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INSTRUMENTATION FOR THE MONITORING OP GASEOUS AIR POLLUTANTS

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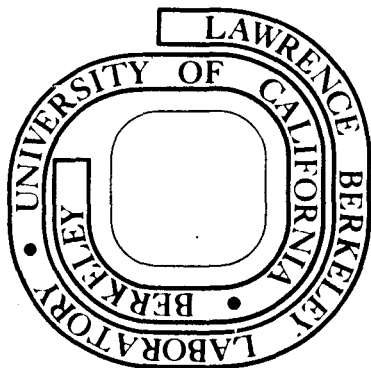
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# INSTRUMENTATION FOR THE MONITORING OF GASEOUS AIR POLLUTANTS

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## I. Introduction

In 1971 the Environmental Instrumentation Group of the Lawrence Berkeley Laboratory received an NSF-RANN (Research Applied to National Needs) grant to carry out a comprehensive survey of instrumentation for environmental monitoring including monitors of air quality, water quality, radiation, and biomedical samples. 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 for producing methodology and development of new instrumentation. The need for such a survey can be appreciated when it is realized that for the major gaseous atmospheric pollutants ( $\text{SO}_2$ , oxides of nitrogen, oxidants, carbon monoxide and hydrocarbons) there are over 300 monitors now commercially available from approximately 100 manufacturers involving over 20 distinctly different principles of operation.

This article briefly describes the techniques which form the basis of current commercial instrumentation for the five major gaseous atmospheric pollutants:  $\text{SO}_2$ , oxides of nitrogen, oxidants, carbon monoxide and hydrocarbons. More complete information on current instrumentation and principles of operation can be found in "Instrumentation for Environmental Monitoring: AIR," LBL-1, Vol. 1,

available from the Technical Information Division, Lawrence Berkeley Laboratory, Berkeley, CA 94720.

## II. National Air Quality and Emission Standards

No discussion of monitoring would be complete without a brief review of present air quality and emission standards. Federal powers to protect and enhance the quality of the nation's air resources and to promote public health and welfare are contained in the Clean Air Act Amendments of 1970. Under this act the Environmental Protection Agency (EPA) is charged with setting national air pollution standards. The national standards are only highlighted here, and one should refer to the Federal Register for the complete texts of these regulations.

"National Primary and Secondary Air Quality Standards" was published in the Federal Register on April 30, 1971. Primary standards to protect public health and secondary standards to protect public welfare (against effects on vegetation, animals, materials, etc.) were promulgated for sulfur oxides (measured as sulfur dioxide), particulate matter, carbon monoxide, photochemical oxidants, hydrocarbons, and nitrogen dioxide. A summary of the standards is shown in Table 1. The regulations also include reference methods for the measurement of the six pollutants.

"Standards of Performance for New Stationary Sources" was published in the Federal Register on December 23, 1971. These standards are for five categories of new and modified stationary sources which started construction as of August 17, 1971. The five categories and their emissions standards

TABLE 1.

National Air Quality Standards<sup>a</sup>

Pollutant	Averaging Time	Primary <sup>b</sup> Standards	Secondary <sup>c</sup> Standards	Reference <sup>d</sup> Method
Sulfur Dioxide	Annual Arithmetic Mean	80 $\mu\text{g}/\text{m}^3$ (0.03 ppm)	60 $\mu\text{g}/\text{m}^3$ (0.02 ppm) <sup>e</sup>	Pararosaniline Method
	24 hours	365 $\mu\text{g}/\text{m}^3$ (0.14 ppm)	260 $\mu\text{g}/\text{m}^3$ <sup>f</sup> (0.10 ppm)	
	3 hours	---	1300 $\mu\text{g}/\text{m}^3$ (0.5 ppm)	
Particulate Matter	Annual Geometric Mean	75 $\mu\text{g}/\text{m}^3$	60 $\mu\text{g}/\text{m}^3$ <sup>f</sup>	High Volume Sampling Method
	24 hours	260 $\mu\text{g}/\text{m}^3$	150 $\mu\text{g}/\text{m}^3$	
Carbon Monoxide	8 hours	10 $\text{mg}/\text{m}^3$ (9 ppm)	Same as Primary Standards	Non-Dispersive Infrared Spectroscopy
	1 hour	40 $\text{mg}/\text{m}^3$ (35 ppm)		
Photochemical Oxidants (corrected for NO <sub>2</sub> & SO <sub>2</sub> )	1 hour	160 $\mu\text{g}/\text{m}^3$ (0.08 ppm)	Same as Primary Standard	Gas Phase Chemiluminescent Method
Hydrocarbons (corrected for methane)	3 hours	160 $\mu\text{g}/\text{m}^3$ (0.24 ppm)	Same as Primary Standard	Flame Ionization Detection Using Gas Chromatography
Nitrogen Dioxide	Annual Arithmetic Mean	100 $\mu\text{g}/\text{m}^3$ (0.05 ppm)	Same as Primary Standard	New Reference Method Under Study

- a. National standards other than those based on annual arithmetic means or annual geometric means are not to be exceeded more than once per year.
- b. National Primary Standards: The levels of air quality necessary, with an adequate margin of safety, to protect the public health.
- c. National Secondard Standards: The levels of air quality necessary to protect the public welfare from any known or anticipated adverse effects of a pollutant.
- d. Reference method as described by the EPA. An "equivalent method" means any method of sampling and analysis which can be demonstrated to the EPA to have a "consistent relationship to the reference method."
- e. Proposed to be revoked.
- f. For use as a guideline in assessing implementation plans.

TABLE 2.

