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Publication Date

1974-09-01

Submitted to Environmental Science
and Technology

LBL-3204
Preprint c.1

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September 3, 1974

Prepared for the U. S. Atomic Energy Commission
under Contract W-7405-ENG-48

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Instrumentation for Water Quality Measurements*

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The dangers of polluted water have been recognized for at least as long as recorded history. Contaminated water has been known to be responsible for countless deaths. For example, catastrophic epidemics of such diseases as cholera and typhoid were traceable to water. There have in the past been isolated attempts to solve the problem of obtaining good water. As early as the third century B.C.E. Hippocrates (460 to 354 B.C.E.) stated that "water contributed much to health" and went on to assert that rain water should be boiled and strained because otherwise it would have a bad smell and cause hoarseness. In ancient times much effort was spent in building aqueducts, cisterns and reservoirs to provide water for cities and towns, but little was done towards controlling the purity of this water. Certain brief references were made to boiling, filtering, sedimentation and treatment of water with salts, however no definite standards of quality other than clarity and patatability were recorded. This was partly due to a lack of knowledge of the problem and to a poor understanding of a systems approach in solving large

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*This work was funded under Grant AG-271 from Research Applied to National Needs, National Science Foundation, and performed in facilities provided by the U.S. Atomic Energy Commission.

scale problems; however this was also due to the lack of availability of instrumentation to quantitatively measure water quality. It is this instrumental aspect of the problem which is the subject of this report.

On October 21, 1914, the U.S. Treasury Department accepted the recommendation of the Surgeon General of the Public Health Service, and adopted the first U.S. standards for drinking water. These standards specified the maximum permissible limits of bacterial impurity, and the recommended procedures for their measurement. Since 1914, water drinking standards have been revised four times, and the EPA is expected to issue new standards shortly. Currently, the latest set of standards are those promulgated in 1962, with the tentative addition of mercury to the list of toxic constituents which must be monitored in 1970. In 1969, the American Water Works Association recommended changes and additions to Public Health Drinking Water Standards to include maximum permissible concentrations of boron, uranyl ion, and pesticides. On September 7, 1973, the EPA published a list of toxic pollutants for which effluent discharge standards will be established. Techniques for water quality monitoring must be developed to take into account both standards. The following briefly describes both standards as they apply to metals, nutrients (nitrogen and phosphorus), pesticides and oxygen demand (biochemical oxygen demand, chemical oxygen demand, total organic carbon).

The need to maintain the pristine nature of the waters of the United States has resulted in laws which require measurements of an increasing number of water quality parameters and with increasing number of samples. Besides this growth in the number of measurements required is added the burden of identifying and quantitatively determining concentrations of water constituents named as harmful or potentially harmful at low levels. The recent developments in laboratory and field instrumentation are making possible this combined need for increased work load and higher sensitivity.

Early water analysis was performed either at the field site, or in the laboratory on samples gathered from the site. It was found quite early that taste, smell and visual inspection were inadequate to determine the chemical, physical and biological characteristics, and, that as a minimum, constituents or properties known or deemed harmful must be measured by wet chemical methods. The dual demands of time and care required trained personnel to perform even the most routine analysis; this has resulted in an increasing need for instrumentation to aid in the measurements. The results have taken several forms. In some cases an electrically accuated array of pumps and tubing still performs the wet-chemical analysis, albeit automatically. The Technicon AutoAnalyzer is an example of this direction of development. In other cases sensors or transducers respond to specific physical or chemical parameters converting intensities into electrical signals; these signals are in turn processed and converted to readings using convenient units of measurement. The atomic absorption spectrophotometer is an example of this type of instrument.

In the future, instruments will approach the characteristics of an "ideal" water analyzer. The ideal water monitoring instrument would perform automatic measurements of specific parameters without interference from other parameters at the existing ambient concentration level; analysis would be rapid, accurate and economical. Obviously much remains to be done before we achieve this goal for all parameters of interest.

Water Standards and Criteria

Historically, the quality of water intended for various uses (e.g., beverages, or paper manufacturing) is specified in terms of the concentrations of contaminants which are permissible, or constitute grounds for rejection of a particular water supply.

