continuous quantitative measurements of BOD-related parameters. For these, automated and semi-automated methods have been developed. Some examples of such methods will be discussed in the following section.

As used in this paper the term *automated methods* will refer to those methods employing analytical instrumentation in the continuous (or, at least, semi-continuous) measurement of BOD and related parameters. Any measuring device provided with a *sensor* or transducer, *signal-conditioning* circuitry, and a means of *read-out* constitutes an *instrument*. If the instrument may be used in a continuous or semi-continuous fashion, it will be regarded as an *automatic* instrument. This is an admittedly arbitrary use of the term "automatic", since "continuous" and "automated" are not necessarily synonymous or interchangeable terms. In practice however, this terminology has been found convenient.

A variety of automated instruments and methods now exist for the determination of OD in natural and wastewaters as well as in sewage effluents.

1. Oxygen Demand

Oxygen demand techniques are based either on oxygen consumption or on its equivalent. This is in turn interpreted as reflecting sample carbon content. However, this interpretation is valid only in the absence of other reduced, i.e., oxygen consuming or *oxidizable* substances. Whether the test used is chemical or biochemical, the system will ultimately be stabilized thermodynamically in some lower energy state. When this state is reached for a chemical system, less carbonaceous material will remain. Thus the chemical system provides a better approximation to the total carbonaceous materials originally present, whereas the biochemical test system reflects that portion of the organic material present which was biodegradable and may thus be more representative of the actual processes occurring in a receiving stream or a sewage treatment plant.

2. Chemical Oxygen Demand (COD)

The standard COD test employs a wet chemical oxidation with acid-dichromate and a silver sulfate catalyst. The oxidized solution is then back-titrated with ferrous ammonium sulfate and the dichromate consumption calculated in terms of oxygen (Ref. 1, pp. 290, 495). The oxidation efficiency of the method varies with classes of organic compounds present. Non-carbonaceous constituents (reduced states of N and S), some halides and many metals also react (see H2O-COD, section 3.2).

The COD test has been applied to problems of industrial waste treatment; it has also found use in areas of process control (Refs. 2 - 6 incl.). It has been used in the assessment of toxic conditions interfering with the normal BOD test, and for detection of biologically resistant organic pollutants. Used as an adjunct to the BOD test, COD can assess the biological stability of an aquatic system often providing a rapid estimate of its BOD. Measurement of COD provides an estimate of the *total organic content* of the sample -- not just the carbon portion of it. Thus compounds containing organically-bound nitrogen, phosphorous, halogens and sulfur may be measured using the COD method.

3. COD: Automated Methods

Automated Chemical Oxygen Demand methods may be classified as: a) *wet combustion* or b) *dry combustion* methods. These will be discussed in the following sections.

3.1 Wet Combustion Method

Molof and Zaleiko (Ref. 7) have successfully automated the standard dichromate method (the Technicon Autoanalyzer) extending the utility of the test for routine continuous pollution monitoring, control and testing. Thus, the normal time span for a complete manual COD determination is from 3 - 5 hours, with semi-quantitative results often obtainable in less than 2 hours (see H2O-COD, section 4.1). The automated version of the procedure was designed to provide complete analyses in less than 1/2 hr. (*ca.* 10 min./sample, 10 samples/hr.).

3.1.1 Spectrophotometric Principle

The basis of the procedure is the color change from the *oxidized* state of dichromate (Cr^{+6}, yellow) to the *reduced* state (Cr^{+3}, green) which is measured photometrically.

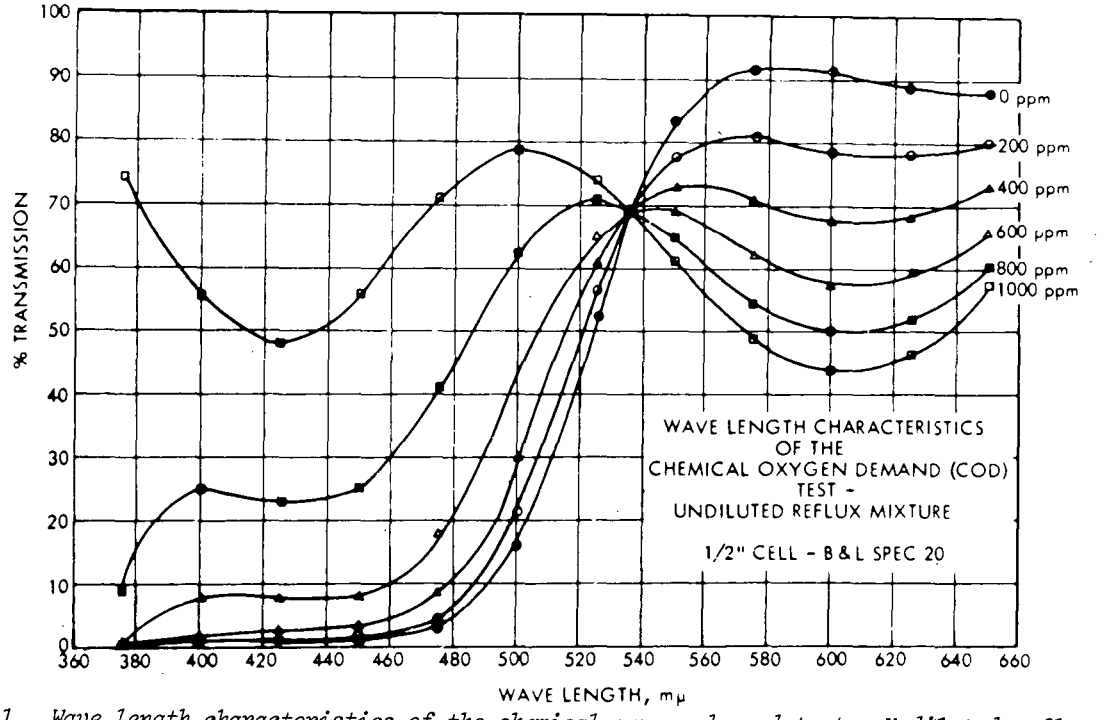


Figure 1. Wave length characteristics of the chemical oxygen demand test. Undiluted reflux mixture (Ref. 7, p. 542).

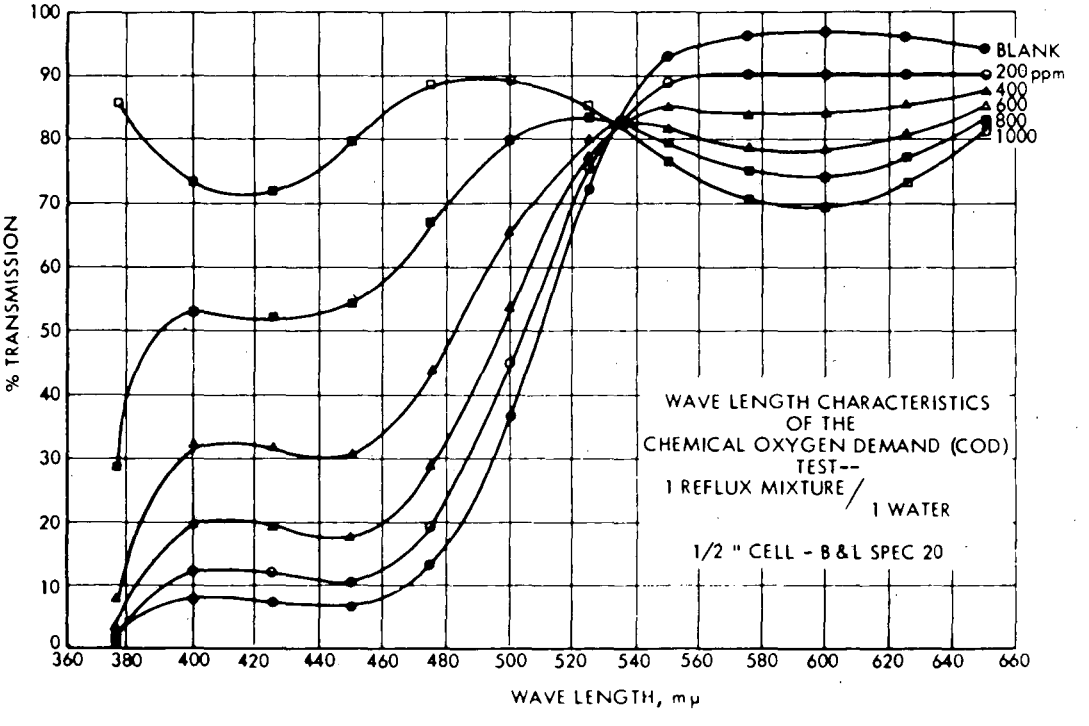


Figure 2. Wave length characteristics of the chemical oxygen demand test. 1 reflux mixture/1 water (Ref. 7, p. 543).

The system presents an interesting example of the existence of two forms of Cr in equilibrium; the sum of the oxidized and reduced forms present constitutes the total amount of Cr in solution. The spectrum obtained thus represents the sum of absorptions of the two states of Cr present in solution.

In Fig. 1 the wavelength characteristics of the undiluted dichromate reflux mixture are shown, revealing the *isosbestic point* characteristic of systems involving equilibria. At this point the sum of the oxidized and reduced forms of Cr is constant *(invariant)*, and the curves for all concentrations intersect. For systems containing more than one equilibrium, there will be an equal number of isosbestic points.

The photometric measurement may be made on either side of the isosbestic point which in this instance occurs at 535 mμ. In practice the wavelength 440 mμ was used to measure percent transmission of diluted samples, since at this wavelength *Beers law* was followed for the diluted sample and the difference in percent transmission between oxidized and reduced forms was greater (Fig. 2).

Photometric measurement of COD has been found to yield results comparable with those obtained using the standard dichromate titration technique. It has the further advantages of greater speed in addition to which it requires less skill of the technician. Table 1 compares COD values obtained using colorimetric and titrimetric methods on a variety of waste waters (Ref. 8).

3.1.2 Automated COD: Method and Apparatus

The apparatus consists of (1) a continuous digestion module used in conjunction with (2) a reagent pump, (3) measuring and mixing module, (4) a heating bath, (5) a

Table 1

Comparison of COD Values Obtained by Colorimeter and by Titration (Ref. 8, p. 925)

No.	Description of Sample	Chemical Oxygen Demand mg/l		$\frac{COD_C}{COD_t}$
		Colorimeter[1]	Titration	
1	Raw Sewage, Stillwater	555 (684)[2]	516 (540)	1.076 (1.267)
2	Primary Effluent, Stillwater	488 (550)	511 (563)	0.955 (0.977)
3	Refinery Waste, Tulsa	5210 (5530)	5256 (5715)	0.991 (0.968)
4	Primary Effluent, Okla. City	693 (470)	662 (430)	1.047 (1.093)
5	Mixed Liquor, Okla. City	2970 (2662)	2965 (3290)	1.002 (0.809)
6	Hardboard, Plant Effluent	1109 (1185)	1090 (1155)	1.014 (1.028)
7	Hardboard, Digester Liquor (1/25 Dil.)	1318 (1489)	1458 (1520)	0.905 (0.979)
8	Hardboard, White Water (1/10 Dil.)	511 (568)	507 (562)	1.008 (1.010)

[1] Values obtained using glucose calibration curve.

[2] Values in parentheses are results obtained using Ag_2SO_4 added at the beginning of the reflux period.

colorimeter and (6) a recorder (see flowsheet, Fig. 3). The waste water may be introduced continuously from the sampler cups or discrete samples (10-20/hr) may be introduced by automatic samplers. Wastewater and dichromate are introduced simultaneously by means of a pump fitted with a flexible tube for each reagent. The use of tubes of calibrated diameter facilitates the measurement of small quantities of reactants into the system. Reagents and sample are mixed in a helical glass coil, heated, and moved on to the digester. In order to prevent the escape of volatiles before oxidation and to provide for the initial digestion of the more easily degradable substances, the heating bath is set at 95-155° with a retention time of ∿ 5 minutes.

The digester itself is a rotating glass helix placed above 2 stages of electrical heaters arranged in series. Internal helix temperatures are controlled by means of two variacs, and the rotation of the helix is at a constant (preset) speed, such that the digestant remains in the helix between 2 to 6 minutes. The mixture volume is a small volume which is distributed throughout the rotating heated helix as a thin film, allowing for rapid heat transfer and efficient digestion of the sample.

After digestion the mixture is pumped, diluted with distilled water, cooled and passed through a continuous flow differential (dual beam) colorimeter, and the electrical signal is recorded as percent transmission (%T) or absorbance.*

A series of standard solutions put through the above procedure provide the

*absorbance:optical density = -log %T

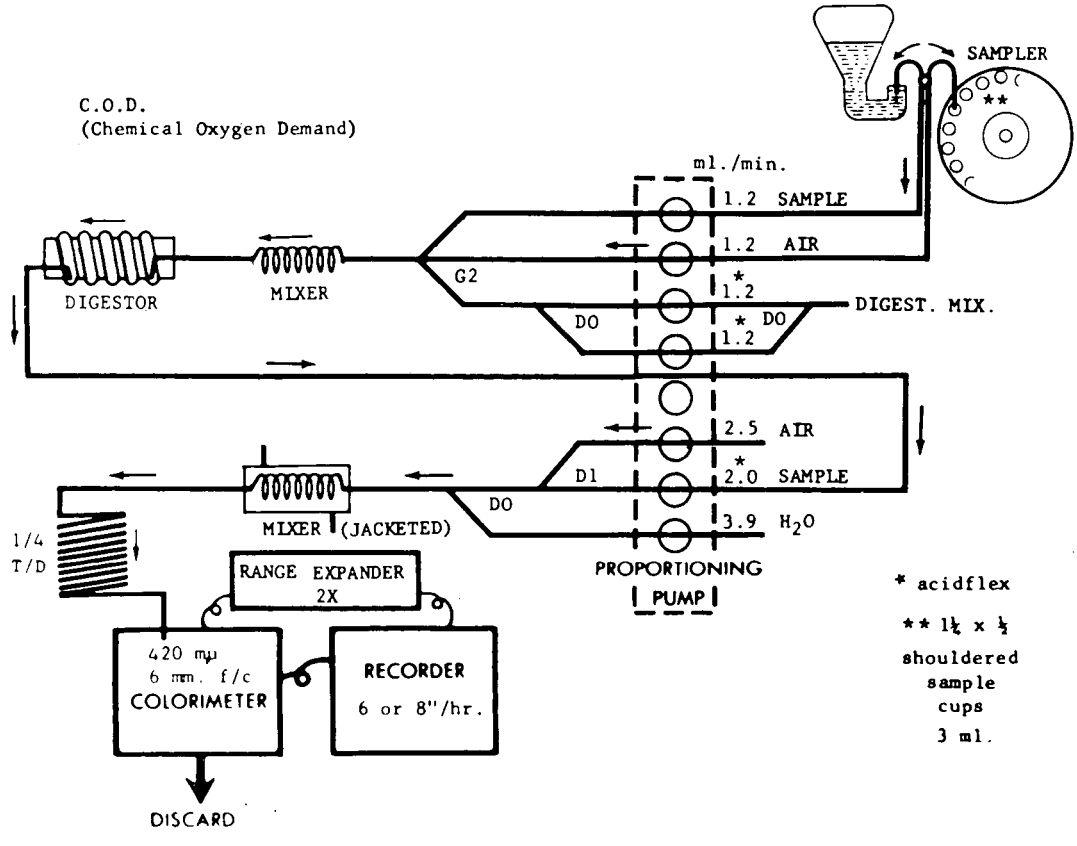


Figure 3. Automated COD flowsheet (Ref. 7, p. 545).

conversion data from %T to mg/liter COD. Because of the segmenting air bubbles and continuous flow of oxidant between samples, the system is self-cleaning. Fig. 4 below illustrates typical COD response patterns for two different concentrations of dextrose.