Standards of Performance for New and Modified Stationary Sources<sup>a</sup>

Fossil-Fuel Fired Steam Generators

Particulate matter (mass loading)  
0.10 lb per million BTU

Particulate matter (opacity)  
20% (40% for not more than 2 minutes)

Sulfur Dioxide  
Oil Fired: 0.80 lb per million BTU  
Coal Fired: 1.2 lb per million BTU

Nitrogen Oxides (expressed as NO<sub>2</sub>)  
Gas Fired: 0.20 lb per million BTU  
Oil Fired: 0.30 lb per million BTU  
Coal Fired: 0.70 lb per million BTU

Incinerators

Particulate matter (mass loading)  
0.08 grain per cubic foot, corrected to 12% CO<sub>2</sub>

Portland Cement Plants

Particulate matter (mass loading)  
From kiln: 0.30 lb per ton of solids fed to the kiln  
From clinker cooler: 0.10 lb per ton of solids fed to the kiln

Particulate matter (opacity)  
10%

Nitric Acid Plants

Nitrogen oxides  
3 lb (expressed as NO<sub>2</sub>) per ton of acid produced  
Opacity: 10%

Sulfuric Acid Plants

Sulfur dioxide  
4 lb per ton of acid produced

Acid mist  
0.15 lb (expressed as H<sub>2</sub>SO<sub>4</sub>) per ton of acid produced  
Opacity: 10%

<sup>a</sup>Standards are expressed as the maximum 2 hour average.

are summarized in Table 2. On June 11, 1973, the EPA published in the Federal Register proposed standards of performance for seven new categories of stationary sources. These are shown in Table 3. The regulations for stationary source performance standards include sampling and analysis methods for determining emissions.

EPA has thus far identified and promulgated on April 6, 1973, national emission standards for three hazard air pollutants -- asbestos, beryllium and mercury.

Regulations covering 1972 through 1975 model year light duty vehicles and heavy duty engines were collected in a compendium and published in the Federal Register on November 15, 1972. Gasoline-fueled light duty vehicle emission standards are summarized in Table 4. These regulations cover emissions of hydrocarbons, carbon monoxide and oxides of nitrogen. Standards of emission for heavy duty gasoline-fueled and diesel-fueled engines beginning with the 1973 model year were collected and published also in the Federal Register on November 15, 1972. On July 6, 1973, the EPA promulgated standards for control of air pollution from aircraft and aircraft engines. A summary of the status of exhaust emission standards for mobile sources is presented in Table 5. All mobile source regulations include sampling and analysis methods for determining emissions.



TABLE 3.

Seven Additional Categories of Stationary Sources  
for Which Standards of Performance Have Been Proposed

(Stationary Sources and Emissions to be Monitored)

Asphalt Concrete Plants

Particulate matter (mass loading and opacity)

Petroleum Refineries

Particulate matter (mass loading and opacity)

Carbon Monoxide

Sulfur Dioxide

Storage Vessels for Petroleum Liquids

Hydrocarbons (evaporative)

Secondary Lead Smelters

Particulate matter (mass loading and opacity)

Secondary Brass and Bronze Ingot Production Plants

Particulate matter (mass loading and opacity)

Iron and Steel Plants

Particulate matter (mass loading and opacity)

Sewage Treatment Plants

Particulate matter (mass loading and opacity)

TABLE 4.  
Federal Gasoline-Fueled Light Duty Vehicle  
Exhaust Emission Standards

Model Year	Test Method	HC (g/mile)	CO (g/mile)	NO <sub>x</sub> (g/mile)
1970	7-Mode Cycle *	2.2	23	-
		4.1	34	-
1971	7-Mode Cycle *	2.2	23	-
		4.1	34	-
1972	CVS-I *	3.4	39	-
		3.0	28	-
1973	CVS-I *	3.4	39	3.0
		3.0	28	3.1
1974	CVS-I *	3.4	39	3.0
		3.0	28	3.1
1975	(original standards)	0.41	3.4	3.1
	(interim "49 state" standards)	1.5	15	3.1
	(interim "California" Fed. and State standards)	0.9	9.0	2.0
1976	CVS-II	0.41	3.4	0.4

\* Standards shown through 1974 are equivalent standards based on the 1975 Federal test procedure (CVS-II technique).

TABLE 5.

Federal Mobile Source Exhaust Emission Standards

Mobile Source	Initial Year of Standards	Status	Exhaust Emissions
Gasoline-Fueled Light Duty Vehicles	1968	Promulgated	HC, CO, NO <sub>x</sub>
Diesel Light Duty Vehicles	1975	To be proposed	-
Gasoline-Fueled Light Duty Trucks	1975	To be proposed	-
Gasoline-Fueled Heavy Duty Engines	1973	Promulgated	HC, CO
	1974	Promulgated	HC, CO, NO <sub>x</sub>
Diesel Heavy Duty Engines	1973	Promulgated	Smoke
	1974	Promulgated	Smoke, HC, CO, NO <sub>x</sub>
Aircraft Turbine Engines	1974	Promulgated	Smoke
	1979	Promulgated	Smoke, HC, CO, NO <sub>x</sub>
Aircraft Piston Engines	1979	Promulgated	HC, CO, NO <sub>x</sub>

### III. Gaseous Air Monitoring Systems

It is the concern of this paper to discuss the instruments and techniques used for the analysis of gaseous air pollutants. Although the analyzer is necessary for monitoring, it is never sufficient by itself. A discussion of an entire monitoring system cannot be presented here; however, the following should acquaint the reader with the general concepts.

It cannot be overemphasized that considerable care must be exercised in designing a complete monitoring system. Depending upon the specific application, systems vary widely in requirements and complexity. Nevertheless, the basic building blocks serve for (1) sampling, (2) analysis, (3) calibration, and (4) data acquisition and reduction. Each is equally important, and the entire monitoring system must be fully understood in order to define its capabilities.

Gaseous monitoring systems can be classified for either ambient air monitoring, stationary source monitoring, or vehicular emissions monitoring. Ambient air instruments are those designed for monitoring in urban areas or industrial sites. Stationary source monitors are those suitable for analyzing the effluents of flues, stacks and exhausts. Vehicular emissions monitors are those suitable for certification testing of vehicles (bag sampling) and for diagnostic purposes in automotive maintenance and surveillance (exhaust probe sampling). These gaseous monitoring systems may be further divided into two classes: manual and automatic.