Standards for discharges of industrial wastes actually pre-date those for drinking water, and are contained in the Refuse Act of 1899. However, this Act was not rigidly enforced until about 1970 when the U.S. Army Corps of Engineers, and, subsequently, the EPA required industrial discharge permits. "Toxic Pollutant Effluent Standards" were published in the Federal Register on September 7, 1973. The criteria used to generate this list were to protect the general welfare against materials which may result in the following: (1) reproductive impairment in any important species, or concentration in food sources in excess of applicable Federal tolerance levels; (2) materials likely to be carcinogenic, mutagenic, or teratogenic to man; (3) substances with a high order of toxicity as measured by short-term lethality tests. The current list includes the metals Cd and Hg, cyanide, and pesticides.

The discussion and tables of instrumentation which follow will center around the important water quality parameters which are listed in the current U.S. Public Health Drinking Water Standards, and the EPA lists of pollutants in effluent discharges. Instrumentation covered will be confined to presently employed methods such as those given in Standard Methods for the Examination of Water and Wastewater, 13th Edition and the EPA Methods for Chemical Analysis of Water and Wastes, and to certain other instruments being developed.

Instrumentation

The techniques which are discussed below form the basis of current commercial or developing techniques for measuring four major categories of water pollutants: (1) metals, (2) nutrients, (3) pesticides, and (4) oxygen demand. The discussion is not exhaustive, but rather gives a general picture of the instrumentation which is available. More complete information on current instrumentation and principles of operation may be found in the references.

Instruments for water quality measurements can be classified in a number of ways. It is convenient to separate them as follows: (1) manually operated laboratory analyzers, (2) automated laboratory instrumentation,

(3) manual field monitors; and (4) automatic field monitors. Laboratory manual analyzers as the name implies, must be operated in the laboratory owing to the constraint of operator intervention, operational environment, fragility or high maintenance requirements. Automatic laboratory instruments do not require human intervention other than to provide samples, maintain calibration and interpret the data. Manual field monitors are portable, and contain any power source that may be required. Such instruments are more rugged than manually operated laboratory instruments, and include the reagents necessary for any chemical reactions. Automated field monitors measure the pollutant without human assistance or intervention on an uninterrupted basis under field conditions. Sampling and calibration are performed automatically, and human intervention is required only for data interpretation and to ascertain the integrity of the data collected. Table 1 lists these four classes of instrumental techniques generally used for measuring metals, nutrients, pesticides and oxygen demand 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. The EPA has found that automated instruments such as the Technicon AutoAnalyzer permit up to 75 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 (e.g., unexpectedly high concentration) sample condition. The set-up 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.

Water Quality Measuring Systems

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 worse than no data at all!

Water quality measuring systems can be classified for use in either fresh, waste or saline waters. Fresh water 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. Waste water monitoring systems are those suitable for analyzing the discharges from point sources such as industrial or municipal effluents. They may require, for example, filtration of the sample to remove floating particles and other debris which 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 and 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 will permit assessment of mass concentration, mass flow and water composition.

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 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.

Rather than listing all of the laboratory manual instruments which might be employed to analyze for metals, nutrients, pesticides, and oxygen demand in water, we have limited our discussion to the most widely employed techniques in water quality monitoring. Commercially available instruments will be discussed for the following methodology: (1) atomic absorption spectrophotometry, (2) ultra-violet and visible absorption spectrophotometri (colorimetry), (3) emission spectrometry, (4) gas chromatography, (5) gas membrane electrodes (e.g., NH_3, O_2), and (6) chemical oxidizers (e.g., chemical oxygen demand, total organic carbon).

Atomic Absorption Spectrophotometry

Flame atomic absorption spectrophotometry is a convenient and reliable means for measuring the metal content of water samples. Basically, monochromatic light is generated with a spectral content characteristic of the metal being analyzed. On passing through a flame containing atoms of the metal the light is absorbed and the diminution in intensity recorded by a data handling system. The attenuation in light intensity due to absorption by the metal atoms in the flame, corrected for background effects, is related to the metal concentration in the water sample by calibration data. In cases where the metal content is below the instrumental sensitivity, a pre-measurement concentration step is required. For example, the contaminant can be extracted into a water-imiscible solvent of smaller volume than the sample, and the solvent layer containing the metal then aspirated into the flame.