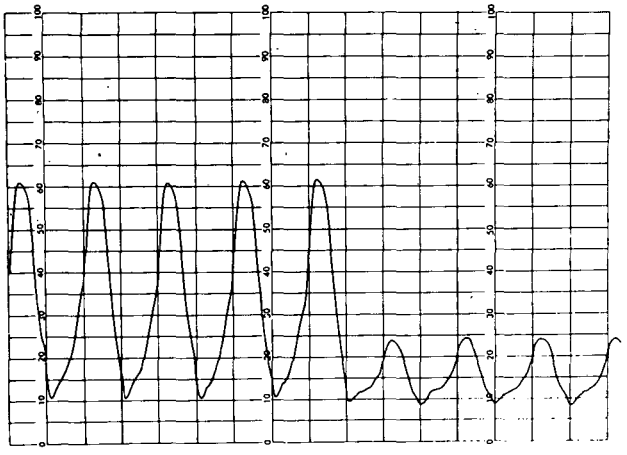


Figure 4. Response pattern for automated COD at two different concentrations (from Ref. 7, p. 546).

Figure 5 illustrates a diagram of a more recent version of the autoanalyzer used for low level COD detection.

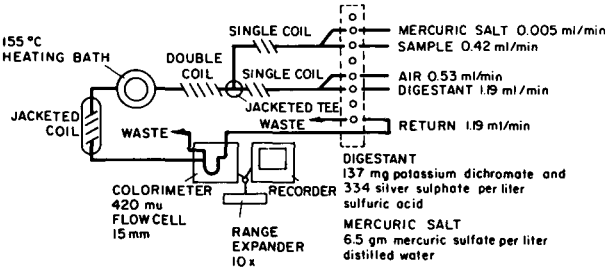


Figure 5. Low level COD detection by use of AutoAnalyzer (Ref. 9).

In another* version of the Automatic COD Analyser, designed for unattended on-line operation, a 10 ml sample is obtained automatically from the sample stream and dispensed into the reaction vessel. Sulfuric acid, potassium dichromate and mercuric sulfate reagents are then added and the solution refluxed for a preset period of from 1/3 to 2 hours. Formation of the green Cr^{+++} is photometrically monitored during the entire heating cycle, the final reading being a measure of the sample's COD (Ref. 10).

*Formerly marketed by Ionics as the Auto COD Analyzer Model 335.

3.1.3 Factors Affecting Automated Wet COD Method

In general the same factors affect the oxidative digestion whether the method employed is automated or manual. Silver sulfate catalyzes oxidation of straight chain aliphatics, but has little effect on aromatics such as benzene which resist the reagent.

Silver sulfate precipitates as the halide in the presence of halogen, resulting in incomplete oxidation and low results. In the absence of the catalyst, chlorides are completely oxidized and results can be corrected for chlorides if they are determined separately as well.

Mercuric sulfate ($HgSO_4$) has been used to complex chlorides, thus avoiding the risk of incomplete oxidation and the necessity of analyzing for Cl^- (Ref. 11).

Temperature is an important factor affecting digestion. The acid concentration determines the boiling point of the mixture (and therefore the reaction temperature, $\sim$ 145°C, in the manual method. This temperature limitation determines the length of time required for complete digestion. Since the automated method is read colorimetrically, the pH limitations imposed when a titration method is used for measurement no longer apply. This allows the use of both high acid concentrations and temperature, shortening the required digestion times (Ref. 12).

3.1.4 Autoanalyzer: Evaluation

A variety of samples, including individual organic chemical compounds and composite waste-stream samples from a treatment plant, were tested by the standard manual and the automated methods. Industrial waste samples were digested for the customary 1 hour for the manual analysis. Results of these comparisons are shown in Table 2. Ballinger and Lishka (Ref. 13) report a precision of ±8% of the accepted value for the manual COD method. The results

Table 2

Comparison of Automated with Manual COD (from Ref. 7, p. 547)

Sample Source	AutoAnalyzer COD, ppm	Manual (by Industrial Plant) COD, ppm
Trickling Filter Effluent		
#1	530	540
#2	522	520
#3	770	705
#4	445	385
Activated Sludge Effluent		
A	200	208
B	218	212
Trickling Filter Effluent	430	416
Waste Influent, Raw	3000	2960
	9600	7560
	1700	1960
	4500	4240
	2120	2300
Trickling Filter Effluent with Lower Heat Input to Digester (to Show Temperature Effect)		
F1	435	480
F2	362	415
F3	370	445
F4	252	265

Unpurified U.S.P. Grade Reagents	COD, ppm AutoAnalyzer	COD, ppm Theoretical	Per Cent Recovery	
			AutoAnalyzer	Literature* (Manual)
Ethyl Alcohol 1/2000 dil.	379	994	38.2	29.7
Acetic Acid " "	60	533	11.4	2.4
Lactic Acid " "	243	533	45.6	45.4
Citric Acid " "	393	393.5	100.0	96.8
Toluene 1/4000 "	90	782.5	11.5	14.9
Phenol 1/3000 "	705	678.3	100.0	—

NOTE: Calibration based on fresh Dextrose solution, 440 mμ, 4 mm cell.

*Moore, W.A., et al., (2,3).

obtained for both activated sludge (A.S.) and trickling filter (T.F.) effluents showed good agreement, with differences between the automatic and manual methods averaging less than 5%. The fact that in most instances the automated method gave the higher COD value would indicate that digestion was more complete under these conditions. Reducing heat input resulted in lower automated COD values than for the manual method (loc. cit.).

With influent wastes between 1700-9600 mg/1, the results obtained were similar, albeit not as good (∿ 11%). Some of this discrepancy was attributed to sampling problems because of the presence of suspended solids and therefore not directly related to the automation itself. The solution here rests with the use of proper mechanical samplers (Ref. 7).

In a recent evaluation of the methodology employed in the AutoAnalyzer® II system, Tifft & Cain concluded that reproducibility and recovery was excellent, but that not all industrial and municipal wastes yielded the same degree of oxidation as that obtained in the manual procedure (Ref. 14).

3.1.5 Automated Wet COD Method: Summary

Control, monitoring and pollution testing using a continuous, automated COD system is feasible. It is also highly desirable where the quality or safety of streams or plant process control operations are involved. Although automation of COD does not inherently alter the COD test, the substitution of an automated for a manual system will facilitate the maintenance of optimum waste-treatment plant operation. The use of automated COD testing reduces the risk of *shock loading* by furnishing an immediate warning.

Automated wet COD, by substituting colorimetry for titration, further reduces the time required for measurement and eliminates certain disadvantages inherent in any titration technique (e.g., the need for special indicator reagents and subjective error).

3.1.6 Advantages and Disadvantages of the Automated Wet Method for COD

Advantages of the method are:

A. Acceptable precision and much shorter analysis time: the original method required several hours per analysis; the automated method, less than 10 minutes/sample (∿ 10 samples/hr). This potential for lower labor input per sample exists where there is a sufficiently large number of samples involved. However, the time-saving and efficiency advantages of automated COD are lost unless a large number of sample measurements or continuous monitoring are required.

The automated method has the disadvantages inherent in the wet method. They are:

A. As in the manual case, automated COD does not differentiate between organic and inorganic reducing species, or between degradable and non-biodegradable organic carbon.

B. There is some continued sensitivity of the procedure to organic structure (e.g., benzene, pyridine, etc.).

C. Automated wet COD analysis requires a high level of technical competence and judgment in carrying out the procedure and interpreting the data.

3.2 Vapor Phase Oxidation: Dry Combustion Methods

Some organic chemicals resist biochemical methods of oxidation; others are resistant to the wet chemical (COD) approach. None resist catalytic combustion which is the basis of the *Total Organic Carbon (TOC)* method discussed in Section 3.2.1 below. Strictly speaking TOC is not an "oxygen demand" method. However, since much of the research carried out with the TOC analyzer has been oriented toward the correlation of this parameter with traditional oxygen demand parameters, it is reasonable to consider the method at this time.

3.2.1 Total Organic Carbon (TOC)

One of the earliest instruments designed for the measurement of the carbonaceous content of waters was described by Van Hall, Safranko and Stenger (Ref. 15). This total carbon analyzer provides a carbon analysis in two minutes and requires only microliter quantities of sample. The procedure entails the injection of a sample by means of a microsyringe into a catalyst-packed combustion tube housed in a high temperature furnace maintained at 950°C. When the carrier gas is pure oxygen, organics are converted to CO_2, H_2O and N_2. On leaving the tube furnace the combined product and sample water is condensed out and the remaining non-condensible gases are passed through the continuous flow sample cell of a nondispersive infrared (NDIR) spectrophotometer sensitized to CO_2. The quantity of CO_2 recorded is proportional to the carbon content of the original sample, and is detected as an electrical imbalance by the CO_2 analyzer (Ref. 16). The flow diagram for a typical Total Carbon Analyzer is shown in Fig. 6.

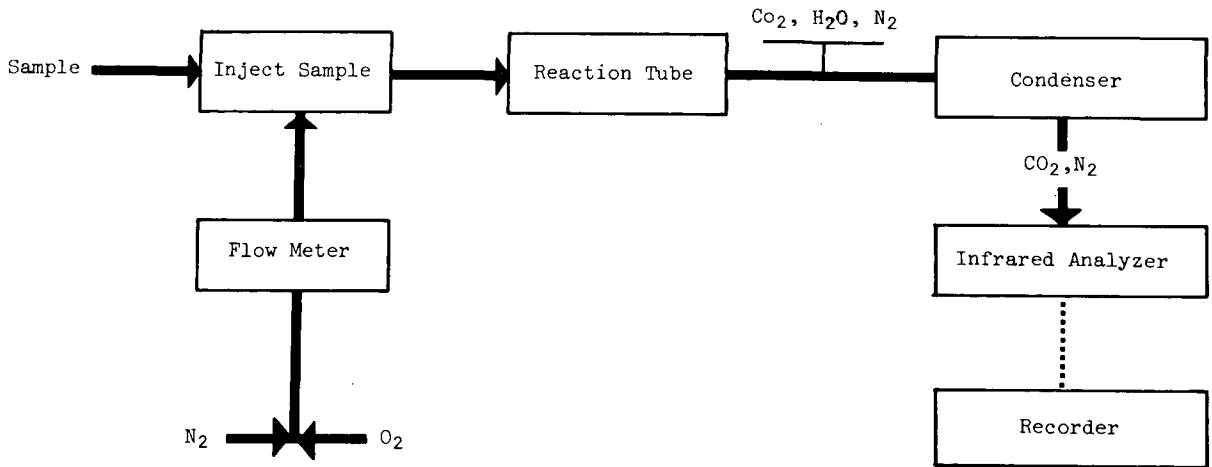


Figure 6. Total Carbon Analyzer flow diagram (Ref. 17, p. 130).

This procedure does not distinguish between organic and inorganic carbon, since inorganic carbonates will also yield CO_2 at the elevated temperature. The differention is made by initial acidification and sparging of the sample prior to combustion, or by use of the dual channel analyzer (Ref. 18) described in the following section.

3.2.1.1 TOC Analyzer: Dual Channel System

The TOC system described under 3.2.1 comprises the single channel version which requires prior chemical removal of inorganic carbonate. However, there is also available a dual channel instrument in which a second sample of equivalent size to the first is injected into a flowing air-stream which carries it to a second combustion tube, this one packed with quartz chips wetted with 85% phosphoric acid* and heated electrically to 150°C. At this lower temperature organic compounds are not oxidized, but CO_2 is released from the inorganic carbonates by the acid-treated packing, and the water is vaporized. The steam and CO_2 are swept out of the furnace by the air, steam is condensed and removed, and the CO_2 measured as in the single channel case. Organic carbon is then calculated by difference.

A completely automated version of the TOC instrument has been reported by Boucher and coworkers (Ref. 19). It is similar to the instrument reported by Van Hall et al. (Ref. 15, 20).

*Catalyst packing in the high temperature tube furnace is cobalt oxide-impregnated asbestos.

The analyzer has two automated features; namely, carbonate is removed via an acidification and nitrogen sparging process, and heterogeneous samples are homogenized in an on-line homogenizer.

3.2.1.2 TOC Procedure: Analytical Considerations

A. TOC Sample Handling

The TOC method was designed for use with true solutions. However suspensions have been analyzed by the use of larger bore syringes. As with BOD and COD analyses, samples must be analyzed quickly or stored at low temperature (∿ 4°C) in the dark. Addition of mineral acid to a pH of 2 inactivates most bacteria. Mercuric chloride has also been employed as a biostat. If the sample is first filtered through a 0.45 μ membrane filter, most of the cellular materials are removed, and the filtrate may then be safely frozen prior to analysis. However, the latter procedure is not recommended for sewage or effluents.

B. TOC Sample Analysis

Since the carbonaceous analyzer measures all the carbon present in the injected sample, prior treatment of the sample will determine the kind of carbon measured by it. In general, there are 3 main classes of carbonaceous materials: 1) soluble organic carbon (i.e., sugars, organic acids, organic bases), 2) insoluble organic carbon such as cellulosic materials, oils and waxes, and 3) other organic matter, soluble or

insoluble, present in an adsorbed and/or otherwise entrapped state. Any or all of these classifications may also contain volatile organics. Categories 2) and 3) may be quantified using the carbonaceous analyzer, but rather complex sampling procedures and pretreatment are required.

The TOC analysis of a water sample is generally carried out on the clear supernatant fraction remaining after removal of inorganic carbonate as CO_2 from the acidified sample (HCl, pH 2). This is accomplished by sparging the acidified sample with an inert gas such as water-pumped N_2. Oil-pumped N_2 is not employed for obvious reasons. For non-homogeneous samples a high-speed blender type homogenizer is often used to reduce particle size and homogenize the sample simultaneously. A magnetic stirrer may be used to maintain proper particulate dispersion in the sample so that a representative aliquot is introduced into the syringe. Syringes with a number of different bore sizes are available for use with samples containing suspended solids (70, 140, 400 µ) (Helms, Ref.28).

In addition to the detailed instructions provided by most instrument manuals, the Federal Water Pollution Control Administration has published a stepwise description of the TOC method applied to both single and dual furnace TOC instruments (Ref. 21).

For further details of sampling, sample preservation and the preparation of standard solutions the reader should consult Refs. 18 and 22.