Manual operation implies human involvement in order to progress from one step in the analysis to another; automatic operation implies that a great deal of the operations are self initiated. Automatic operation may be further subdivided into continuous and semi-continuous operation.

Manual monitoring systems usually involve sampling by mechanical devices followed by laboratory analysis. This class of instruments will not be discussed here.

In continuous analyzing instruments the uninterrupted output response is a direct function of the concentration of the unknown constituent being analyzed; however, depending upon the detection technique, certain integration times and chemical or signal processing delays may be involved. Flame ionization detection is an example of a continuous process.

Semi-continuous analyzing instruments are those where a representative fraction (sample) of the unknown is taken and analyzed and the process automatically repeated on a regular basis. In the ideal case the analyzing period is sufficiently short so that no significant chemical changes take place before another sample is measured. Automated gas chromatographs may be considered semi-continuous instruments.

Of primary concern are the reliability, durability, and ruggedness of the complete system. The reliability is determined by such factors as specificity, sensitivity, and accuracy. It will usually be necessary to settle for less than maximum reliability because of limitations in time available for inspection, maintenance, and repair. This is especially true

in stationary source 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. The trade off between a number of instruments each measuring a specific pollutant and one instrument with multiparameter capability should also be considered -- both with a view to the economics of procurement and the cost of operation and maintenance.

To complete the system, one might need instruments to measure the temperatures, pressures, humidities, and flow characteristics of both the sample and parent gas streams. Data from such instruments would allow assessment of mass concentration, mass flow, and gas composition.

#### IV. Instrumentation

One need only examine the multitude of Federal air pollution and emission standards and their monitoring requirements to realize the tremendous and immediate importance of air pollution monitoring instrumentation.

The discussion here is confined to air pollutant analyzers that detect pollutants in the gaseous phase. Each of the following brief descriptions of instrumentation applies principally to an analyzer. An analyzer, the heart of the monitoring system, is where the actual determination of the pollutant concentration occurs. Besides the analyzer, a system may need some or all of the following: sampling probes to obtain the sample; sampling lines to transport the sample; conditioning units to dry, heat, cool, or otherwise pretreat the sample before analysis; selective filters to remove gases or particulates that can affect accuracy or operation;

pumps to move the sample; calibration devices; and data-handling electronics such as strip chart recorders. Some or all of these components may be included with the basic analyzer. Only continuous and semi-continuous analyzers are discussed here. The principles of operation range from the automated wet chemical analyzers to highly sophisticated spectroscopic techniques. The pollutants (either  $\text{SO}_2$ ,  $\text{NO}_x$ , oxidants, CO, or hydrocarbons) which can be monitored by a particular technique are indicated.  $\text{NO}_x$  refers to total oxides of nitrogen; however, analyzers may be specific for NO,  $\text{NO}_2$ , or both. Oxidant measurements are corrected for  $\text{NO}_2$  and  $\text{SO}_2$ , and measurement is primarily an indication of ozone.

#### Conductimetric Analyzers ( $\text{SO}_2$ )

Basically, the conductimetric analyzer measures the conductance of an absorbing solution into which  $\text{SO}_2$  has been dissolved by contact of the solution with air. An increase in conductance is caused by ions formed as  $\text{SO}_2$  combines with the solution. The two kinds of solution used are (1) deionized or distilled water and (2) dilute, acidified hydrogen peroxide solution. The observed increase in conductivity is proportional to the  $\text{SO}_2$  concentration in the air if there are no interferents.

#### Colorimetric Analyzers ( $\text{SO}_2$ , $\text{NO}_x$ , Oxidants)

Colorimetric analyzers measure a solution's optical absorbance spectrophotometrically as an indication of the pollutant concentration in the sampled air. The pollutant is dissolved in aqueous solution and complexed to form a highly colored compound. Within limitations, the absorbance is linearly proportional to the concentration of the colored species in accordance with Beer's Law.

### Amperometric (Coulometric) Analyzers (SO<sub>2</sub>, NO<sub>x</sub>, Oxidants)

Amperometric analyzers measure the generating current necessary to maintain a constant halide concentration in a solution into which a sample containing a pollutant gas has been absorbed. The pollutant may be an oxidizing agent (NO<sub>2</sub>, O<sub>3</sub>) or a reducing agent (SO<sub>2</sub>). The magnitude of the current required is proportional to the amount of absorbed pollutant. Although commonly called coulometric analyzers, they are more properly referred to as amperometric analyzers because it is the current and not the charge that is measured.

### Paper Tape Analyzers (SO<sub>2</sub>, NO<sub>x</sub>, CO)

The basis for detection is a chemical reaction which takes place on test paper which has been impregnated with suitable chemicals to obtain specificity for the pollutant of concern. The result of this reaction is to produce a colored stain which is monitored photoelectrically. The test paper is in the form of a continuous motor-driven reel of paper tape which allows for continuous monitoring.

### Catalytic Oxidation Analyzers (CO, HC)

Catalytic oxidation analyzers are used for the detection of CO and HC. A variety of catalysts are used, but most often the detection method is the same; namely a temperature difference is sensed between a cell where oxidation is taking place and one which is the same in other respects but no oxidation is taking place. The catalyst which is usually used to oxidize CO is Hopcalite which is a mixture of MnO<sub>2</sub> and CoU, although other catalysts have been used.



For HC detection Purad\* uses a bed of vanadia-alumina as a catalyst for more reactive hydrocarbons followed by a platinum alumina catalyst for CO detection. Figure 1 shows the thermocatalytic sensor. The temperature difference is sensed by two thermocouples and this signal is amplified by solid state electronics.

#### Chemical Sensing Electrode Analyzers (SO<sub>2</sub>, NO<sub>x</sub>)

Chemical sensing electrode analyzers sample a known volume of air with a pH buffered absorbing solution. The solution, containing the dissolved gas pollutant then passes to an ion-selective electrode where the ion concentration, proportional to the pollutant concentration, is measured potentiometrically.