Besides the flame method, atomizing the metal for absorption photometry by hot or cold flameless atomization methods appears promising. In the hot atomization method microliter aliquots of the water sample are pipetted into a carbon, graphite or tantalum ribbon furnace. The sample is sequentially dried, ashed (if necessary) and heated to incandescence to atomize the metal. The hot atomization method is more sensitive than the flame for many metals and may have potential applications for specific problems encountered in water analysis, but its usefulness for routine practical analysis of water of varied composition -- especially by laboratories engaged in the analysis of large numbers of samples -- is limited. Attenuation of light intensity can be caused by scattering due to smoke or salt particles produced during the heating steps thereby requiring additional means for compensation (e.g., H_2, D_2 lamps). The cold vapor atomization method is used in the analysis of mercury; Hg is generated by chemical reduction using, e.g., stannous ion, and subsequently is swept out by an air stream into the optical cell for measurement. This is by far the most widely used method for Hg because of its sensitivity and accuracy at the μg/l levels normally encountered in Hg determinations. See Table 2 for typical commercially available laboratory atomic absorption spectrophotometers.

Ultraviolet-Visible Absorption Spectrophotometry (Colorimetry)

Colorimetric methods generally involve forming a colored species by means of chemical reactions between a reagent and the metal or nutrient 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 due to absorption is corrected for background effects and related to concentration in the water sample through calibration data. Optimum results 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 solvent extraction techniques which often involve more than one extraction are commonly used. Sensitivity is obtained by extracting the metal from a large volume of sample into a smaller volume of organic solvent. Extraction techniques involve use of laboratory glassware and several reagents, which can introduce contamination and cause sample losses. To minimize sample loss or contamination by handling, all glassware must be scrupulously clean, and all reagents must be of high purity.

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. Table 3 lists representative commercial instrumentation.

Emission Spectrometry

Elements emit light with characteristic wavelengths when their outer electrons return to the ground state from a higher excited state. The outer electrons of metals are more easily excited than nonmetals, so that emission spectroscopy is most commonly applied to the analysis of metals and metal salts. Certain nonmetals such as silicon, phosphorus, and carbon also give measurable emission. Quantitatively, the intensity of emission at characteristic wavelengths is proportional to the amount of the respective element within a specified concentration range. The intensity may be measured using a densitometer to compare line blackenings on a photographic plate, or by direct-reading photoelectric devices. The intensity of emission is related to concentration by comparing sample and calibration data. Emission spectrometers thus consist of an excitation source, a monochromator using a grating and/or prism, and a photographic film or phototube detector.

Trace metals in fresh waters are generally present in concentrations too low to be measured directly using conventional emission spectroscopy. Thus, pre-measurement concentration techniques (e.g., evaporation) are required. Plasma excitation gas discharge sources can overcome the lack of sensitivity of conventional emission spectroscopy.

Gas discharge light sources can be made which are much brighter in the desired portions of the spectrum than are the more conventional emission sources, thereby greatly increasing the sensitivity of the system. These sources usually take the form of a radiofrequency excited gaseous plasma (i.e., a discharge with balanced positive and negative charges). Better efficiency and control of the discharge can be obtained if the plasma is formed in the presence of a magnetic field.

An induction coil is used in the Applied Physics Laboratory instrument to excite an electrodeless plasma discharge. A high voltage Tesla coil helps to initially break down the gas and start the discharge. The effective temperature in this type of discharge may be as high as 9000 or 10,000°K with very high probability of ionization of the gas and little or no selective volatilization. Atoms have a long residence time within the plasma, leading to a higher excitation probability and more intense readout. This high residence time accounts in part for the increased sensitivity. See Table 4 for a listing of commercially available instrumentation.

Gas Chromatography

In water quality assessments gas chromatography (GC) is used to analyze both qualitatively and quantitatively for constituents such as pesticides. The great power of this technique is the outstanding ability to separate mixtures into individual components. In principle GC physically separates a complex mixture into its components by passing the mixture through a glass column containing a stationary phase with a high-surface-to-volume ratio. The stationary phase is usually a solid support material coated with a thin liquid film. An inert carrier gas passes through the column under carefully controlled conditions transporting with it the components of the sample. Components are retained for varying lengths of time by the liquid films. The compounds emerge from the column at times related to their degree of retention by the liquid phase. For pesticide determinations, a glass column (e.g., silanized pyrex) is almost mandatory because other materials can catalyze sample decomposition within the column; this is especially true in the case of Cu tubing used for chlorinated pesticides. Besides glass tubing, another difference in pesticide monitoring is the possible use of two or more columns with different stationary phases for confirmatory identification of the pesticides.