The following equipment is required for TOC analysis:

a) a precision hypodermic syringe, capacity 0-50 µl

b) a blender

c) a carbonaceous analyzer, single or dual channel type.

C. Packing for the Total Carbon Tube

20 g of $Co(NO_3)_2 \cdot 6H_2O$ (Cobaltous nitrate hexahydrate) is dissolved in 50 ml distilled water and mixed with 15 g long-fiber asbestos in a porcelain evaporating dish. The mixture is evaporated to dryness on a steambath and the dish then placed in a cold muffle and brought up to 950°C and kept at this temperature for 1 to 2 hours. Any large lumps which form are broken up. The combustion tube is then lightly packed with 5 to 6 cm of the catalyst mixture (ca. 1 gm), held in place by small plugs of untreated asbestos. The gas flow rate for the packed tube is then measured at room temperature and at 950°C. The rate should not be more than 20% lower at the elevated temperature.

D. Packing for the Carbonate Tube (Dual Channel System)

A small wad of asbestos or quartz wool is placed at the exit end of the tube and the tube lightly packed with about 10 cm of 6-12 mesh quartz chips. An excess of 85% H_3PO_4 (phosphoric acid) is poured through the packed tube which is allowed to drain in the vertical position.

E. Method

The IR analyzer and recorder are switched on allowing sufficient warm-up time for drift-free operation (about 2 hours).* The total carbon furnace is heated to 950°C; the carbonate furnace, to 175°C. An oxygen flow rate of 80-100 ml/min is maintained through the TC tube. Amplifier gain is adjusted so that a 20 µl sample of the 100 mg/l organic C standard (KH phthalate - $KHC_8H_4O_4$) gives a peak height of approximately 1/2 scale (or an alternate standard concentration may be used, depending on the sample to be measured). For these settings, noise level should be < 0.5% full scale.

Just prior to analysis or calibration, several portions of the selected standards are injected to obtain constant readings.

E-1: Dual channel analyser: Twenty (20) µl each of the organic C standard (and a blank), and of the sample, are successively injected into the system and the peak heights recorded. The recorder pen is allowed to return to its baseline between injections.

Similarly, a series of diluted carbonate standards are prepared, ranging from 20-100 mg of inorganic carbon (IC)/liter.

*If the analyzer is used every day it may be left on continuously.

The (4 way) valve of the apparatus is then so oriented as to direct gas flow through the low temperature furnace, again adjusting flow rate to between 80-100 ml/min. Again, the baseline is allowed to stabilize. Standard, sample, and water blank are then successively introduced into the low temperature furnace and the peak heights recorded.

3.2.1.3 Precision and Accuracy

On clear samples, or those that have been filtered prior to analysis, a precision of 1 to 2% or 1 to 2 mg/l -- whichever is the greater -- may be attained. Unfiltered samples yield a precision of 5-10% (Ref. 1).

For a single laboratory (Ref. 18), the coefficients of variation at TOC levels of 20 and 30 mg/l were ±3.08% and ±0.02% respectively, when the single channel instrument was employed.

3.2.1.4 TOC: Advantages and Disadvantages

Advantages

The advantages of TOC rest in the following characteristics of the method:

1) TOC analyses are rapid, yielding results in a matter of minutes. The method is particularly useful in process control where even the wet COD method may be too slow in terms of the required response time to a changing process situation.

2) A TOC analysis requires very little sample; 20-50 µl usually suffices.

3) The TOC procedure is generally applicable to organics and relatively specific in nature (Ref. 23).

4) The method is more reproducible than either BOD or COD, displaying an oxidation efficiency of 98 to 100% for a large variety of materials (e.g., acetic acid, arylamines, substituted phenols and pyridine). (Ref. 20).

Disadvantages and Limitations

a) The procedures apply to homogeneous samples only, i.e., those which can be injected into the apparatus reproducibly by means of a syringe. The diameter of the syringe needle limits the size of the particles (Ref. 24). Furthermore it is sometimes difficult to obtain reproducible results from homogenized samples probably because of variation in particle size.

b) TOC measures organic carbon without regard to its biodegradability and this may not accurately reflect true oxygen demand.

c) As a corollary to b), TOC measures only the carbon in organics and does not indicate ecologically important interactions. Thus the value often bears little relevance to the BOD of the system. In general, TOC more nearly reflects the COD than it does the BOD of a system.

d) The method requires a considerable degree of chemical knowledge and skill on the part of the analyst.

e) At the high sensitivity required for potable water, IR analyzer stability has been a problem in the TOC method.

3.2.2 The AquaRator: CO_2D

A variant of the COD analyzer known as the "AquaRator" (Refs. 25, 26) uses oxygen-free CO_2 as the oxidant. Carbon dioxide, deoxygenated by preheating in a carbon furnace (440°C) is then catalytically reacted with the organic sample at ∿ 900°C (Pt gauze cat.), and is itself reduced to CO:

$$C_xH_yN_zO_w + nCO_2 \rightarrow (n + x)CO + \left(\frac{y}{2}\right)H_2O + \left(\frac{z}{2}\right)N_2 \qquad \text{(Eq. 1)}$$

The CO is detected by means of an infra-red analyzer. For the corresponding oxidation reaction with O_2, Equation 2 may be written:

$$C_xH_yN_zO_w + \left(\frac{v}{2}\right)O_2 \rightarrow x\ CO_2 + \left(\frac{y}{2}\right)H_2O + \left(\frac{z}{2}\right)N_2 \qquad \text{(Eq. 2)}$$

It can be shown by the stoichiometric comparison of Equations 1 and 2 that $v = n + x$, and that v/2 moles (or v atoms) of oxygen required for the complete oxidation of $C_xH_yN_zO_w$ is equivalent to (n + x) moles of CO resulting from use of CO_2 in the oxidation. A comparison of values

obtained with the AquaRator (termed CO_2D values to differentiate them from those obtained in the conventional COD procedure) is shown in Figure 7. With the exception of a number of nitrogen compounds,* the values are comparable to those obtained in standard COD determinations reported (Refs. 25 and 3).

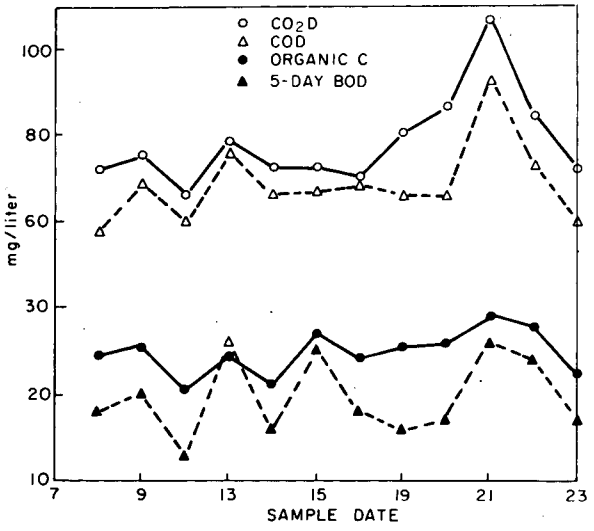


Figure 7. Comparison of CO_2D analysis with the COD, Organic C and 5-day BOD, values obtained on secondary effluent (Ref. 27).

3.2.2.1 CO_2D Analysis Procedure

In practice a 20 µl sample of the wastewater (homogenized, if solids are present) is injected into the instrument by means of a syringe and the sample swept through the (Pt) catalytic furnace by means of a stream of 'bone dry' CO_2 gas. This oxidizes organics to CO and H_2O. The latter is stripped from the mixture by means of a drying tube, the residual products further heated over Pt and the [CO] measured by means of a nondispersive integral IR (NDIR) analyzer. The reading is converted to COD units by means of a standard calibration chart. Figure 8 illustrates the flow diagram of the AquaRator.

*See Section 3.2.2.4

FLOW DIAGRAM

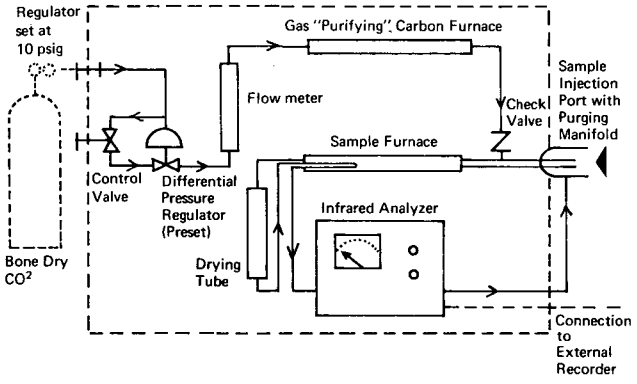


Figure 8. Precision AquaRator CO_2D Analyzer (Ref. 26).

3.2.2.2 AquaRator Design and Measurement Capabilities

The WPCA-suggested concentration limits (10 to 300 mg/l) for COD fall well within the purview of the instrument. Precision is good (± 3%) compared with BOD tests which may deviate from one another by as much as ± 15%. Figure 9 below illustrates AquaRator CO_2D values plotted against corresponding COD and five

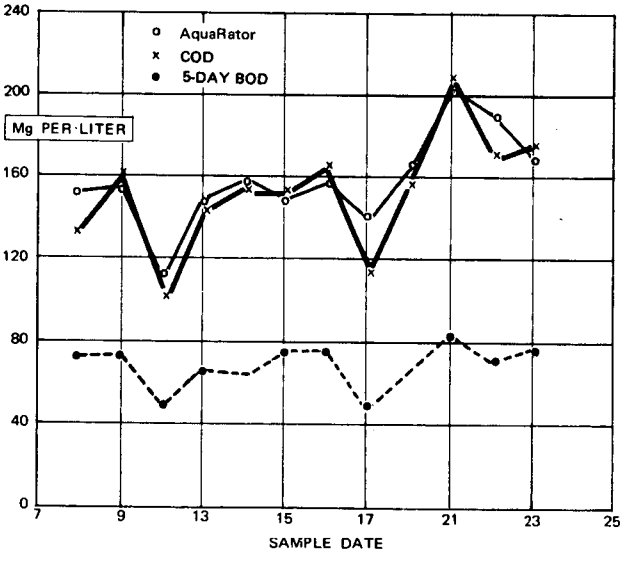


Figure 9. Primary effluent (Ref. 26).

day BOD values. Not unexpectedly, the CO_2D values parallel COD and are higher than 5 day BOD values, the latter measuring only those organics which are biodegradable.

3.2.2.3 Advantages of the CO_2D Method

1) The AquaRator is designed for continuous duty and for use in mobile laboratories.

2) It is fast (2 minutes), enabling the operator to take corrective action quickly.

3) It may be correlated with the standard COD values in a large number of instances.

4) It is applicable over a wide range of COD concentrations (10-300 mg/1) and may, of course, be used outside of this range by appropriate dilution.

3.2.2.4 Limitations of the CO_2D Method

A. Stenger and Van Hall (Ref. 27) reported that the CO_2 oxidations were only linear for standard solutions containing more than 100 mg/1, and that their results closely paralleled those obtained with the standard COD methods, the chief differences stemming from a divergence of characteristics displayed by nitrogen-containing compounds in the two systems. Thus, carbon dioxide is reduced at high temperatures by NH_3 and urea (NH_2CONH_2), but these compounds do not affect the chromic acid reagent in the standard COD procedure. Ammonium chloride (NH_4Cl) yielded anomalously high results in this (CO_2D) method, possibly because of some intermediate reaction of the HCl formed, reducing the CO_2 to CO and forming a transient platinum halide. Stenger and Van Hall (Ref. 25) suggested either measuring chloride separately and making a correction, or "spiking" standards with known amounts of chloride.

B. At high temperatures, nitrates, phosphates and sulfates release O_2 which in turn reoxidize CO to CO_2. Sulfate may be removed prior to sample injection. Nitrates are the chief offenders, but the authors noted that they would yield available oxygen in BOD tests and therefore "should not be regarded as interfering if actually a valid part of the sample." (*Loc. cit.*, p. 210). However, Helms (Ref. 28) considers this positive interference by oxygen-containing anions common in wastewater a disadvantage, and states that the methods used to compensate for the interference produce unacceptable side effects.

3.2.3 Total Oxygen Demand

Another instrument based on a dry combustion process, which correlates oxygen demand with organic content, employs catalytic burning of the sample (Pt catalyst) in a carefully controlled mixture of N_2 and O_2 (see Fig. 10) (Refs. 29, 30). Oxygen depletion is detected by means of a fuel cell (Pb-Pt) and *TOD (Total Oxygen Demand)* is recorded as a change in cell current. The change in fuel cell current output is a function of the oxygen concentration in the N_2 stream, and this depends linearly on TOD. Sensitivity of the method is ca. 10 mg/l (ppm). A solution of potassium acid phthalate, $KHC_8H_4O_4$, is used for calibration of the system. The correlation between TOD and COD for two systems is shown in Figures 11 and 12.

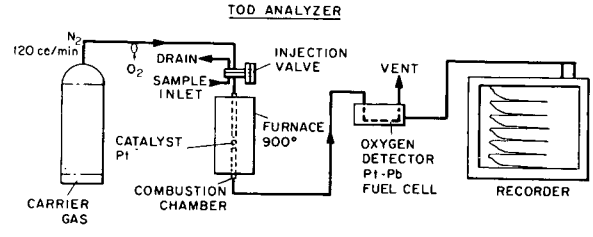


Figure 10. Schematic diagram of the TOD Analyzer (from Ref. 30).

Another version of the TOD analyzer (EnviroControl) has a fluidized bed type reactor with fine aluminum particles furnishing greatly increased surface area to promote the oxidation of carbon compounds. Here combustion occurs at 850°C, the products of combustion are cooled to 30°C and the condensed water vapor removed. Noncondensibles then enter a chamber where an oxygen sensor measures remaining oxygen. This system features a high sample flow rate of 3-4 ml/min and can handle solid particulates of diameters ≤ 100 μ. Throughput per sample is about 8 minutes. TOD values are expressed in mg/1.

TOD overcomes some of the difficulties encountered in the standard COD test such as the variation in sample susceptibility to dichromate oxidation (Ref. 1). In addition, inorganic carbonates are not included as organic carbon using this method. However, nitrates decompose to give nitric oxide (NO) and O_2, and would thus reduce the apparent OD of the sample.