#### Electrochemical Cell Analyzers (SO<sub>2</sub>, NO<sub>x</sub>, CO)

Analyzers using electrochemical cells measure the current induced by the electrochemical oxidation of SO<sub>2</sub>, NO<sub>x</sub> or CO at a sensing electrode. Electrochemical cell analyzers avoid the wet chemistry of the traditional conductimetric, colorimetric, and aperometric analyzers by using a sealed module, the electrochemical cell, inside which all chemical reactions occur.

Figure 2 shows a simplified schematic of a Dynasciences electrochemical cell analyzer. Other electrochemical cell analyzers are of a similar design. The gas to be detected diffuses through the semipermeable membrane into the cell. The rate of diffusion is proportional to the gas concentration. At the sensing electrode, the gas undergoes electrochemical oxidation causing electrons to be released. The production of electrons at the sensing

\*The mention of a commercial product does not constitute an endorsement by the National Science Foundation nor the Lawrence Berkeley Laboratory.

electrode causes this electrode to be at a lower potential relative to the counterelectrode. Thus, an electron current can flow from the sensing electrode through the amplifier to the counterelectrode. The current is proportional to the sample  $\text{SO}_2$ ,  $\text{NO}_x$  or  $\text{CO}$  concentration. Selectivity of the cell is determined by the semipermeable membrane, the electrolyte, the electrode materials, and the retarding potential. The retarding potential is adjusted to retard oxidation of those species that are less readily oxidized than the gas of interest.

#### Chemiluminescent Analyzers ( $\text{NO}_x$ , Oxidants)

Chemiluminescent analyzers are based on the emission characteristics of a molecular species formed in the reaction between the gas pollutant being monitored and a gas or solid species. Ozone when allowed to react on a surface (organic dye on silica gel) or with  $\text{NO}$  or ethylene gas produces chemiluminescence which is measured with a photomultiplier tube. This reaction is specific for ozone. A schematic of a typical gas phase ozone chemiluminescent analyzer is shown in Figure 3.  $\text{NO}$  when reacted with ozone produces excited  $\text{NO}_2$  which proceeds to the ground state with the emission of radiant energy, measured with a photomultiplier tube. A schematic of a typical oxides of nitrogen chemiluminescent analyzer is shown in Figure 4.

#### Flame Photometric Detection and Gas Chromatography-Flame Photometric Detection Analyzers ( $\text{SO}_2$ )

Flame photometric detector (FPD) analyzers measure the emissions from sulfur compounds introduced into a hydrogen-rich flame. A narrow-band optical filter selects the 394 nm  $\text{S}_2$  emission band. Figure 5 is a schematic of

a flame photometric detector. For  $\text{SO}_2$  monitoring, FPD analyzers are susceptible to interference from other sulfur compounds. Although  $\text{H}_2\text{S}$ ,  $\text{H}_2\text{SO}_4$  aerosols, and mercaptans are commonly found in the atmosphere, their contribution to the total sulfur content is usually 10% or less. However, if sulfur compounds other than  $\text{SO}_2$  are present in appreciable concentrations gas chromatography-FPD (GC-FPD) analyzers can be used to distinguish among the sulfur compounds. A schematic of a typical GC-FPD is shown in Figure 6.

#### Flame Ionization Detection Analyzers (HC)

The sensor which is involved in over 90% of the HC monitoring systems in use today, is the FID. In some cases, it is used in a system which makes no attempt to separate the various hydrocarbons. These systems are referred to as total HC monitors. In, roughly, an equal number of cases, it is used as the sensor following gas chromatographic separation. These systems allow for methane detection separate from the rest of the hydrocarbons. They may also allow for the monitoring of a number of other hydrocarbons. In addition this sensor has been used as a CO detector by first converting the CO to  $\text{CH}_4$ .

The principle of operation of the FID can be seen by referring to Figure 7. The sample is introduced into a combustion region created by the reaction of hydrogen with a surplus of oxygen. The combustion occurs between electrodes which have a voltage drop of a few hundred volts between them (polarization voltage). The ionized combustion fragments are attracted to the positive electrode which results in an electrical current whose magnitude is related to the concentration of hydrocarbons introduced into the sensor.

There is no simple relationship between the response of the FID and the various organic compounds being monitored. Therefore, the data from this detector are usually expressed in terms of some calibration gas, i.e., ppm of total hydrocarbons, measured as hexane.

#### Gas Chromatography-Flame Ionization Detection Analyzers (CO, HC)

The need to separate methane from total HC and interest in total HC composition is responsible for the use of GC-FID in air pollution monitoring. A typical gas chromatography-FID analyzer is shown in Figure 8. The coiled column is packed with an inert solid support upon which is distributed a liquid solvent. A carrier gas moves the sample through the column. If the sample consists of a mixture of hydrocarbons different components of the mixture will require different times to move through because of differing affinities for the liquid solvent. This method of operation requires intermittent sampling since a few minutes is required for passage through the column.

#### Nondispersive Infrared Absorption Analyzers (SO<sub>2</sub>, NO<sub>x</sub>, CO, HC)

A nondispersive absorption spectrometer is an instrument which is based on broad-band spectral absorption and which is sensitized for a particular gas of interest by means of a detector, a special cell, or a filter. Commercial instruments are available which use this technique in the infrared, ultraviolet, and visible regions.

Typical nondispersive infrared (NDIR) analyzers use an arrangement of the type shown in Figure 9. Infrared radiation from the filaments is directed onto two cells: (1) a reference cell filled with a noninfrared

absorbing gas, such as nitrogen or argon, and (2) a sample cell through which the sample air is continuously drawn. The detector consists of a gas-impermeable double chamber with a flexible metal diaphragm as a partition. Both chambers are filled with the gas being measured. The infrared radiation which passes through the reference cell enters one chamber of the detector, and the radiation passing through the sample cell enters the other chamber. The gas in each chamber of the detector is heated by the incoming energy. This heating causes a pressure increase in the two chambers. The pressure rise is greater in the chamber receiving radiation from the reference cell, since a portion of the radiation transmitted through the sample cell has been absorbed by the gas before entering the chamber on the sample cell side. This difference in pressure causes a diaphragm displacement which is electronically measured as a capacitance change. The infrared radiation is chopped by an optical chopper to cause a periodic capacitance change, which modulates a radio-frequency signal from an oscillator. This signal is subsequently demodulated, amplified, and the output is fed to a meter or a recorder.