Mass spectrometers (MS) have recently been combined with GC and the resulting instrument applied to pesticide detection. In the combined GC/MS instrument, a glass separator generally serves as the interface for the carrier gas between the outlet of the GC and the inlet to the MS. The glass separator is maintained under vacuum causing the pressure to drop from approximately 1000 torr in the GC column to about one torr in the MS inlet. In the process the pesticide concentration in the carrier is somewhat enhanced because the light molecules of the carrier gas are pumped off faster than the heavier pesticides. Pesticides separated by the GC column then pass into the ionization chamber of the MS where fragmentation occurs into ions characteristic of the pesticide. The ion fragments are accelerated into the analyzer section and resolved according to their mass/charge ratio to provide a mass spectrum which identifies the pesticide. In the Finnigan, Extranuclear and Hewlett-Packard GC/MS instruments, the mass analyzer is an electrostatic quadrupole; the DuPont and Varian instruments have electrostatic and magnetic sector analyzers; while CVC employs a time-of-flight analyzer. Table 5 lists commercially available gas chromatographs applicable to pesticide monitoring.

Gas Membrane Electrodes

In gas membrane electrode analyzers, the gas pollutant dissolved in water diffuses through a permeable membrane (e.g., Teflon) into an electrochemical cell compartment. The electrochemical cell is comprised of a sensing electrode, a reference electrode, and a supporting electrolyte such as ammonium chloride or potassium hydroxide. The semipermeable membrane serves a dual function: it separates the electrochemical cell from the water sample, and it permits 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 a current flow. 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.

The ammonia electrode is affected by other dissolved gases in the water sample if these gases change the pH of the supporting electrolyte. The gases present must diffuse through the membrane, and must 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 no longer in the gaseous form.

The Orion model 95-10 ammonia selective instrument is an example of a device using this principle. It has an operating range of 0.017 to 17,000 mg/l and an accuracy listed as 2% or better. Interferences in the operation of the electrode include volatile amines such as methyl amine or ethyl amine which diffuse thru the membrane and cause a change in the pH of the electrolyte. Also organic solvents and wetting agents may shorten the membrane electrode life. The time required for a 99% response to a change in ammonia concentration is 8 minutes. See Table 6.

All dissolved oxygen (DO) membrane electrodes include the following: (1) an electrochemical cell consisting of a metal cathode (e.g., Au, Ag, Pt) and an anode (e.g., Pb), (2) a thin layer of supporting electrolyte (e.g., 1 M KOH) in which the cathode and anode are immersed, and

(3) a thin oxygen permeable membrane such as Teflon or polyethylene which serves to separate the water sample from the electrolyte and electrodes. In operation, oxygen dissolved in the water sample diffuses through the membrane into the electrolyte, where it accepts electrons and is reduced at the cathode to peroxide or hydroxyl ions. Concomitantly, electrons are given up at the anode (e.g., by oxidation of Pb to PbO), thereby causing an electrical current to flow which is measured in the external circuit by a meter or other recording device. The magnitude of the current is a measure of the DO in the water sample. The polymeric membranes are permeable only to gases, so that other electroactive water constituents (e.g., Cu, Hg, Cd) do not interfere. See Table 6 for typical commercial DO probes.

Biochemical Oxygen Demand (BOD)

BOD is a test used to determine the oxygen requirements of the water under examination: it is an empirical bioassay test which involves measurement of the quantity of oxygen required for the biochemical oxidation of the decomposable matter (e.g., organic material) at a given temperature (20°C) within a given time (usually 5 days). The reduction in dissolved oxygen concentration after the five day incubation period is a measure of BOD. Measurements of the oxygen uptake during a BOD test may be carried out using a DO probe. The DO probe and modified Winkler are normally employed.