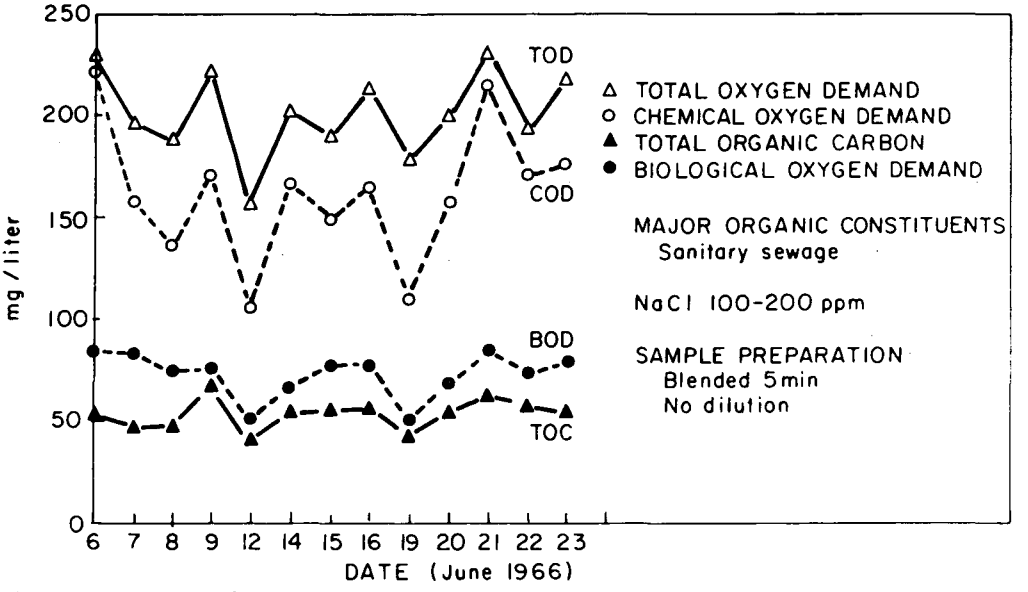


Figure 11. Comparison of TOD with COD, BOD and TOC in primary effluent (Ref. 29).

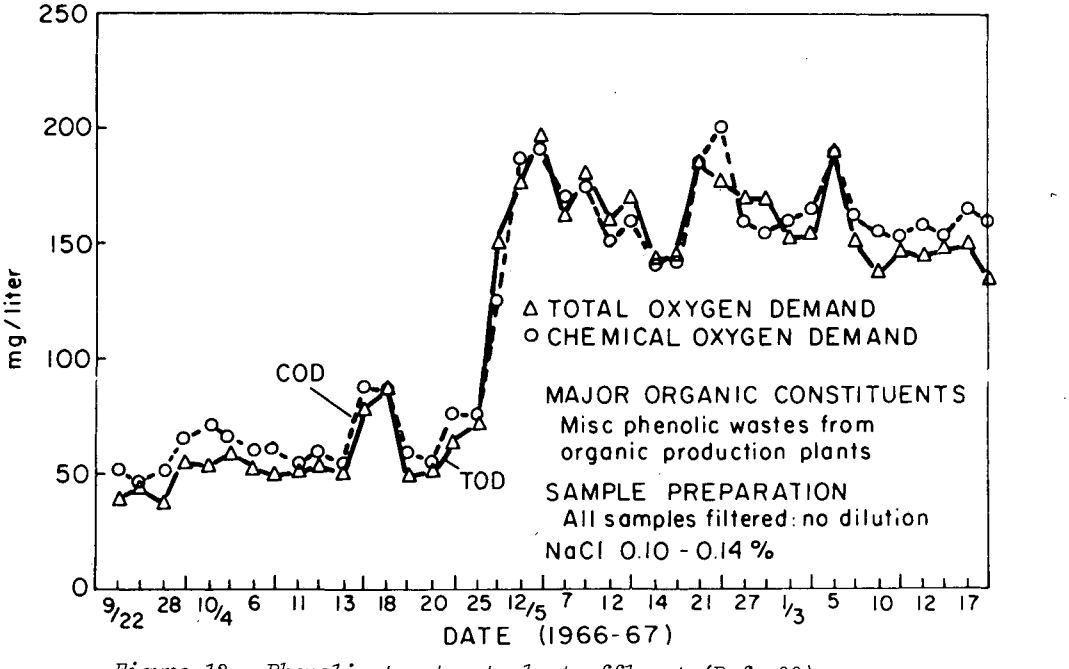


Figure 12. Phenolic treatment plant effluent (Ref. 29).

3.2.3.1 TOD Method

A typical water analysis entails the simultaneous introduction of a 20 µl sample and a stream of an inert gas into the combustion tube of an electric furnace maintained at 900°C. The carrier gas contains ca. 200 ppm of oxygen. Two reactions occur at the surface of the Pt catalyst:

1) sample impurities are oxidized by adsorbed oxygen at the catalyst surface, thereby momentarily depleting the Pt surface of its adsorbed oxygen;

2) oxygen equilibrium is restored on the catalyst surface by replacement of its depleted O_2 furnished by the carrier gas. This temporarily lowers the concentration of O_2 present in the inert gas stream.

It is this momentary O_2 depletion which is accurately measured by the lead-silver fuel cell and recorded as cell current which is thus a function of the oxygen demand of the sample. In practice the peak height measured for the unknown is compared with a standard calibration curve.

3.2.3.2 Applications and Limitations

The TOD method measures oxygen consumed in the following reactions:

$$C + O_2 \rightarrow CO_2 \qquad \text{(Eq. 3a)}$$

$$H_2 + 1/2\ O_2 \rightarrow H_2O \qquad \text{(Eq. 3b)}$$

$$N_{(\text{reduced forms})} + 1/2\ O_2 \rightarrow NO \qquad \text{(Eq. 3c)}$$

N_2 carrier gas does not react and the lower oxidized states of sulfur form a fixed ratio of an SO_2-SO_3 mixture under TOD conditions. The oxidation of urea, for example, may be represented by the following equation:

$$2\ NH_2CONH_2 + 5O_2 \rightarrow 2CO_2 + 4NO + 4H_2O \qquad \text{(Eq. 4)}$$

Correlation of TOD with COD is good where the latter measurement does not suffer from interference (Ref. 31).

Because of greater catalytic oxidation efficiencies of the method, TOD values are normally higher than their COD counterparts, particularly on mixed or nitrogenous wastes (Ref. 32). Correlation with BOD will, of course, vary with the sample, since there is often little relationship between *biochemical* OD processes and *catalytic* oxidations at high temperature. Further, unless sample has been purged of dissolved oxygen, the TOD value obtained will represent that OD which is *in excess* of the DO present in solution.

Heavy metals may poison the Pt catalyst. This problem was taken into consideration by providing a large area of catalyst in the combustion chamber (Ref. 32).

Common anions found in natural and wastewaters do not interfere seriously, as shown in Table 3 below, where 1000 ppm of the anions in question were added to 200 ppm of organic standard in de-ionized water (Ref. 32). The presence of nitrates would, however, interfere for reasons already discussed in section 3.2.3.

3.2.3.3 Summary

Table 4 summarizes the salient characteristics of some automated oxygen demand type systems. TOD analyzers have been used to measure organics in a variety of plant and municipal effluents (Refs. 29, 32) and a number of comparisons with BOD, COD, and TOC made (Fig. 11).

Table 3.

Effect of Common Anions on 200 PPM TOD Standard (Ref. 32)

Anion Source	1000 PPM of Anion	PPM TOD Calculated	PPM TOD Found	No. Detn.	Rel. Std. Deviation
NaCl	Cl^-	200	198.2	4	± 1.41%
$NaHCO_3$	HCO_3^-	200	204.5	4	± 2.28%
K_2SO_4	$SO_4^=$	200	191.4	4	± 0.79%
$KHSO_4$	HSO_4^-	200	196.8	4	± 1.43%
Na_2HPO_4	$HPO_4^=$	200	195.2	4	± 1.54%

Table 4.

Summary of Oxygen Demand and Carbonaceous Analyzers (adapted from Ref. 33).

Parameter	Sample Treatment	Instrumental Detection		Sample Size, µl	Anal. time, min	Range	Sensitivity, ppm	Continuous Automated Operation	Requirements	Supplier
		Species	Sensor							
COD										
Standard COD	Chromate oxidation	Cr^{3+}	Colorimeter	Variable	6[a]	0-55,000 ppm of O_2	1	Yes	Reagents	Technicon
TOD Analyzer	Catalytic combustion	O_2	Fuel cell	20	3	0-1000 ppm of O_2	10	Yes	N_2, air	Ionics
AquaRator CO_2D	Catalytic combustion	CO	Infrared	20	2	10-300[b] ppm of O_2	10	Not Claimed	CO_2	Precision Scientific
TOC[d]										
Automated Analyzer	Catalytic combustion	CO_2	Infrared	(500 ml/min, 5 ml/min)[c]		25-400 mg/liter C	10	Yes	N_2, O_2, HCl (conc.)	Raytheon/AES
TOC Analyzer	Catalytic combustion	CO_2	Infrared	20-200	2-4	0-10 0-4000 mg/liter C	> 10	Not Claimed	Air or CO_2	Beckman
Total Carbon Analyzer[d]	Catalytic combustion	CO_2	Infrared	40	3	0-100 0-5000 mg/liter C	5	Yes	N_2, air	Ionics[f]
Organic Analyzer	Pyrolysis	Organic pyrolyzate	Flame ionization detector	to 50	2[e]	0-3000 mg/liter C	> 1	Not Claimed	N_2, H_2	Envirotech

[a] At a rate of 10 samples/hr.

[b] Higher concentration by dilution.

[c] 500 ml/min nominal flow rate to sample and a fraction taken for treatment at 5 ml/min.

[d] All analyzers except total carbon analyzer distinguish between organic and inorganic carbon.

[e] 6 min between analyses.

[f] formerly Union Carbide

3.3 Vapor Phase Pyrolysis

Pyrolytic fragmentation of organic compounds in the presence of water is the basis of still another total carbon analysis in an instrument marketed by Rocketdyne. A hydrogen flame ionization detector is used in the detection of the fragments produced. Dissolved CO_2 and inorganic carbonates do not interfere (Ref. 17).

Lyzyj et al. (Ref. 34) used the following procedure: The aqueous sample was introduced into the system which consisted of (1) a pyrolysis chamber maintained at 800°C; (2) a flow stabilizer column of glass beads; and (3) a detector (FID). The carrier gas was steam. An ion current signal produced by the pyrolyzed hydrocarbon fragments was detected by the FID and integrated. Glucose-glutamic acid was used as the primary calibration standard.

The method has been used to calculate the BOD values for sewage systems based on the prior establishment of ratios between the BOD measurements and the instrument response obtained for the systems examined.

Another pyrolytic system (Ref. 35), somewhat similar to the one previously described, utilizes prior conversion of the organics to methane (CH_4) in a nickel tube heated to 800°C. The carrier gas is N_2 in this instance.

The methane formed is passed through a column (H = 10 ft.) at 50°C packed with 50-80 mesh porous glass.

Methane equivalents obtained for industrial wastes using this method were consistantly higher than methane/organic equivalents obtained for natural streams.

3.3.1 Limitations of Vapor Phase Pyrolysis

The FID measures carbon concentration in terms of electric current generated (i.e., the number of ions formed). It apparently responds to all organics with the exception of formic acid (HCOOH) (Ref. 36), the response being greatest with the hydrocarbons, and diminishing as the substitution of hetero-elements increases. Properly operated, the method yields highly accurate analysis of trace levels of carbonaceous materials. However, for the routine monitoring of wastewaters, the carbonaceous analyzers of Van Hall et al. are preferred.

3.4 Summary and Evaluation of Carbonaceous Analyzers

1. With one exception, all of the vapor phase carbonaceous analyzers operate on the same basic principle: namely, oxidation of carbonaceous material and detection of the products by IR. The instruments may be calibrated in terms of carbon content or OD (BOD or COD). In the absence of systematic error(s), the form of the standard calibration has essentially no effect on the precision or the accuracy of the results obtained (Ref. 28).

2. There is no universal correlation between carbonaceous content and OD. However, for a given kind of waste, with predictable composition, the carbonaceous content bears a relationship to BOD and/or COD values, and thus can be expressed in these familiar terms.

3. Removal of interfering inorganic carbonate is effected preferably by sample precipitation of the carbonate with $Ba(OH)_2$. The two-furnace system has disadvantages associated with possible additive errors.

4. The CO_2D instrument of Van Hall and Stenger can be classified as a carbonaceous analyzer performing the function of the single furnace adaptation of the TOC analyzer. The change in oxidant from O_2 to CO_2 does not impose any fundamental furnace-design differences: it merely requires that a change in CO content be detected instead of CO_2. The basic calibration remains mg/l, although the instrument was originally calibrated in terms of COD (Ref. 25). Those anions which yield oxygen on decomposition interfere significantly in the CO_2D analysis, and the suggested methods of correction have unacceptable side effects in that oxygen production from them may vary with the sample, making the correction unreliable (Ref. 28).

5. The pyrolytic method employing FID to measure trace levels of carbonaceous materials can yield very accurate data under carefully controlled conditions. However, the simple furnace carbon analyzer is more suited to the routine monitoring of waste waters. The FID response is reported to be greatest with hydrocarbons and occurs with all organic compounds except formic acid (HCOOH). Groups I and II elements are also ionized by a hydrogen flame and will interfere.

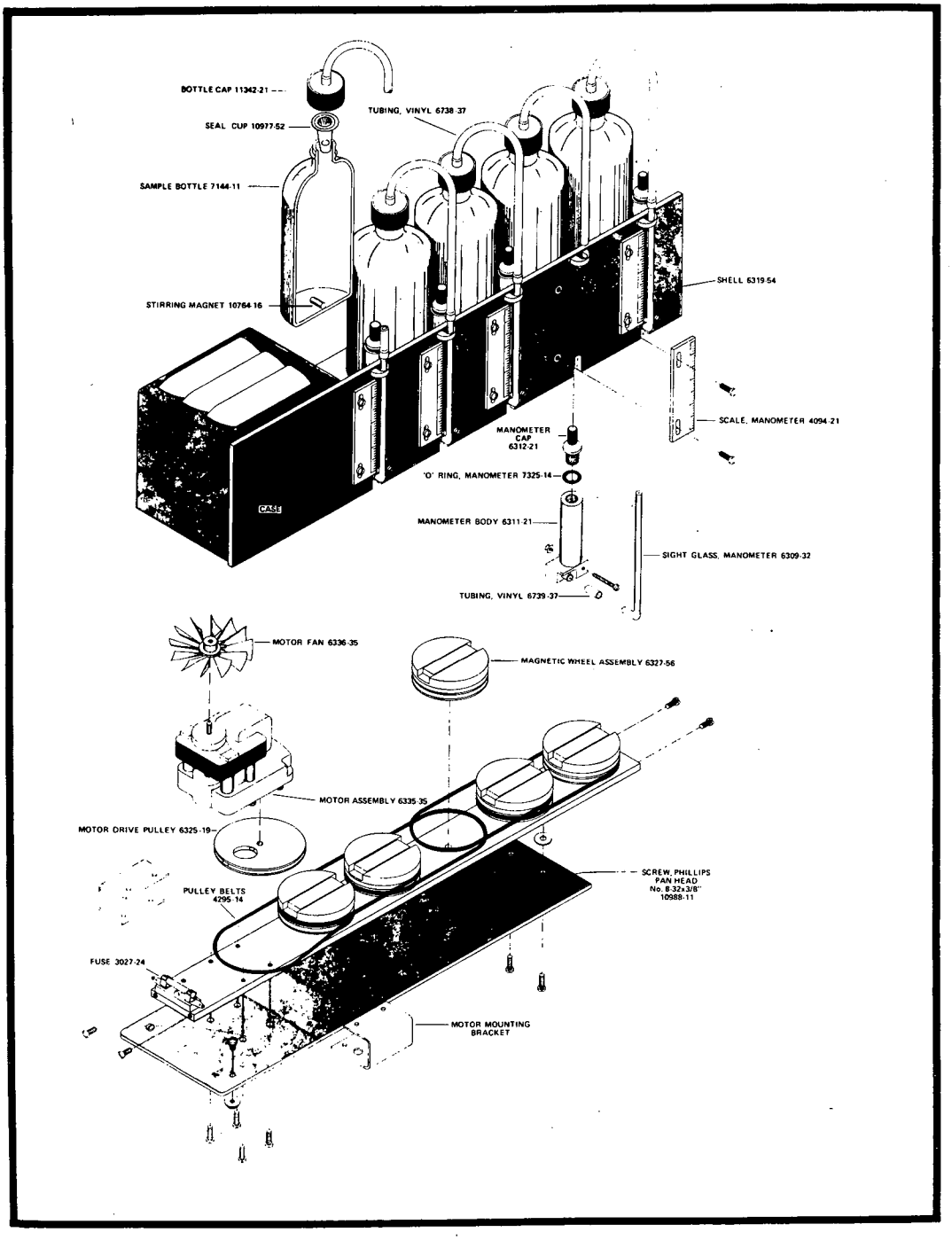


Figure 13. Assembly diagram of the Hach Model 2173, BOD respirometer (Ref. 40).