All NDIR analyzers use principally the above technique, but the optical and detection arrangements vary somewhat. One series of NDIR analyzers uses a detector consisting of two chambers in series separated by a diaphragm. Chopped radiation from the reference and sample cells are recombined before reaching the detector. Both detector chambers are filled with the gas being measured. The gas in the forward chamber is heated by the center of the absorption band; the gas in the rear chamber, by the edges of the band. The gas in the sample will absorb primarily in the band center and cause the front chamber to become cooler. The

pressure change causes a displacement of the diaphragm, which is measured as an electronic capacitance change.

#### Fluorescent NDIR Analyzer (CO)

An improvement in the NDIR method for CO monitoring has been made using the principle of dual isotope fluorescence NDIR which is shown in Figure 10. In this method infrared fluorescence from  $C^{16}O$  and  $C^{18}O$  is alternately passed through the sample. Since all CO contained in the sample will be  $C^{16}O$  the ratio of the intensity of the fluorescence will be a measure of the CO in the sample. The effects of interferences will be minimized since their effect will be to diminish the intensity of the fluorescence from the two species equally without greatly changing the ratio of intensities.

#### Nondispersive Ultraviolet Absorption Analyzers ( $SO_2$ , $NO_x$ , Oxidants)

Instruments use nondispersive absorption techniques also in the ultraviolet and visible regions. Several instruments employ a double-beam arrangement through two cells (reference and sample) and photomultiplier tubes for detection. Some instruments are based on the measurement of the difference in absorption by the sample at two separate wavelengths, one an absorbing wavelength of the gas and the other a non-absorbing wavelength. A schematic is shown in Figure 11.

#### Mercury Substitution Ultraviolet Absorption Analyzer (CO)

A mercury substitution UV absorption analyzer utilizes the heterogeneous reaction between carbon monoxide and mercuric oxide to generate mercury vapor in the sample gas stream at a concentration proportional to the CO concentration. UV photometry is used to measure the resultant Hg vapor.

### Ultraviolet Fluorescence Analyzer (SO<sub>2</sub>)

A UV fluorescence analyzer for SO<sub>2</sub> monitoring is based on the measurement of the intensity of the fluorescence in the ultraviolet of SO<sub>2</sub> which is excited by the Zn 213.8 nm or Cd 228.8 nm line.

### Dispersive Absorption Spectrometers (SO<sub>2</sub>, NO<sub>x</sub>, CO, HC)

A dispersive absorption spectrometer is an instrument which can be set to pass any small wavelength interval within its range and differs from a nondispersive type instrument which looks at a broad spectral region. The dispersive type instrument is able to measure any gas that absorbs within its spectral region and is not limited to a single, preselected gas as is usually the case with the nondispersive type instrument. The disadvantage of a dispersive type instrument is that in situations where a number of absorbing gases are present, it may be difficult to locate an absorption wavelength for the gas of interest which is in a spectral interval where other gases do not absorb. A schematic of a dispersive infrared absorption optical system is shown in Figure 12.

### Correlation Spectrometers (SO<sub>2</sub>, NO<sub>x</sub>)

A correlation spectrometer uses either skylight or artificial light for measurement of selected gases. There are numerous possibilities for ambient air and stationary source monitoring: data may be obtained remotely or on-site and may be long-line average or point values. Long-line data are obtained in units of concentration times distance such as ppm-meters (ppm-m). To convert to conventional ppm data, one divides the ppm-m value by the observed pathlength in meters.

Figure 13 shows a correlation spectrometer for remote sensing. Sky-light is collected by a telescope, collimated, dispersed by a prism or grating, and focused onto a correlation mask. The pattern of the mask is formed by depositing aluminum on glass and then removing slits of aluminum corresponding to absorption lines of  $\text{SO}_2$  and  $\text{NO}_2$ . If the mask is repeatedly shifted relative to the incident spectrum, then the photomultiplier tube will observe a minimum when the mask lines correlate with the  $\text{SO}_2$  or  $\text{NO}_2$  lines and a maximum when the mask is shifted off. The difference in light intensities seen by the photomultiplier is a measure of the  $\text{SO}_2$  or  $\text{NO}_2$  concentration between the light source and the instrument.

If an artificial light source such as quartz iodine or xenon lamp is used, monitoring across a defined distance is achieved. The distance may be across a stack or across a courtyard. An artificial source also allows monitoring at night when there is insufficient skylight.

#### Second Derivative Spectrometers ( $\text{SO}_2$ , $\text{NO}_x$ , Oxidants)

A second derivative spectrometer processes the transmission versus wavelength function of an ordinary spectrometer to produce an output signal proportional to the second derivative of this function. A schematic of such a spectrometer is shown in Figure 14. Ultraviolet light of continuous wavelength is collected and focused onto an oscillating entrance slit of a grating spectrometer. By slowly changing the grating orientation, the exiting light has a slowly scanning center wavelength with sinusoidal wavelength modulation created by the oscillating entrance slit. This radiation passes through a gas sample and is detected with a photomultiplier tube. The signal is then electronically processed to produce a second derivative spectrum.



### Condensation Nuclei Formation Analyzers (SO<sub>2</sub>)

A commercial condensation nuclei formation analyzer for SO<sub>2</sub> monitoring is currently available. The unit consists of two parts: a converter for changing SO<sub>2</sub> molecules into condensation nuclei and a condensation nuclei monitor. In operation, an air sample is drawn through a glass filter into the converter. The glass filter removes condensation nuclei from the sample. In the converter, the SO<sub>2</sub> molecules in the presence of water vapor and ultraviolet radiation are converted into H<sub>2</sub>SO<sub>4</sub> aerosol. The H<sub>2</sub>SO<sub>4</sub> aerosol, which consists of condensation nuclei, is then drawn into the condensation nuclei monitor where constant volume expansion in the presence of water vapor produces a cloud. The optical transmittance of the cloud indicates the number of condensation nuclei per cubic centimeter (CN/cc). A calibration curve relates the CN/cc value to a corresponding SO<sub>2</sub> concentration value.