Total Organic Carbon (TOC)

TOC is a test used to assess the potential oxygen-demand load of organic material from waste discharges into a receiving stream. The usual test procedure involves injecting 20 μl of the wastewater sample into a catalytic combustion tube maintained at a temperature of 950°C. The water in the sample is vaporized and any carbonaceous material is oxidized to CO_2 and H_2O by reaction in a stream of air or oxygen. The air or oxygen flow carries the steam and CO_2 to a condenser where the bulk of the water is removed. The CO_2 and remaining H_2O are then passed through a nondispersive infrared analyzer which measures the CO_2 content. The CO_2 measurement is corrected for any inorganic carbon (e.g., carbonate or bicarbonate) and is then related to TOC by calibration data. The Beckman single channel analyzer is an example of this type of instrument. One method of correction for inorganic carbon is the use of a second furnace; this furnace operates at about 150°C, which suffices to liberate CO_2 from carbonates. Two signals are obtained at the analyzer, and the difference signal is a measure of the total organic carbon. The Ionics Model 1224 is an example of a dual channel analyzer.

Another principal for TOC analyzers is that illustrated by the Dohrmann Model DC-50 system. The carbonaceous material is catalytically oxidized to CO_2, and then reduced to methane with hydrogen on a nickel catalyst. The methane produced is subsequently measured using a flame ionization detector. See Table 6.

Automated Laboratory Instrumentation

Automated laboratory instruments can be classified into the following three categories: (1) central measuring analyzers with automated sampler comprised of a turntable or capsule. The Unicam SP1900 atomic absorption spectrophotometer with a Model SP450 automatic sample changer is an example of an automated turntable sampler. It has a batch capacity of 50 samples, and is capable of handling up to 250 sampler per hour. (2) Central measuring analyzers equipped with data processing units. One example is the Perkin-Elmer PEP-2 system which converts the peaks from a gas chromatograph into a record in a desired format. This system can be used as an automatic integrator. (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 can automatically perform the following functions: sampling, filtering, diluting, reagent addition, mixing, heating, digesting, color development, and measurement of the color produced. For example, the EPA includes a method of determining ammonia colorimetrically 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 Table 7 for typical laboratory automation equipment.

Manual Field Monitors

Manual field monitors are portable instruments that measure pollutants by a variety of methods, two of which are 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. The LaMotte Octet Comparator outfits are examples of the liquid-in-glass comparator measurements. Another approach to colorimetric intensity determination is that employed by the Bausch and Lomb MiniSpec 20 battery-powered spectrophotometer. This instrument measures the attenuation in light intensity due to a sample, and relates the reading to the pollutant concentration by calibration data. Table 8 lists typical currently available manual field monitors which encompass these three classes of analyzers.

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 (e.g., DO electrode) and wet chemical analyzers (e.g., Hach Model 651B silica 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.

Table 9 contains a list of currently available automated field analyzers.

Conclusion

After reviewing current instrumentation in light of the needs of water monitoring, some general observations are appropriate. While the typical currently used instrument is adequate in many respects, it still has a number of shortcomings. The optimum instrumentation system for the next generation of water analyzers should include:

A detector which is specific for the parameter of interest -- the detector should not be subject to interferences.

A monitoring system with multi-parameter capability which can be assembled from individual specific detectors. Conversely, instruments that can measure a number of parameters (e.g., gas chromatograph) is a step in this direction.

Instruments operating on physical principles are preferred to those requiring wet chemical methods.

Methods by which samples are either analyzed quickly or preserved quickly to help insure the reliability of the information; in situ monitoring being preferred. A number of water reactions are time dependent. For example, the pH may change significantly in a matter of minutes; dissolved gases may be lost or gained.

Sensitivity capable of detecting ambient levels of a contaminant is of particular importance. As the emission levels of pollutants decrease, it is necessary that the instrumentation be able to cope with these lower levels. Any steps such as enhanced sensitivity that eliminate pre-measurement concentration are welcome.

The capability of being read out both directly (e.g., for field use) and into remote data-handling facilities for point source or laboratory application.

Sampling and analysis techniques capable of handling suspended and sediment forms of constituents, as well as distinguishing individual forms of a pollutant.

Methods for accurate calibration either in the laboratory or in the field. Where possible, built-in calibration means utilizing standard solutions are particularly desirable.

Instruments that are rugged and thoroughly reliable.

Automated data handling which is properly interfaced to handle large numbers of samples, particularly when intricate calculations are required.

And finally, the price should be one that is economically defensible.

Acknowledgment

Thanks are given to George A. Morton, Lawrence Berkeley Laboratory, for his comments.

References

1. Instrumentation for Environmental Monitoring: WATER, LBL-1, Vol. 2, Technical Information Division, Lawrence Berkeley Laboratory, Berkeley, CA, 94720.