4. Biochemical Oxygen Demand (BOD): Respirometric Methods

A number of attempts have been made to automate BOD, using respirometric methods (Refs. 37, 38, 39). The respirometer measures oxygen uptake and/or gas exchange associated with some biological processes. In practice, oxygen uptake is usually measured by means of a manometer in a closed system, and the CO_2 produced in the reaction is absorbed by an appropriate reagent. The Hach Model 2173, BOD respirometer is typical of this kind of device (see Fig. 13 preceding). The measured sample is placed in a brown bottle fitted with a mercury (Hg) manometer. As the air above the sample is depleted of its oxygen by bacterial activity the pressure drop is registered by the manometer. Carbon dioxide produced is absorbed by a 45% potassium hydroxide solution placed in the seal cap. During the test period the sample is continuously agitated by means of a magnetic stirring bar activated by a pulley system connected to a motor. Clark (Ref. 41) has developed an electrolytic respirometer which generates O_2 electrolytically in response to the change in pressure which occurs during oxygen uptake. When the O_2 pressure is equal to $P_{atmospheric}$, electrolysis ceases, and the current used is a measure of oxygen uptake. The E/BOD Respirometer (Oceanography International) is based on the above principle (see Fig. 14 below).

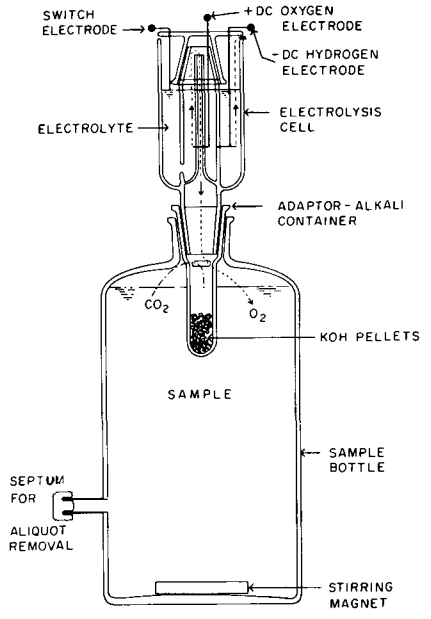


Figure 14. Schematic diagram showing the basic operation of the electrolysis system for measuring BOD (Ref. 42).

Liebmann and Offhaus (Ref. 43), using a similar technique (the Sapromat A6 Respirometer) reported obtaining oxygen uptake with 5% precision. The time advantage of obtaining BOD data using such respirometric methods (48 to 72 hours) is obvious.

Another respirometric system bubbles gaseous oxygen through the sample and the disappearance of oxygen is measured by means of an oil manometer (Ref. 44). Arthur and Hursta (Ref. 45) have correlated the 4- and 7-hour O_2 uptakes with 5-day BOD. Eye, Ritchie and others (Refs. 46, 47) have used membrane electrodes to measure changes in [DO] as an OD indicator. One such device is an ordinary BOD bottle fitted with a polarographic membrane and stirrer for continuous monitoring of DO. Good data correlation was reported when this system was compared with the usual BOD method (Refs. 45, 46).

Lamb and coworkers (Ref. 48) employed a respiration cell equipped with the galvanic cell oxygen analyzer of Mancy and Westgarth (Ref. 49) and magnetic stirring, in a study of the biological treatment of industrial wastes (Fig. 15). This led to the subsequent development of a short term (STOD) test for BOD (Lamb et al., Ref. 48).

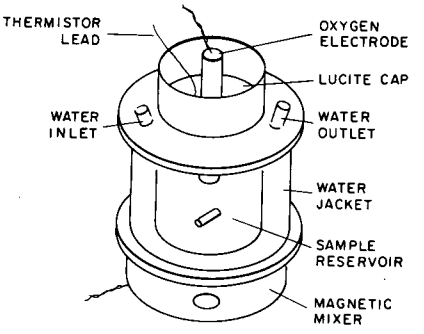


Figure 15. Respiration cell (Ref. 48).

5. Miscellaneous Monitoring Methods: Bio Parameters

Attempts have been made to correlate a number of physical parameters with the oxygen demand characteristics of biosystems. Among these, temperature plays a vital role which has been discussed (see BOD section 2.1 Temperature; DO section 1.2 Temperature Effects). Temperature measurement is discussed under Physical Parameters in this volume and will therefore not be considered in this section.

Similarly, factors such as pH and salinity affect DO and BOD (see H2O:DO, 1.3 Electrolyte Effects; H2O:BOD, 2.5 Nutrients). Again, description of these physical parameters and their measurements appear elsewhere (this volume, PHY), and so will be omitted from this chapter.

In the following section we will describe the use of *oxidation-reduction potential (ORP)* as a biometric tool in evaluating the state of aqua-systems.

5.1 Oxidation-Reduction Potential (ORP) in the Monitoring of BIO Systems

Biological systems are complex and dynamic in nature, and the biochemical changes occurring within them are frequently of a thermodynamically reversible kind. Their reactions are strongly environment-dependent, with *oxygen-reduction potential (ORP)*, hydrogen ion concentration (pH), and temperature ranking as the three most fundamental environmental variables or parameters. Measurement of ORP provides an over-all system potential, which embraces many interrelated reactions and phenomena, not all of them amenable to individual measurement. By the indication of the redox state of an aqua-system one can obtain an insight into the biological condition of that system (Refs. 50, 51, 52). For in-depth discussions of ORP theory as it applies to biological systems, the reader is referred to the works of Clark (Ref. 53) and Barron (Ref. 54).

5.1.1 Theory of ORP

The *electrochemical potential* of a system is associated with its *driving force* or tendency to lose or gain electrons. At equilibrium the free energies of products and reactants will be equal and the system potential depends solely on the concentration of the reactant and product species remaining. Using the standard hydrogen electrode* as a reference for potential measurement, the reduction potential for a system

$$M^{b+} + (b - a)e \rightleftarrows M^{a+} \qquad \text{(Eq. 5)}$$

where $b > a$, may be written as the Nernst expression:

$$E_{M^{b+}M^{a+}} = E^0_{M^{b+}M^{a+}} - \frac{RT}{(b - a)F} \log \frac{a_{M^{a+}}}{a_{M^{b+}}} \qquad \text{(Eq. 6)}$$

where:
- E^0 = the standard reduction potential for the system, i.e., (for $a_{M^{b+}} = a_{M^{a+}} = 1$) compared with the standard hydrogen electrode,
- $(b - a)$ = the number of electrons transferred,
- R = the gas constant,
- T = absolute temperature, and
- F = the Faraday, in appropriate units.

To measure $E_{M^{b+}M^{a+}}$ for the half cell reaction of the system, the following cell assembly is employed:

$$Pt|H_2,\ 1\ atm|H_3O^+,\ a = 1||M^{b+},\ M^{a+}|Pt \qquad \text{(A)}$$

The following half cell reactions occur in this cell assembly:

Anode: $\frac{1}{2} H_2 \rightleftarrows H^+ + e,\ E^0_{H_2} = 0.000\ V$ (Eq. 7)

Cathode: $M^{b+} + (b - a)e \rightleftarrows M^{a+},\ E^0_{M^{b+}M^{a+}}$ (Eq. 8)

For a system using the standard electrode ($E^0_{H_2} = 0$) both the magnitude and sign of the overall cell potential are identical with its ORP. The sign will of course depend on the sign of the E^0 term in Eq. 6 and the relative concentrations of the charged species in question.

For the cell system (A) shown, the ORP will be negative if the electrons flow from the H electrode to Pt, $M^{b+}M^{a+}$ and the reaction of Equation 6 will then go spontaneously. For the case of opposite electron flow (i.e., to the H electrode), the following equations (i.e., half cell reactions) maintain:

Anode: $M^{a+} \rightleftarrows M^{b+} + (b - a)e$ (Eq. 9)

Cathode: $H^+ \rightleftarrows \frac{1}{2} H^0_2 - e$ (Eq. 10)

Here the ORP will be positive.

Since the convention used is based on the standard hydrogen electrode, the notations ORP and E are used interchangeably.

*The standard hydrogen electrode is assigned zero potential for $a_{H^+} = 1$, $P_{H_2} = 1$ (at 25° C). (a = activity; p = pressure in atmospheres)

Still another expression for the ORP parameter is in terms of pE. This is analogous to the expression for pH and takes the form

$$pE = pE^0 + \frac{1}{(b - a)} \log \frac{M^{b+}}{M^{a+}} \qquad \text{(Eq. 11)}$$

Here,

$$pE = \frac{E_{M^{b+}M^{a+}F}}{RT} \qquad \text{and} \qquad \text{(Eq. 12)}$$

$$pE^0 = \frac{E^0_{M^{b+}M^{a+}F}}{RT} \qquad \text{(Eq. 13)}$$

pE is a measure of equilibrium *redox intensity*, where a large positive value is indicative of a strongly oxidizing condition in an aqua-system. Conversely, a low positive--or negative--pE indicates reducing conditions. For water solutions the pE range is -10 to +14.

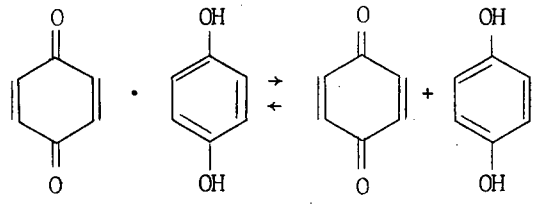
Since the standard H electrode is not a convenient reference electrode, other electrodes are generally employed, one of the most widely used being the *calomel electrode*. For 1 molar KCl ($a_{Cl^-} = 1$), $E^0_{calomel} = +0.268$ V. Expressed in terms of the standard hydrogen electrode,

$$E_H = E_C + 0.268 \text{ V} , \qquad \text{(Eq. 14)}$$

where:

E_H = the ORP value of the system using a H reference electrode,
E_C = the ORP value in terms of the calomel reference electrode, and
0.268 V = the standard reduction potential for the calomel reference electrode (1 M KCl).

Quinhydrone may be used to standardize the ORP cell by allowing the indicator electrode (Au or Pt) to come in contact with a saturated quinhydrone solution. This is a simple technique, depending on the rapid dissociation reaction of the molecular compound to quinone (Q) and hydroquinine (HQ):



(QH) (Q) (H)

(Eq. 15)

A potential develops rapidly, and the QH electrode is relatively resistant to poisoning. However, standardization must be carried out between pH 1-8 (Ref. 33, p. 1482).

5.1.2 ORP Measurement

Measurements of ORP are made with an electrode pair consisting of a noble metal non-polarizing indicator electrode and a reference electrode, such as Ag-AgCl or the calomel electrode ($Hg-Hg_2Cl_2$). The indicator electrode to which electrons are transferred by the redox system may be in the form of a button or wire. Measurement of the emf developed may be by means of a potentiometer or voltmeter (Fig. 16c). Details of the procedure are given in Ref. 24b. (ASTM Standard test D1498-59). Depending on the accuracy required, one of three types of meters may be used. Table 5 gives electrical characteristics for three assemblies.

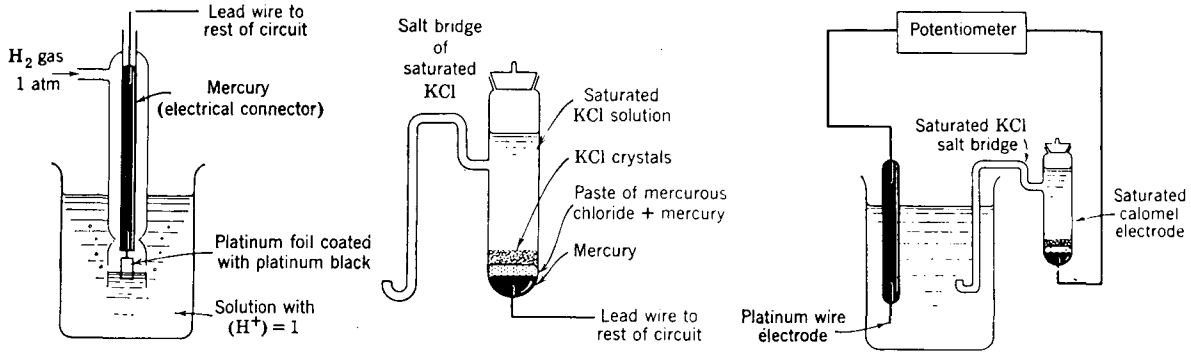
The ASTM method employs a saturated calomel reference electrode with an excess of solid KCl and of calomel surrounding the pure Hg component. It requires that a fresh junction be formed between the saturated KCl solution of the reference electrode and each new test solution. The a.c. resistance at the junction may not exceed 5000 Ω, and the area of the noble metal in contact with the test solution should be approximately 1 sq. cm.

Sampling procedures are those described in H2O-DO-2.1 and HSO-BOD-12.4, or ASTM method D-510.

Calibration will depend on the type of meter employed (see D 1498-59.9).

New metal electrodes are cleaned with aqua regia warmed to 70°C for 1 minute. Since this treatment attacks the noble metal as well as removing impurities, the time specified must be closely observed. This same treatment may be applied with caution to an aged electrode whose performance has become unreliable.

Just prior to use the electrode is cleaned with (1:1) HNO_3 by gradually warming to boiling, maintaining just below the boiling point for five minutes, then allowing the assembly to cool. The electrode is then washed repeatedly with distilled water before immersion in the sample solution. The voltage is read after the cell has reached thermal equilibrium. Readings using different oxidation-reduction electrodes should agree within ± 5 mV.



(a) Standard hydrogen electrode. *(b) Saturated calomel electrode.* *(c) Cell for measurement of an oxidation potential.*

Figure 16. Electrodes and cells (adapted from Ref. 55, p. 28-36).

Table 5.