### Bioluminescence Analyzers (SO<sub>2</sub>, NO<sub>x</sub>, CO)

In bioluminescence analyzers an air sample is drawn over the surface of a sensor containing luminescing organisms. The light intensity change effected by specific vapors is monitored by a photocell whose output indicates changes, if any, in the concentration of a specific pollutant gas.

### New Developments in Air Monitoring Instrumentation

The most promising instrumental developments for air monitoring are those techniques based upon the application of well-known spectroscopic methods. The instruments discussed here are either in early commercial stages or in an advanced prototype stage. The following comments are

intended only to acquaint the reader with recent developments in air monitoring instrumentation and indicate the type of new commercial instrumentation which will probably be available in the near future.

Fourier interferometry uses a dispersive technique; however, unlike the grating type, the technique first generates a frequency spectrum by light interference in an optical system. The frequency spectrum is mathematically converted into the conventional wavelength spectrum by Fourier transforms. By this technique all wavelengths are scanned concurrently in time and are measured directly as a frequency spectrum. This approach is capable of producing high resolution in the infrared.

Mass spectrometers are marketed by many manufacturers, and a few have recently been developed specifically for air pollution monitoring. The sensitivities of such instruments are on the order of 0.1 ppm and response times are less than 1 second.

Laser techniques show good promise for the remote monitoring of air pollutants. Several recent studies have considered the application of laser resonance absorption for air monitoring. Resonance scattering and Raman scattering also show potential use for gaseous air pollution monitoring. Sensitivity and cost presently limit their ability to compete in today's market; however, there are indications that they may have much wider usage in the future.

Several other techniques are being studied for their applicability to gaseous pollutant monitoring. These include microwave spectroscopy, nondispersive vacuum ultraviolet absorption techniques, ESCA (electron spectroscopy for chemical analysis), and semiconductor devices.

V. Tables of Gaseous Pollutant Monitors

Tables 6, 7 and 8 list the commercially available gaseous pollutant monitors arranged according to their principles of operation. The instruments are divided into ambient air monitors (Table 6), stationary source monitors (Table 7), and vehicular emissions monitors (Table 8).

VI. Additional Reading

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C. D. Hollowell, G. Y. Gee, and R. D. McLaughlin, "Current Instrumentation for Continuous Monitoring for SO<sub>2</sub>," Anal. Chem., 45 (1) 63A, January, 1973

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Environmental Protection Agency, "Interim Standards for 1975 Model Year Light Duty Vehicles," Federal Register, 38 (126) 17441, July 2, 1973

TABLE 6. AMBIENT AIR MONITORS

	SO <sub>2</sub>	NO <sub>x</sub>	Oxidants	CO	HC
<u>Conductimetric</u>					
Calibrated Instruments	X				
Casella/London <sup>1</sup>	X				
CEA Instruments	X				
Devco	X				
Intertech	X				
Kimoto <sup>2</sup>	X				
Scientific Industries	X				
Scott Aviation	X				
<u>Colorimetric</u>					
CEA Instruments	X	X			
Enraf-Nonius	X	X	X		
Kimoto <sup>2</sup>		X			
Precision Scientific		X			
Scientific Industries		X			
Technicon	X	X		X	
Wilkens-Anderson	X				
Xonics	X	X			
<u>Amperometric (Coulometric)</u>					
Barton	X				
Beckman	X	X		X	
Intertech		X			
Mast		X		X	
Philips	X				
Process Analyzers	X				
Welsbach					X
<u>Paper Tape</u>					
Houston Atlas (via conversion to H <sub>2</sub> S)	X				
Universal Environmental Instruments <sup>3</sup>		X			X
<u>Catalytic Oxidation</u>					
Devco					X
Energetics					X
Matheson					X
<u>Chemical Sensing Electrode</u>					
Geomet	X	X			
Orion	X				
<u>Electrochemical Cell</u>					
Dynasciences	X	X			
EnviroMetrics	X	X			X
Mast	X				
Theta Sensors	X	X			
<u>Chemiluminescence</u>					
Aerochem		X		X	
AID				X	
Beckman		X		X	
Bendix/PID		X		X	
Intertech		X			
Kimoto <sup>2</sup>				X	
LECO		X			
McMillan		X		X	
Meloy		X		X	
Monitor Labs		X		X	
REM		X		X	
Thermo Electron		X		X	

TABLE 6. (contd)

	SO <sub>2</sub>	NO <sub>x</sub>	Oxidants	CO	HC
<u>FPD</u>					
Bendix/PID	X				
Meloy	X				
<u>GC-FPD</u>					
AID	X				
Bendix/PID	X				
Hewlett Packard	X				
Process Analyzers	X				
Tracor	X				
Varian	X				
<u>FID</u>					
Antek					X
Beckman					X
Bendix/PID					X
Delphi					X
Gow-Mac					X
Meloy					X
MSA					X
Power Designs					X
Process Analyzers					X
Scott Aviation					X
Scott Research					X
Teledyne					X
Thermo Electron					X
<u>GC-FID</u>					
AID				X	X
Beckman				X	X
Bendix/PID				X	X
Byron				X	X
Hewlett-Packard				X	X
<u>NDIR</u>					
Beckman				X	
Bendix/PID				X	
Calibrated Instruments				X	
Ecological Instrument				X	
Horiba				X	
Intertech				X	
MSA				X	
<u>Fluorescent NDIR</u>					
Andros				X	
<u>Nondispersive UV Absorption</u>					
Canadian Research	X				
Dasibi			X		
<u>Hg Substitution UV Absorption</u>					
Bacharach				X	
<u>Dispersive IR Absorption</u>					
Wilks (IR)				X	
<u>UV Fluorescence</u>					
REM	X				