2. Standard Methods for the Examination of Water and Wastewater, 13th edition, American Public Health Association, 1015 Eighteenth St., NW, Washington, D.C., 20036 (1971).

3. Methods for Chemical Analysis of Water and Wastes, U.S. Environmental Protection Agency, Analytical Quality Control Laboratory, National Environmental Research Center, Cincinnati, OH, 45268 (1971).

4. E. Brown, M.W. Skougstad, M.J. Fishman, Methods for Collection and Analysis of Water Samples for Dissolved Minerals and Gases, Book 5, Chapter A1, U.S. Geological Survey (1970). Available from Superintendent of Documents, U.S. Government Printing Office, Washington, D.C., 20402.

5. Annual Book of ASTM Standards, Part 23, Water; Atmospheric Analysis, American Society for Testing and Materials, 1916 Race St., Philadelphia, PA 19103 (1973).

6. Guidelines Establishing Test Procedures for the Analysis of Pollutants, Federal Register, 38 (199), Page 28758, October 16, 1973.

Table 1: Typical instrumental methods for measurement of metals, nutrients, pesticides, and oxygen demand

Instrument Method	Pollutant Measured
Manual Laboratory Analyzers	
Atomic Absorption	Metals
Colorimetric	Metals; nutrients (ammonia, nitrate, nitrite, phosphate) chemical oxygen demand; total organic carbon
Emission spectrometry	Metals; phosphorous
Gas chromatography	Pesticides
Gas membrane electrodes	Dissolved oxygen; ammonia, nitrite; BOD
Ion selective electrode	Nitrate
Activation analysis	Metals; nitrogen; phosphorus
X-ray fluorescence	Metals
Gas chromatography/Mass spectrometry	Pesticides
Thin layer chromatography	Pesticides
Infrared spectrophotometry	Total organic carbon
Automated Laboratory Analyzers	
Atomic absorption	Metals
Colorimetric	Metals; nutrients
Gas chromatography	Pesticides
Manual Field Monitors	
Colorimetric	Metals; nitrite; phosphate
Electrode	DO; metals
Volumetric Titration	DO; nitrate

Table 1. Continued

Automated Field Monitors	
Atomic absorption	Hg
Colorimetric	Cr; MnO_4^-; $PO_4^{\equiv}$; Fe; Cu; NH_3; NO_3^-; NO_2^-; total phosphorus; chemical oxygen demand
Electrometric	Cu; dissolved oxygen; NH_3; NO_2^-
Flame Ionization; Infrared	Total Organic Carbon

Table 2. Representative commercially available manual laboratory analyzers for measuring metals, nutrients, pesticides, and oxygen demand.

METALS

Atomic Absorption Spectrophotometers

Manufacturer	Model No.
Bausch & Lomb, Inc.	AC2-20
Beckman Instruments Inc.	485; 495
Bendix Corporation	A1740
Corning Glass Works	240
Fisher Scientific Co.	Dial Atom II; 810
GCA/McPherson Instrument Corp.	EU-703
Hilger and Watts	H 1170
Instrumentation Laboratory Inc.	151; 251; 253; 353; 453; 151/455
Perkin-Elmer Corp.	103; 107; 300; 305B; 305BG; 306; 360; 403; 503
Phillips Electronics (see Pye-Unicam)	
Pye-Unicam	SP90; SP1900; SP1950
Rank Precision Industries, Inc. (see Hilger and Watts)	
Shandon Southern, Ltd.	A3400
SpectraMetrics, Inc.	SpectraSpan 101, 210
Spectro Products Inc.	HG-2AG
Varian Techtron	1000; 1100; 1200; AA-6

Table 3. Representative commercially available manual laboratory analyzers for measuring metals, nutrients, pesticides, and oxygen demand

METALS AND NUTRIENTS

Ultraviolet-Visible Absorption Spectrophotometers (Colorimeters)