Electrical Characteristics of Meters and Operating Performance of Assemblies (Ref. 24)

	Type A Meter	Type B Meter	Type C Meter
Vacuum tube operation	Yes	Yes	No
Type of measuring circuit	Potentiometric	Direct Reading	Potentiometric
Method for detection of balance point	Null indicator (galvanometer or electron-ray tube)	Direct	Galvanometer[a]
Maximum current flowing in input circuit	10^{-10} amp	10^{-10} amp	
Standard cell for calibration	Yes	Optional	Yes
Scale units	Millivolts	Millivolts	Millivolts
Minimum range	0 to ± 1100	0 to ± 1100[b]	1 to ± 1100
Maximum value of smallest ruled interval	10 mV	10 mV	10 mV
Power supply: batteries or 115 Vac	Either	Either	Batteries

[a]Minimum sensitivity equivalent to 0.0005 μA at 1 m.

[b]A double scale may be provided.

Oxidation-reduction potential for the sample (in mV) is calculated with reference to the hydrogen scale:

$$ORP = E - C \quad ,$$

where

E = emf in mV for the cell, and
C = potential of the saturated calomel electrode (also in mV), referred to hydrogen.

It is to be noted that C must be corrected for deviation from standard temperature (25°C).

Precision obtained is reported as ±5 mV with type A and C meters, ±10 mV with type B.

5.1.3 Scope and Limitations of ORP

Experimental measurement of E_H in natural waters, and interpretation of the significance of the value obtained presents serious problems (Ref. 56). Firstly, natural waters harbor a broad spectrum of substances, organic and/or inorganic, in dissolved, colloidal, or suspended states, which may affect or interfere with the ORP measurement. Secondly, the recurrent cyclical input of solar energy results in a photosynthetic cycle, and characteristically low rate for redox reactions. Thus the system is an *open* one -- i.e., does not attain equilibrium. The numerous redox systems present are furthermore not distributed homogeneously throughout the aqua-environment, so that the attainment of an overall equilibrium for the system is highly unlikely. The *open* or *dynamic* nature of the aqua-system exists both on a localized (*micro-* or molecular) and non-localized (*macroscopic* or environmental) level and the bio-systems within these natural waters may be viewed as functioning on both levels.

On the molecular level, the response of living organisms to an ORP system may be viewed in terms of the presence (or absence) of electroactive substances (*mediators*) -- i.e., trace metals, and/or the latter in combination with appropriate enzyme systems. Bacterial systems have been classified on the basis of their electroactive response (Barron). On the macro level, microorganisms function at a much more complex level, since other environmental substances present, and their interaction with metabolites, can be affected by the other physical and chemical parameters and by their own surface activity. Even given a hypothetically uniform distribution not possible under dynamic stream conditions, many redox systems would not couple in the normal course of events. Thus, although the ORP measurement is a valid one on a macro scale, it is unrealistic to assume that an ORP measurement reflects any micro (i.e., *molecular*) system.

The number and complexity of the redox systems present also contribute to the problem of interpretation of experimental measurements since an E_H value may reflect the sum of the potentials of a number of biosystems *(mixed potential, E_m)*, and thus cannot possibly yield any information on individuals, even of a qualitative nature. Interaction between systems can lead to a slowly changing E_m value, and low concentrations of certain redox species can interfere with the successful measurement of E_H. Differing half cell reactions may show these effects to a varying degree. The following factors are involved:

a) exchange current i_0;

b) electrode area, A (cm^2);

c) electroactive species involved (the products of their concentrations: $C_{ox}C_{red}$ (mol cc^{-1})).

The dependence of i_0 is given in Equation 16 below:

$$i_0 = AnFK' C_{ox}^{(1 - \alpha)} C_{red.}^{\alpha} \quad , \qquad \text{(Eq. 16)}$$

where

n = the number of electrons in the half cell reaction;
F = the Faraday, and
α = the transfer coefficient (usually ~ 0.5).
K' = a reaction rate constant (cm/sec).

For systems with $i_0 > 10^{-7}$ amp., E_H is a reasonably measurable quantity. By the use of electrodes with large surface areas, the low exchange currents, i_0, resulting from slow reaction rates may be measured. There are practical limitations to increased electrode areas, since they adsorb surface active pollutants, thereby suffering reduction in electroactive area.

The value of E_H is further affected by *poising capacity* -- a quantity similar to the buffering capacity in acid-base solutions. The *poising index* is defined as the

"increment of oxidizing agent in equivalents/l, divided by the incremental change in E_H" (Ref. 53). Without poising capacity, potential instabilities hamper measurement. This is often a problem in muds and lake waters (*electrode poisoning*). It may also result from sample dilution with distilled water.

For solutions which have poor poise, the Pt electrode surface area is critical. In addition, an electrode may require a long adaptation period before attaining equilibrium in a given system. However, once equilibrium is achieved, the response for the system in question becomes satisfactory.

5.1.4 Summary and Conclusions

The dynamic (non-equilibrium) states of natural water systems, the multiplicity of redox couples, and the existence of numerous experimental difficulties, have all militated against the use of the ORP as a water monitoring parameter. Nevertheless ORP does have some value in defining conditions under which some algal and/or bacterial species are favored. This can be very important in sanitary engineering process control and in some environmental investigations (Ref. 50).

The eco-concept states that there is a mutual interrelationship between all parts of a bio-system. Although bio-systems are dynamic and classified as open, they are nevertheless viewed as existing in some sort of *quasi-steady state* (Ref. 33, p. 1485), other than true equilibrium, however. Lee and Hoadley (Ref. 57) found that the micro-organisms in an ecosystem, for example, figure significantly in determining the mineral content of their aquatic environment.

Hydrogen ion concentration (pH) is also an important parameter of microbial viability. Also, because of the importance of pH in the solubility relationships of enzymes, pH can effect the presence of essential nutrients in solution, thereby having a profound influence on metabolic rates and processes, not to mention the half-cell reactions.

The chief chemical species engaged in these redox reactions in the aquatic system are the metallic species Fe, Mn, and the compounds of C, N, O and S. An increase in ORP may indicate one of a number of metabolic processes, such as the oxidation of NH_3 to NO_2^- or NO_3^- (nitrification), the oxidation of sulfides to sulfites (or to $SO_4^=$) and/or photosynthetic reactions. Conversely, reductive processes such as the conversion of ferric to ferrous ion ($Fe^{+3} \rightarrow Fe^{+2}$), nitrate to nitrite ($NO_3^- \rightarrow NO_2^-$), and/or of sulfate to its lower oxidation states ($SO_4^= \rightarrow SO_3^=$, etc.), will reduce the ORP value, E_H.

Edox (oxidation) reactions furnish the energy required for bacterial syntheses in bio-systems. The *reducing* power needed for photosynthetic assimilation of CO_2, and the means of obtaining and utilizing energy in cyclic processes are provided by coupled *redox* systems.

The micro-fauna and flora of greatest significance in the ecocycles of natural waters are probably the iron-bacteria, the sulfate reducing and so-called *thio-bacteria*, and certain algae, with the photosynthetic (*green* and *purple*) bacteria, nitrifying (and de-nitrifying -- i.e., reducing) species playing relatively secondary roles. The interrelationships of these organisms are illustrated in Fig. 17 and discussed in Ref. 58.

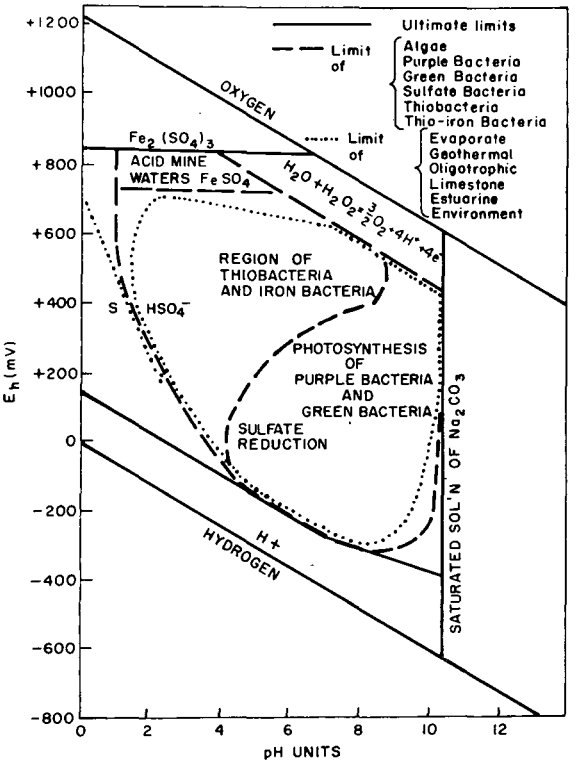


Figure 17. E_H-pH limits of the natural environments (Ref. 58).

5.1.5 Heterogeneity of Ecosystems and E_H

Measurements of different locations in an ecosystem reveal its heterogenous and dynamic aspects. E_H measurements vary with depth and with the nature of flora, lithos, etc. Fillos (Ref. 33, p. 1486) recorded variations in E_H in benthic muds. The dynamics of microbiological processes in estuarine bottom muds, as evidenced by variation in E_H, is also discussed by Wood (Ref. 58).

The reduction of $SO_4^=$ in sea water occurs at ∿-100 mV in the presence of an adequate supply of decomposed organic matter. Thereafter the E_H may be reduced to ∿ -350 mV by further reduction of $SO_4^=$ and/or extensive anaerobic digestive processes. Such a decrease in E_H may delimit the organisms which survive, favoring those groups which flourish at the lower potential. The value of E_H is believed by Wood to be influenced by respiration on the positive side and by organic reducing systems on the negative side.

Thus, by the examination of E_H data from an aquatic ecosystem some indications of existing overall environmental conditions may be obtained.

5.1.6 The Future of ORP in Waste Water Applications

The complexities of activated sludge systems limit the utility of ORP as a parameter in them. However, ORP measurements have been used as qualitative control indicators during anaerobic digestion (Ref. 54). To date, redox data have not been used strictly quantitatively in wastewater systems (Ref. 59) but rather as a means of detecting gross changes, such as the conversion from aerobic to anaerobic conditions in the system.

The aeration of wastewaters will usually result in reasonably constant E_H values above a DO content of ∿ 1 mg/1. Below this value, there is a marked decrease in E_H (see Fig. 18). Redox readings are therefore useful in monitoring anaerobic digestion processes, where they can be used to detect trends which may then be correlated with other parameters (Ref. 53). The potential value ranges for some sanitary engineering processes are shown in Fig. 18.

E_H has also been used successfully in monitoring cyanide and chromate oxidation (Ref. 60).

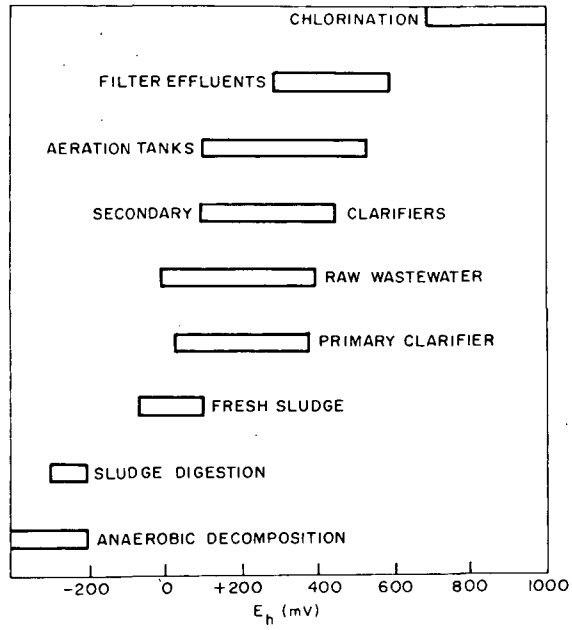


Figure 18. Potential values of some sanitary entineering processes. The E_H values are referred to the hydrogen half cell (Ref. 59).

5.1.7 Spectrophotometric Measurement of Organic Pollutants

Since many pollutants have characteristic ultraviolet (UV) absorption spectra, it is possible to use these spectra to estimate gross pollutants from industrial effluent. Bramer, Walsh, and Caruso (Ref. 61 a,b) have taken advantage of this fact in their development of a continuously monitoring UV spectrophotometer for the detection of UV-absorbers such as benzene, phenol and pyridine (10-50 µg/1). In other instances, phenolic compounds in plant effluents have been monitored by means of the bathochromic shifts* in their wavelength maxima. Similarly the composition of reaction mixtures from certain industrial processes and effluents has been determined. The latter procedure is based on the spectral characteristics of aromatics and conjugated systems (Ref. 17). Under relatively constant pollutant conditions. with

*bathochromic shift -- a shift to longer wavelength.

such UV absorbers in effluent waters it should be possible to establish at least some rule of thumb relationships between the chemical parameters of specific absorbers and their BOD, while keeping in mind the quantitative limitations to these extrapolations.

5.2 Summary: Future Trends

With the increasing demands in the management of water quality, instrumental monitoring of natural waters and industrial effluents is clearly the trend of the future. Biological parameters remain the most important indicators of water quality, but they are also the slowest to measure and the most difficult to automate. While samples collected from natural and waste waters undergo more and more sophisticated analysis, the biological methods used are often of necessity those that were in vogue more than half a century ago.

Although the crux of many current water quality investigations is biological examination, it is highly unlikely that indicator organisms, which have proven their worth as *qualitative* criteria in the monitoring of aquatic ecosystems, will soon provide us with *quantitative* data -- and it is even less likely that such methods will be readily amenable to automation. Nevertheless, it is not inconceivable that some of the control methods employed by the drug industry, for example, in the synthesis of antibiotics may ultimately be applicable to water pollution monitoring -- or for that matter, the biochemical methods developed in photosynthetic studies with radioisotope-labelled nutrients. But these are approaches of the future. For the present, identification of the biota collected in a grab sample is still a slow process and requires in addition a good deal of expertise. The number of samples which can be processed by such methods is strictly limited, as is their frequency. For this reason, there will of necessity be an increased reliance on more rapid, short term, but biologically correlated measurements. Among these, parameters such as STOD and ΔCOD, using mass culture aeration techniques and some of the more rapid respirometric methods described here and in the BOD chapter, have already shown promise and should be further developed.

Automated wet chemical methods have already proved their utility in COD and amino acid analysis, where large numbers of samples are involved. However, the dry combustion COD techniques generally have the advantage of requiring less complicated sample treatment, fewer steps, and fewer reagents.

As a rule, automated methods require a good fundamental comprehension of the chemical processes involved and the nature of the problems encountered in specific systems. They also demand a degree of technical expertise and a knowledge of electronics not usually in the arsenal of the routine analyst. Thus, these methods are best suited to larger laboratories with the economic capabilities necessary for the most effective use of these tools, as well as their continuous maintenance in good working order.

Biochemical redox systems such as DPN* and TPN* employing reactions such as the TPTZ-ATP* test also deserve further scrutiny. For a more detailed discussion of automated enzymatic analyses and the use of bio-activators and inhibitors, see Ciaccio et al., Vol. 4 in Ref. 33, Chapter 27, pp. 1515-1523. Finally, the wealth of expertise developed in the antibiotics industry and in photosynthesis studies may well furnish us with some valuable approaches in the future.