TABLE 6. (contd)

	SO <sub>2</sub>	NO <sub>x</sub>	Oxidants	CO	HC
<u>Correlation Spectroscopy</u>					
Barringer	X	X			
<u>2nd Derivative Spectroscopy</u>					
Spectrometrics/Lear Siegler	X	X	X		
<u>Condensation Nuclei Formation</u>					
Environment/One	X				
<u>Bioluminescence</u>					
RPC	X	X		X	

<sup>1</sup> U.S. Distributor: BGI

<sup>2</sup> U.S. Distributor: Instruments International

<sup>3</sup> U.S. Distributor: MDA Scientific

TABLE 7. STATIONARY SOURCE MONITORS

	SO <sub>2</sub>	NO <sub>x</sub>	CO	HC
<u>Conductimetric</u>				
Calibrated Instruments	X			
<u>Colorimetric</u>				
F & J Scientific		X		
<u>Amperometric (Coulometric)</u>				
Barton	X			
<u>Paper Tape</u>				
Houston Atlas (via conversion to H <sub>2</sub> S)	X			
<u>Catalytic Oxidation</u>				
Devco			X	
Matheson			X	
MSA			X	
<u>Chemical Sensing Electrode</u>				
Geomet	X	X		
Orion	X			
<u>Electrochemical Cell</u>				
Dynasciences	X	X	X	
EnviroMetrics	X	X	X	
Theta Sensors	X	X		
<u>Chemiluminescence</u>				
Aerochem		X		
Beckman		X		
Bendix/PID		X		
Intertech		X		
LECO		X		
McMillan		X		
REM		X		
Scott Research		X		
Thermo Electron		X		
<u>FPD</u>				
Meloy	X			
<u>FID</u>				
MSA				X
Process Analyzers				X
Scott Research				X
Teledyne				X
Thermo Electron				X
Wemco				X
<u>GC-FID</u>				
Byron			X	X
Hewlett-Packard			X	X

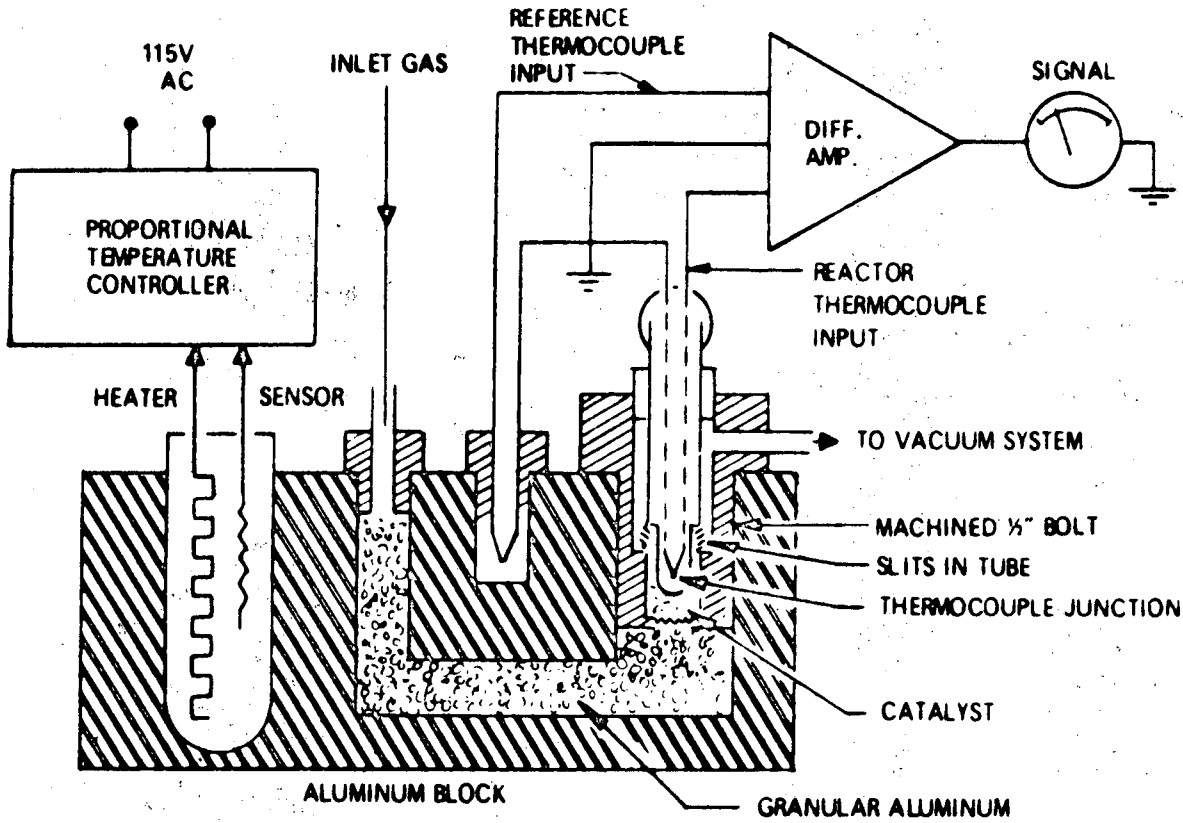
TABLE 7. (contd)

	SO <sub>2</sub>	NO <sub>x</sub>	CO	HC
<u>NDIR</u>				
Beckman	X	X	X	
Bendix/PID	X	X	X	X
Calibrated Instruments	X	X	X	
Ecological Instrument			X	X
Horiba		X	X	X
Infrared Industries	X	X	X	
Intertech	X	X	X	
Leeds & Northrup	X		X	
MSA	X	X	X	
Peerless		X	X	X
Scott Research		X		
<u>Nondispersive UV Absorption</u>				
Beckman		X		
Canadian Research	X			
DuPont (visible for NO <sub>2</sub> )	X	X		
Intertech	X	X		
Peerless	X	X		
Teledyne	X	X		
<u>Hg Substitution UV Absorption</u>				
Bacharach			X	
<u>Dispersive IR and UV Absorption</u>				
Environmental Data (IR/UV)	X	X	X	
Wilks (IR)	X		X	
<u>UV Fluorescence</u>				
REM	X			
<u>Correlation Spectroscopy</u>				
Barringer	X			
CEA Instruments	X			