Manufacturer	Model No.
American Instrument Co.	DW-2
Baird-Atomic, Inc.	FP-100; SF-100
Bausch & Lomb, Inc.	Minispec 20; Spectronic Nos.: 20, 70, 88, 100, 200, 210, 700, 710
Beckman Instruments Inc.	24, 25; ACTA Nos.: CII, CIII, CV, MIV, MVI, MVII; B; DB-GT; DV-2
Brinkmann Instruments Inc.	Probe Colorimeter
Chemtrix, Inc.	Type 20
GCA/McPherson Instrument Corp.	EU-701-D; EU-707; DU-721-D
Gilford Instrument Laboratories, Inc.	240
Hach Chemical Co.	DR/2 2504; DR/2 2582
Hitachi Scientific Instruments	181-7000; 101; 102; 191
Markson Science, Inc.	Solid-state colorimeter
Micromedic Systems, Inc.	MS-2
Perkin-Elmer Corp.	Coleman Junior Series: 54, 55, 124, 156; 295; 323; 356; 402
Pye-Unicam	SP1700; SP1800; SO800
Tektronix, Inc.	RS5
G.K. Turner Associates	110; 111; 330; 430; 510
Varian Instrument Division (Cary Instruments)	17; 118A; 118B; 118C; Techtron 635
Carl Zeiss, Inc.	PMZ3; PM2 D; DMR21

Table 4. Representative commercially available manual laboratory analyzers for measuring metals, nutrients, pesticides, and oxygen demand

METALS AND PHOSPHORUS (Simultaneous Analyzer)

Emission Spectrometers

Manufacturer	Model No.
Applied Research Labs (Bausch & Lomb, Inc.)	Quantometric Analyzer with Inductively Coupled Radio Frequency Plasma Excitation Source
Baird-Atomic, Inc.	SB-1; SH-1; GW-1; GK-1; GX-3; various monochromators
Bausch & Lomb, Inc.	Various monochromators
Jarrell-Ash Division (Fisher Scientific Co.)	1500 Atom counter; 750 Atom counter; 3.4 m. Ebert Spectrograph
National Spectrographic Laboratories, Inc.	Excitation sources
Spex Industries, Inc.	Excitation source; Sample Mixers
Spectrex Corp.	Quantrex; Vreeland 6A

Table 5. Typical Commercially Available Gas Chromatographs for Pesticide Analysis

Manufacturer	Model (option)
Bendix (Process Instruments Division)	
Beckman Instruments Inc.	GC 65(577653)
Chromtronix Inc.	Series 500 (501 UV)
Columbia Scientific Industries	SCI-260 Data System
CVC Products	2655(R)-3(06-008)A
CVC Products GC/MS	Direct-Coupled
GC/MS/Data System	SI-150
Dohrmann Division, Envirotech Corp.	2465-E
DuPont Instruments GC/MS	21-490-B-4
GC/MS/Data System	21-094
Extranuclear GC/MS	SpectrEL
GC/MS/Data System	SI-150
Finnigan GC/MS	3000 D-003; 9500
GC/MS/Data System	6000
Fisher Scientific Co./Victoreen	2400-001; 4400 series
Hewlett-Packard	5713A (055-011-017)
Hewlett-Packard GC/MS	5700A/5930A
GC/MS/Data System	5932A; 5933A
JEOL Analytical Instruments, Inc.	JMS-D100/JMA
LKB Instruments, Inc.	
Nuclide GC/MS	3-60-SECTORR
Packard Instrument Co., Inc.	417(8044)
Perkin-Elmer Corp.	3920(045-006)
System Industries	System/150 Data System
Tracor, Inc.	550(4201-1400-3201)
Varian, Instrument Div.	147520-00
Varian GC/MS	MAT 112
GC/MS/Data System	SS-100 MS

Table 6. Oxygen Demand and Nutrients

Manufacturer	Model No.
Dissolved Oxygen Gas Membrane Electrodes	
Beckman Instruments, Inc.	735
Delta Scientific Corp.	2010
Fisher Scientific Co.	Precision Oxygen Analyzer
International Biophysics Corp.	500-051
Weston and Stack	6, 350, 650
Chemical Oxygen Demand	
Bendix-Environmental Science	
Delta Scientific	260
Fisher Scientific Co.	Precision AquaRator
Total Organic Carbon	
ARRO Laboratories, Inc.	TOC Analyzer
Astro Ecology Corp.	600
Beckman Instruments, Inc.	915
Bendix-Environmental Science	
Ecologic Control	
Enviro Control, Inc.	TOC/TOD Analyzers
Envirotech Corp. Dohrmann Division	DC-50
Oceanography International Corp.	Total Carbon System
Ammonia and Nitrite Gas Membrane Electrode	
Kent Instrument Co.	
Orion Research	95-10, 95-46