*DPN: diphosphopyridine nucleotide
*TPN: triphosphopyridine nucleotide
*TPTZ-ATP: triphenyltetrazolium chloride -- adenosine triphosphate.

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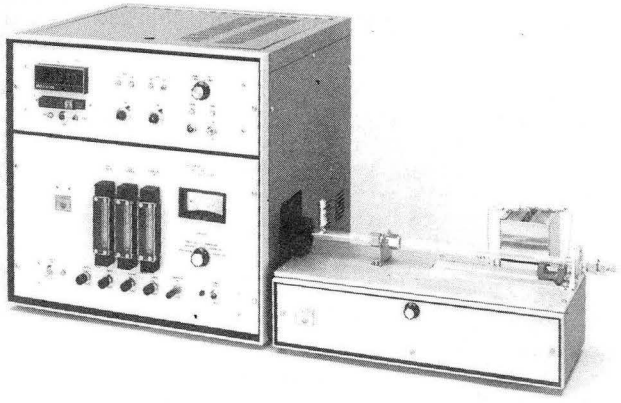
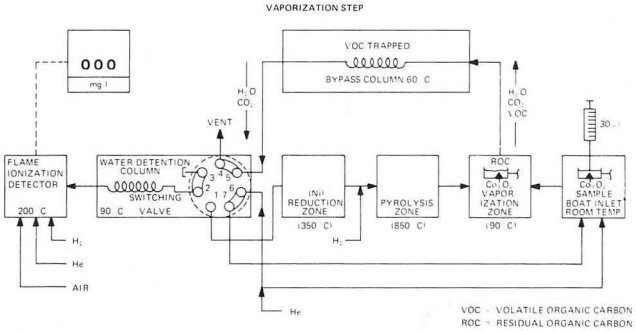
INSTRUMENTATION
FOR ENVIRONMENTAL
MONITORING

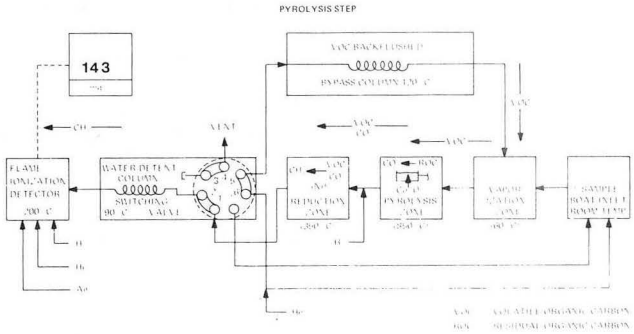
H20-BIO
Field: TOC
Dohrmann 1
June 1975

Total Organic Carbon Analyzer

Dohrmann Model DC-50







Class	Laboratory/portable
Categories of Water	Fresh/Saline/Waste
Principle of Operation	Catalytic reduction of carbon allows materials to methane which is measured by flame ionization detection (FID)
Sensitivity	1 ppm
Range	1 to 2000 ppm; (± 1 ppm ± 2%)
Interferences	Appreciable interferences from: no specific interference Moderate interferences from: Slight or no interferences from:

Multi-Parameter Capability	Also determines total carbon (organic + inorganic) and inorganic carbon (by difference, i.e., TC - TOC)
Sampling	Method: Batch, via calibrated syringe Volume: 30 ul homogeneous water sample (acidified) Collection efficiency: At least 99% with homogeneous sample Sampling module: An inert (Pt) boat charged with oxidant. An interchangeable ball joint connector provides rapid sampler-analyzer couplings.
Performance	Accuracy: Reproducibility: ±1mg/l or 2% whichever is greater Linearity: Equal or better than reproducibility Analysis time: 5 min/sample Drift: Zero drift correction
Operation	Over-all temperature characteristics: Spec: 4.5-35° C (40-95° F) Relative humidity: to 95% Sample processing: Multi-step, operator attended Calibration: Operator-performed using standard solution Procedure: For TOC a 30 ul acidified water sample is injected into a sample boat containing a cobalt oxide oxidizer at R.T. The boat is advanced to the 90° C vaporization zone whence H20, CO_2 and volatile organics (VOC) are swept into the bypass column. Here VOC is trapped on a Porapak Q column maintained at 60° C, while H20 and CO_2 are swept through the switching valve and vented to the atmosphere. After sample vaporization, the valve is automatically switched to the pyrolyzer position and the boat advanced to the pyrolysis zone. Residual organics (ROC) react with the catalyst at 850° C, producing CO_2. The bypass column is simultaneously backflushed at 120° C, sweeping VOC through the pyrolysis zone. Both VOC and CO_2 from the ROC are swept by HO into the H_2-enriched reduction zone over the Ni catalyst. Here all the carbon is converted to CH_4 at 350 °C. The reduction product is swept through the switching valve and water retention column into the FID which responds linearly to CH_4. The detector output is integrated and displayed on a digital meter in mg/l or ppm. For TC, the function switch is set to TOTAL CARBON and the sample is put through the vaporization and pyrolysis steps without prior acidification. With the switching valve remaining in the pyrolyze position, all carbonaceous material is directed to the detector. Maintenance: MnO_2 oxidant replaced daily; Ni catalyst on alumina support replaced periodically (6 mos. to 1 year estimated) depending on use. FID cap assembly, which holds all electrodes, is removable from outside the detector for maintenance. Data display: Digital, 0 to 1999 Outputs: Digital, binary coded; analog, ca. 1 mV/10 ppm (30 µl sample)
Requirements	Power: 12 A at 115 VAC, 50/60 Hz Water: Moderate flow via 1/4" connectors Hydrogen: 70 cc/min (prepurified) @ 20 psig Helium: 175 cc/min (prepurified) @ 20 psig Air: 300 cc/min (prepurified) @ 20 psig Size: 48.2 cm H, 73.5 cm W, 43.1 cm D (19" X 29" X 17") Weight: 43 Kg (95 lbs) net 57.5 Kg (115 lbs) shipping
Features	Contains four temperature-controlled ovens (±0.5° C); the two furnace sections are Triac-controlled and capable of continuous operation at 1000° C. High temperature sections are water-cooled. Detector: 3 section, stainless steel, with sapphire insulated collector electrode. Leakage $<10^{-16}$ A up to 500° C. Reduction catalyst: Ni on activated alumina.

Output: Digital - BCD, 1248 Positive True
Analog - Approx. 1 mV per 10 mg/l from a 30 µl sample
Training: See under Remarks
Options:

PART NO.	DESCRIPTION	PRICE
	DC-50 TOTAL ORGANIC CARBON ANALYZER	
832050	115 VAC, 50/60 Hz	$7875.00
832051	230 VAC, 50/60 Hz	7990.00
	DC-50 TOC ANALYZER WITH THE ABI-1	
832052	115 VAC, 50/60 Hz	8665.00
832053	230 VAC, 50/60 Hz	8780.00
526020	AUTOMATIC BOAT INLET	1420.00
899818	ABI Retrofit Kit (for DC-50 units with Serial Number 8269 and below)	260.00

References

a) Manufacturer's bulletin no. SM-674-072750
b) Y. Takahashi, R. T. Moore, and R. J. Joyce, "Direct Determination of Organic Carbon in Water by Reductive Pyrolysis" Am. Laboratory 4 (7), pp 31-38 (1972).

Cost

$7875.00 (Sept 1974)

Remarks

Analyzer price includes start-up assistance and operator training.
Manufacturer claims the following useful features:
1) Freedom from sample handling in cases of high salt and silt.
2) Volatile organics data can be monitored separately from Total C.

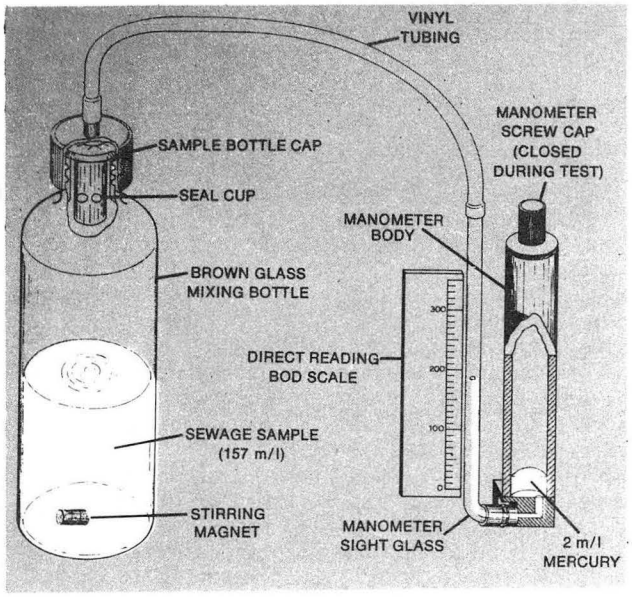
Address

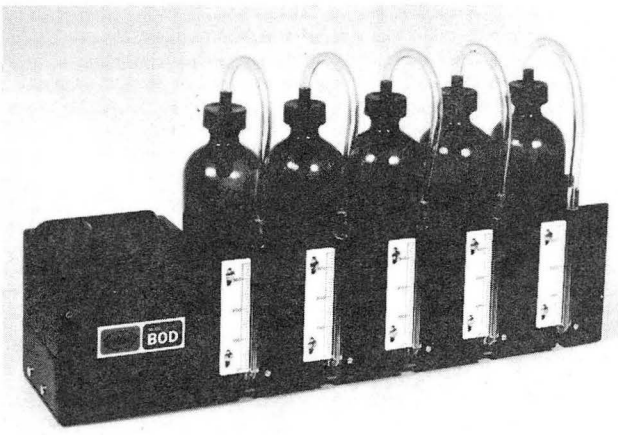
Dohrmann Division
Envirotech Corporation
3240 Scott Boulevard
Santa Clara, California 95050
Attn: Robert J. Joyce, Product Manager or John McCutchen, In-House Sales Mgr.
(408) 249-6000 Cable DOHRMANN

INSTRUMENTATION
FOR ENVIRONMENTAL
MONITORING

H2O-BIO
Field: BOD
Hach 1
Sept. 1975

Biochemical Oxygen Demand
Hach Model 2173 BOD Apparatus





Class	Batch
Categories of Water	Sewage/wastewater
Principle of Operation	A measured sample of sewage or wastewater is placed in one of the bottles (Step 1) and connected to a closed-end Hg manometer. Above the sample is air containing 21% oxygen. Bacteria present in the sample utilize dissolved oxygen for their oxidation of organic matter, thereby depleting the sample of its oxygen. The deficient oxygen is replaced by dissolution of oxygen from the supernatent air, resulting in an air pressure drop over the liquid. This registers on the manometer whence it may be read directly as mg/1 BOD.
Minimum Detectable Sensitivity	∿2 mg/1 on 0-30 range; ∿20 mg/1 on expanded scale
Range	May be selected by varying sample volumes: from 0-35 mg/1 to 0-350 mg/1 BOD
Interferences	Toxic metals, extremes of pH: sample is buffered to pH 7.2 (optional pH range, 6.5-7.5)
Multiparameter Capability	N/A
Sampling	Method: Batch Volume: 157 ml sample in 1 pt. reaction bottle Maximum Temperature Input: 20°C or 35°C Collection Efficiency: N/A Maximum Number of Sample Sources: 5

Performance

Accuracy: ±5%
Reproducibility:
Linearity:
Noise:
Lag Time: N/A
Rise Time: N/A
Retention Time: N/A
Fall Time: N/A
Zero Drift: N/A
Span Drift: N/A

Operation

Ambient Temperature Range: 20°C ±1° (18°F) maintained during test, either in an incubator or by use of a refrigerator unit converted with a Hack "Incutrol/2" conversion unit.
Temperature Compensation: N/A
Relative Humidity Range: up to 100%
Calibration: Calibrated against standard glucose solution
Procedure: After the system containing the sewage or wastewater sample is sealed, it is agitated continually during the test period (usually 5 days) by means of a magnetic stirrer. The stirrer is rotated via a pulley system connected to an external motor. The CO_2 formed during the metabolic process is removed by absorption in 45% KOH solution placed in a seal cup in the neck of the bottle.

The procedure consists of the following steps: 1) a measured sample is added to the bottle; 2) the magnetic stirring bar and seal cup containing KOH are inserted; 3) the bottle is capped lightly and stirring begun; 4) when temperature equilibrium is attained, manometer and bottle caps are tightened to seal the system; 5) the direct reading scale is zeroed and the test begun.

Unattended Period:
Maintenance: Minimal: designed sturdily, with few moving parts. Manufacturer predicts many years of trouble-free operation

Requirements

Power: 115 Vac, ∿60 W; Incutrol/2: Heating element, 300 W max
Fan, ca. 30 W (continuous load)
Weight: Shipping wt, 6.8 kg (15 lb); Incutrol: 3.18 kg (7 lbs)
Dimensions: 5.25 x 27.9 x 11.1 cm

Features

Output: Direct reading manometer calibrated in mg/l
Training: Minimal
Options: Model 2173 Hach BOD Apparatus; 230 V/59 Hz $250.
Model 2597 Incutrol, 115V or 220 V $165.

References

Hach Brochure, "For Wastewater...Simplified BOD Test
H. Raymond Tool, "Manometric Measurement of the Biochemical Oxygen Demand," Water and Sewage Works, 114 (6) 211 (1967) (Repr. 18 pp)
P.L. D'Alessandro & W.G. Characklis, Water and Sewage Works, 119 (9), 106 (1972) (Repr. 2 pp)

Cost

Hach Model 2173 BOD apparatus, complete $250.
Includes: rack, 5 sample bottles, mercury, seal caps, magnetic stirring bars and all required fittings

Remarks

BOD samples incubated at 35°C for 2-1/2 days give analyses comparable with those obtained in the standard (20°C) 5-day BOD test.