Table 7. Automated Laboratory Instrumentation

Manufacturer	Model	Metals	Nutrients	Pesticides	Oxygen Demand
Brinkmann Instruments, Inc.	Sample turntable	X			
Foss America Inc.	Kjel-Foss		Kjeldahl Nitrogen		
Hewlett Packard	3380A Integrator			X	
Ionics, Inc.					TOC
Perkin-Elmer Corp.	Auto 200	X			
Perkin-Elmer Corp.	4900; AS-41 Samplers; PEP-2 data reduction			X	
Perkin-Elmer Corp	Automatic Integrator			X	
Pye-Unicam	SP450; DR10	X	X		
Spectra-Physics	Autolab System I, IV data reduction			X	
Technicon Corp.	Autoanalyzer II	X	X		COD,DO
The London Co.	Multisample Phototitrator PMT2; Autopipetting Titration System ATS-1	X	X		
Varian	51, 36; 485	X		X	

Table 8. Typical manual field monitors

Manufacturer	Model	Metals	Nutrients	Pesticides	Oxygen Demand
Anti-Pollution Technology Corp.	Mercometer 171	Hg			
Aquatronics Inc.	510; 520				DO
Bausch and Lomb	Minispec 20	X	X		
Beckman Instruments Inc.	Fieldlab				DO
Chemtrix, Inc.	Type 30				DO
Consolidated Technology, Inc.					DO;BOD
Delta Scientific Corp.	22; 50; 260; 3000; 85-02; 75; 2010; 2260 Spectrophotometer	X	X		DO;COD; BOD
Ecologic Instrument Corp	106				DO
Environmental Sciences Associates, Inc.	SA 2011	X			
Hach Chemical Co.	DR/2 2504	X			
International Biophysics Corp	490-051				DO;BOD
International Ecological Systems Corp.	1120 Photometer	X	X		
Koslow Scientific Co.	1233; 1282-A; 1280-A; 1248-A	As, Cd, Hg			
LaMotte Chemical Products Co.	AM-02; AM-11; AM-22 to 25	X	X		DO
Martek Instruments, Inc.	DOA *in situ*; DO-S; Mark I and II				DO
Nera, Inc.	4				DO
Rexnord Instruments Div.					DO
Sensorex			X		
Taylor Chemicals Inc.		X			
Tekmar Instruments Inc.	BYK 700-21				DO
Weston and Stack, Inc.	300; A-15				DO
Yellow Springs Instrument Co.					DO

Table 9. Typical Commercially Available Automated Field Monitors

Parameter	Manufacturer
DO	Aquatronics Series 25; Model 525; MIDAS 1000
NH_3, $CrO_4^{=}$, Cu, Fe, Ni, NO_2^-, NO_3^-, $PO_4^{\equiv}$, Si	Delta Scientific Series 8000, Multi-parameter
TOD, NO_3^-, Cu, $CrO_4^{=}$, $PO_4^{\equiv}$, NH_3, Fe, DO	Enviro Control, Inc., Series 500, 1000, 2000
DO	Environmental Devices Corp.; Type 146
Hg	Enraf-Nonius N.V.
Cu, P, MnO_4^-	Fischer & Porter Co.
Hg	Geomet, Inc.
Si, $PO_4^{\equiv}$, $CrO_4^{=}$, Fe, Cu	Hach Chemical Co., Series CR2
DO	Honeywell, Industrial Div., System 200
TOD, TOC, DO, $PO_4^{\equiv}$	Ionics, Inc., Model 1224, 225, 1236, 1131
Hg	Olin Corp./Ionics, Inc.
NH_3, Cd, Cu, Pb, NO_2^-, NO_3^-, Ag	Orion Research Inc., Series 1000
DO	Philips
Cr, Fe, Cu, $PO_4^{\equiv}$, TOC	Raytheon Co., AES, Series 1200, 1400, 1500, 1550, 1600, 1700
$PO_4^{\equiv}$	Siemens Corp.
NH_3, NO_3^-, NO_2^-, $PO_4^{\equiv}$, Total P, Si, Fe, $CrO_4^{=}$, Cu, COD	Technicon Instruments Corp. CSM6 Multi-parameter; Monitor IV
$PO_4^{\equiv}$, $CrO_4^{=}$	Universal Interloc, Inc., Model 1203; 1205
DO	Weston and Stack, Inc., Royal Series; Model 400; Model 5000; Model 3000

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