Address

Main Office:
Hach Chemical Co.
P.O. Box 907
Ames, IA 50010
(515) 232-2533
Attn: General Sales

West Coast Office:
Hach Chemical Co.
P.O. Box 477
Laguna Beach, CA
(714) 494-7421
Attn: Grant Wetzel, Manager West Coast Sales Office

INSTRUMENTATION
FOR ENVIRONMENTAL
MONITORING

Biochemical Oxygen Demand

Oceanography International, E/BOD Respirometer

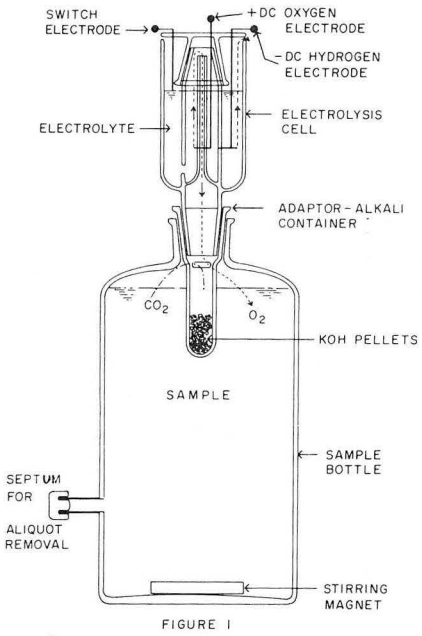
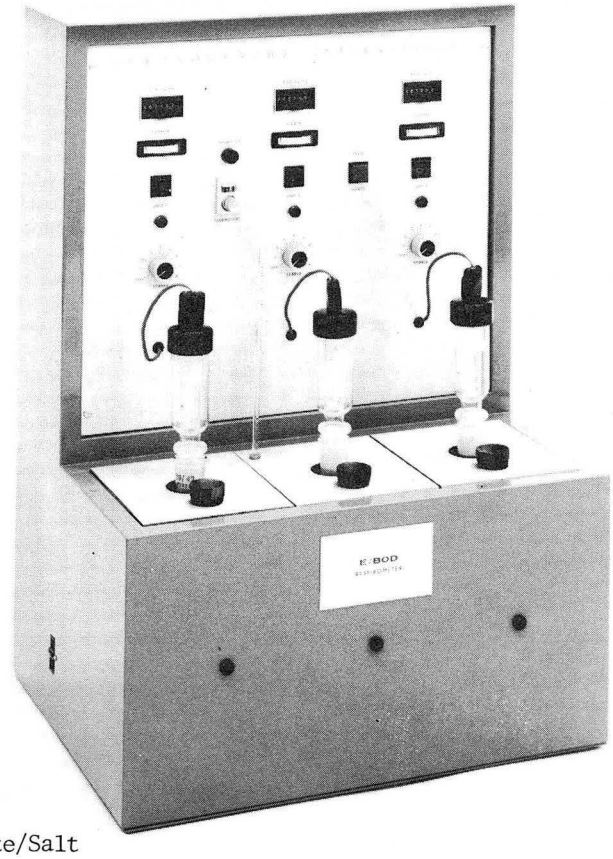


FIGURE I

SCHEMATIC DIAGRAM SHOWING THE BASIC OPERATION OF THE ELECTROLYSIS SYSTEM FOR MEASURING BOD



Class	Batch
Categories of Water	Municipal/Industrial/Waste/Salt
Principle of Operation	Automatically measures BOD by electrolysis. The system contains a reaction chamber, an electrolysis cell, an incubator (proportionately controlled) and a measuring unit. The reaction chamber is a 1.25 l vessel provided with a top-mounted electronic oxygen generator, a stirring bar, and a manometric switch. As oxygen is used up biologically or chemically, any CO_2 produced in the process is absorbed by KOH pellets present in the vessel, producing a slight vacuum in the air space. This triggers the manometric switch and electrolytic oxygen is produced to replace the O_2 consumed. Oxygen generated by electrolysis may be related to the current applied and the time during which O_2 is being generated via Faraday's Law. The cell electrolyte employed is 2N H_2SO_4. Electrolysis (i.e., passage of direct current) results in the generation of O_2 gas at the anode and H_2 gas at the cathode.
Minimum Detectable Sensitivity	0.5 mg O_2
Range	Maximum O_2 Production: 60 mg/hr Stirrer: 50-1700 rpm Incubator: ±15°C from ambient Counter: 9999.9 mg in mg and 1/10 mg

Interferences	Changes in barometric pressure; long lag periods due to toxicity or lack of acclimated organisms. Manufacturer provides pressure correction equation and recommends the use of acclimated seed and the exclusion of toxic materials whenever feasible.
Multiparameter Capability	N/A
Sampling	Method: Discrete sample Volume: 1 liter ±.05 Maximum Temperature Input: 35°C Collection Efficiency: N/A Maximum Number of Sample Sources: N/A
Performance	Accuracy: Depends on sample, within ca. 5-8% of standard methods Reproducibility: 1-2%; sewage samples ∿4-7% Linearity: N/A Noise: N/A Lag Time: 12 sec Rise Time: 12 sec Retention Time: N/A Fall Time: N/A Zero Drift: ±1 mg/5 days Span Drift: ±1 mg/5 days
Operation	Ambient Temperature Range: 20°C or 35°C Temperature Compensation: Incubation and temperature control at 20°C and 35°C is provided Relative Humidity Range: Calibration: Reference standard is a known quantity of Na_2SO_3 which reacts in the presence of $CoCl_2$ catalyst, consuming a stoichiometric amount of O_2. The reaction rate is controlled by limiting the stirring rate, which in turn limits the rate of oxygen transfer. The electrolytic O_2 generator is prepared as described in the manual, except that KOH absorption pellets are omitted. One liter of H_2O is allowed to come to temperature and D.O. equilibrium in the generator, 1 ml of $CoCl_2$ solution and 1 g Na_2SO_3 crystals are added and the generator re-sealed. O_2 is monitored for 3-4 hrs. Cumulative oxygen should attain a value of 126.4, ±2 mg O_2 and uptake should then cease. The system is allowed to run for a short time beyond the endpoint to insure complete reaction. Procedure: A 1 liter sample is allowed to react in an air-tight chamber at constant temperature, with complete mixing. As chemical or bio-oxidation proceeds, the partial vacuum created in the reactor is compensated by the electrolytic production of O_2 in the oxygen generator to replace oxygen consumed. Cumulative oxygen demand may be read directly from counters at any time during the test period. Unattended Period: May be run unattended "for long periods." Maintenance: Occasional cleaning of glassware.
Requirements	Power: 115 Vac, 60 Hz single phase (220 V, 50 Hz optional) Instrument electronics Supply: Electrolysis cell: 20 Vac, 200 ma Incubator: 200 watts Magnetic Stirrer: 115 Vac, 60c, 0.5 amp Counter: 20 VdC Weight: 39.5 kg (87 lbs) Dimensions: Case: 76.2 x 55.9 x 41.9 cm (30" x 22" x 16.5") Glass Reaction Chamber: 27.4 cm H x 9.5 cm ID (8.8" H x 3.7" ID) Sample Port: 1/4" glass tubing; std 29/42 ground glass joint

Features

Output: Connector to optional printer only
Training: Operator training by factory representative optional
Options:

206EP Printout, monitors and cumulative O.D.for 15 or 60 minute intervals. Simultaneous 3-cell OD (to 0.1 mg O_2).	$1,675.
Standard Printout for 3 or 6 cells, Option to 15 cells.	
206S/B Sludge/Benthic O_2 Uptake Accessory	$ 620.
206SBT Silicone Rubber Tubing (per foot)	$ 3.07
2004K Accessory Kit	$ 33.90

Contains:
- 2 ea. BD 2431B, 5 ml syringe
- 2 ea. BD1100, 17 gauge 2" needle
- 2 ea. BD 1108, 15 gauge 3-1/2" needle
- 1 ea. 2 oz. tube stopcock grease
- 1 ea. packet 1/4 lb. KOH pellets
- 20 ea. special septums
- 1 ea. interstice filler bottle
- 1 ea. rack for electrolysis cell

Also Available:

6-206	6-Sample Capacity E/BOD Respirometer	$ 5,350.
9-206	9-Sample Capacity E/BOD Respirometer	$ 7,590.
12-206	12-Sample Capacity E/BOD Respirometer	$ 9,610.
15-206	15-Sample Capacity E/BOD Respirometer	$12,220.

References

1) Manufacturer's Brochure: "The E/BOD Respirometer System."
2) "A Proposed Standard Method Test for Oxygen Demand Determination by Electrolysis in Wastewater," 12 pp., incl. 11 refs. (typewritten booklet provided by the manufacturer.)
3) J.C. Young and J.W. Clark, "Growth of Mixed Bacterial Populations at 20°C and 35°C," *Water and Sewage Works*, 112 (7), pp 251-5 (1965).

Cost

3-Sample Capacity E/BOD Respirometer $2,820.
Includes stirrers, incubator and electronic counters.

Remarks

The reactor is provided with a septum for removal of aliquots with a syringe for the measurement of other parameters. Incubation and temperature control at 20°C and 35°C are provided (according to Young and Clark, a 2-1/2 day BOD at 35° is equivalent to the 5-day BOD at 20°C, within experimental limits).

Address

Oceanography International Corporation
512 West Loop
P.O. Box 2980
College Station, Texas
(713) 693-1711 TWX: 510 - 892 - 7944
Attn: Alan D. Fredericks, Chief Chemist and Vice President, or
Rogers M. Hall, District Sales Rep. Tel: 846-3729, or
Ms. Jane Theis, Secretary to the President

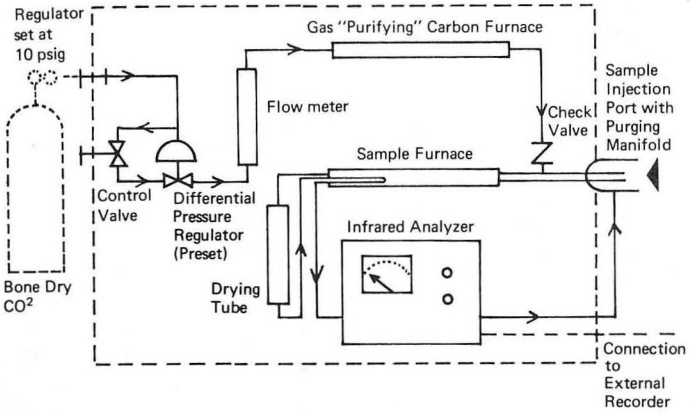
INSTRUMENTATION
FOR ENVIRONMENTAL
MONITORING

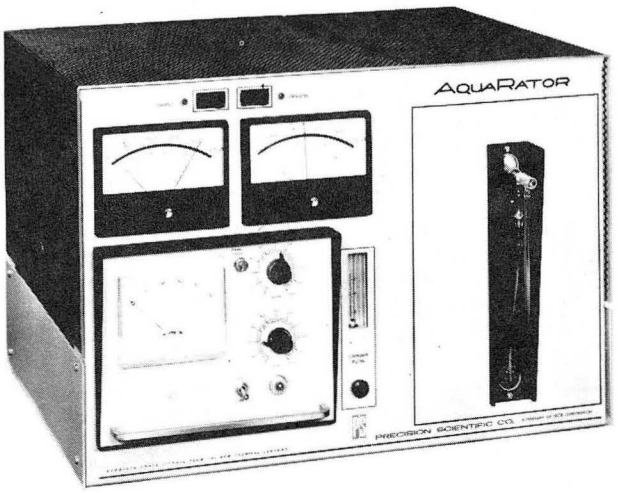
H2O-BIO
Field: COD
Precision Scientific
Sept. 1975

Chemical Oxygen Demand Analyzer

Precision AquaRator

FLOW DIAGRAM





Class	Laboratory/mobile lab
Categories of Water	Waste
Principle of Operation	Combustion of an organic substance in an O_2 and CO_2 atmosphere, respectively, may be expressed by the following equations:

(1) $C_aH_bN_cO_d + (n/2)O_2 \rightarrow aCO_2 + (b/2)H_2O + (c/2)N_2$

(2) $C_aH_bN_cO_d + mCO_2 \rightarrow (m + a)CO + (b/2)H_2O + (c/2)N_2$

The theoretical ultimate COD of the sample is given by the exact quantity of O_2 required to effect complete oxidation of the compound to CO_2 and H_2O. Dichromate oxidation approaches this theoretical value, but the variation in sensitivity of organics to oxidation under the vigorous conditions used by the AquaRator results in values somewhat less than theoretical. Since it has been demonstrated [Stenger and VanHall, Anal. Chem. 39, 206 (1967); Moore, Kroner, and Ruchhoft, *Ibid.* 21, 953 (1949)] that the number of moles of CO formed is equivalent to OD, it is possible to relate COD directly to CO readings.

Minimum Detectable Sensitivity	10 mg/ℓ
Range	10 to 300 mg/ℓ
Interferences	Nitrates, phosphates, sulfates
Multiparameter Capability	None
Sampling	Method: Discrete; via microsyringe Volume: 20 µl Maximum Temperature Input: Not applicable Collection Efficiency: Not applicable Maximum Number of Sample Sources: No restriction

Performance

Accuracy: ±1% full scale
Reproducibility: ±3%
Linearity: Nearly linear
Noise: < 1% full scale
Lag Time: Approximately 50 sec
Rise Time: IR analyzer, 90% of final reading in 5 seconds
Retention Time: 2 minutes
Fall Time: Approximately 55 sec
Zero Drift: Not determined
Span Drift: Not determined

Operation

Ambient Temperature Range: Not determined
Temperature Compensation: None
Relative Humidity Range: Not determined
Calibration: Usually effected by injection of standard solutions of $NaOOCCH_3 \cdot 3H_2O$, for which OD in mg/ℓ may be calculated. A plot of OD vs. recorder output as shown on a strip chart is used to determine OD for the sample.
Procedure: A 20 µl water sample, homogenized if solids are present, is injected into the AquaRator by means of a micro-syringe. The sample is then swept through a catalytic combustion furnace (Pt cat.) by a stream of dry CO_2, oxidizing organic pollutants to CO and H_2O. Water is then removed in a drying tube and the reaction mixture subjected to a second pass catalytic oxidation. [CO] is measured by means of an NDIR analyzer sensitized for CO, and the resultant CO reading is directly converted to COD by means of the calibration chart. Gas flow (CO_2) is set at ~130 ml/min. Any oxygen impurity is removed by reduction in a carbon furnace, yielding a mixture of CO and CO_2 which provides the normal baseline of the recorder.
Unattended Period: Variable, up to 90%
Maintenance: Designed for continuous duty

Requirements

Power: 120 V, 60 Hz or 120 V, 50 Hz. Power consumption 1500 W.
Weight: 41 kg (90 lb); shipping weight 79.5 kg (175 lb)
Dimensions: 61 x 56 x 40.6 cm (24 x 22 x 16 in.)

Features

Output: 0-100 mV
Training: None
Options: Cat. No. 62971 - Stepdown Transformer
240/120 V, 50 or 60 Hz, 2000 W

References

1) V.A. Stenger and C.E. VanHall, "Rapid Method for Determination of Oxygen Demand", Anal. Chem. 39, 206 (1967).
2) Manufacturer's brochure "AquaRator"
3) Manufacturer's letter of May 1974

Cost

Cat. No. 68900 (120 V, 60 Hz)	$8250
Cat. No. 68901 (120 V, 50 Hz)	8250
Cat. No. 62971 (Stepdown Transformer)	134.40

Remarks

Standard equipment includes special sample syringe, extra charcoal, Drierite, and instruction manual.

Not included:
1) AquaRator grade CO_2, cylinder size 1A
2) Two-stage CO_2 regulator, 5-50 psig delivery pressure
3) Tygon tubing for cylinder supply line R3603, 3/16" ID, 3/32" wall
4) Potentiometric recorder, 0-100 mV range with input impedance of $\geqslant$ 5000 Ω; chart speed, 0.2"/min; pen speed 1 to 2 seconds

May be operated on 240 V with suitable transformer.

Address

GCA/Precision Scientific
3737 W. Cortland St.
Chicago, IL 60647
Attn: Dr. Jim Tison
(312) 227-2660