TABLE 8. VEHICULAR EMISSIONS MONITOR

	CO	HC	NO <sub>x</sub>
<u>Colorimetric</u>			
Megatech	X		
<u>Catalytic Oxidation</u>			
Bendix/NEI	X		
Bosch	X		
Matheson	X		
MSA	X		
Purad	X	X	
<u>Electrochemical Cells</u>			
EnviroMetrics	X		X
<u>Chemiluminescence</u>			
Aerochem			X
Beckman			X
Intertech			X
LECO			X
McMillan			X
Meloy			X
REM			X
Scott Research			X
Thermo Electron			X
<u>FID</u>			
Beckman		X	
Delphi		X	
Gow-Mac		X	
Heath		X	
Horiba		X	
Intertech		X	
MSA		X	
Scott Research		X	
Thermo Electron		X	
<u>GC-FID</u>			
Byron	X	X	
Carle		X	
Hewlett-Packard	X	X	
<u>NDIR</u>			
Allen	X	X	
Autoscan	X	X	
Beckman	X	X	X
Bendix/PID	X	X	X
Bosch	X	X	
Calibrated Instruments	X		
Chrysler	X	X	
Commercial Electronics	X	X	
Ecological Instrument	X	X	
Horiba	X	X	X
Intertech	X		X
Marquette	X	X	
MSA	X	X	X
Peerless	X	X	X
Scott Research	X	X	
Sensors	X	X	
Sun	X	X	
<u>Nondispersive UV Absorption</u>			
Beckman			X
<u>UV Emission</u>			
Detector Electronics	X		
<u>Dispersive IR and UV Absorption</u>			
Chrysler (IR/UV)	X	X	X
Wilks (IR)	X	X	



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Fig. 1 Simplified Sketch of Thermocatalytic System (Purad Incorporated)

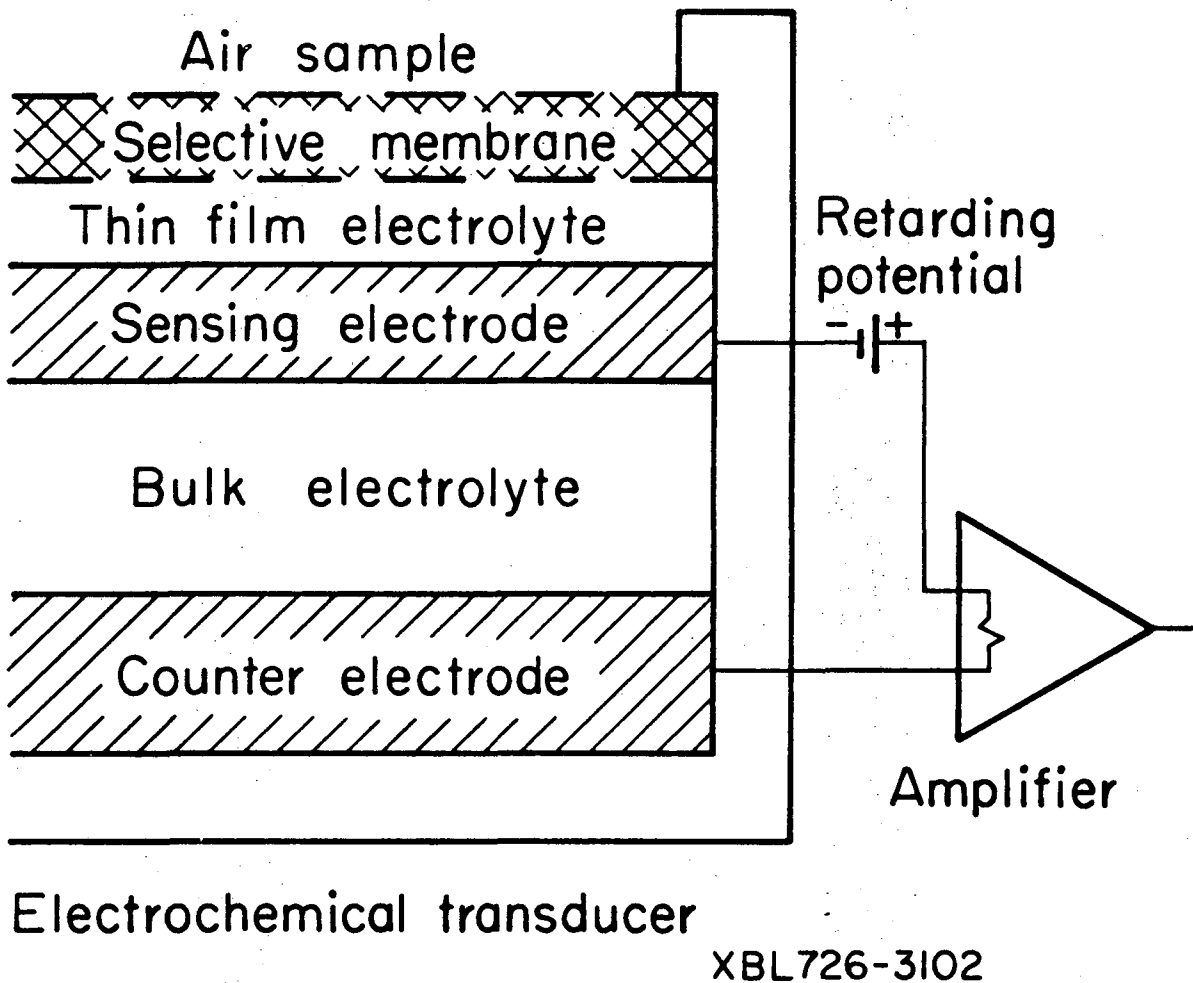
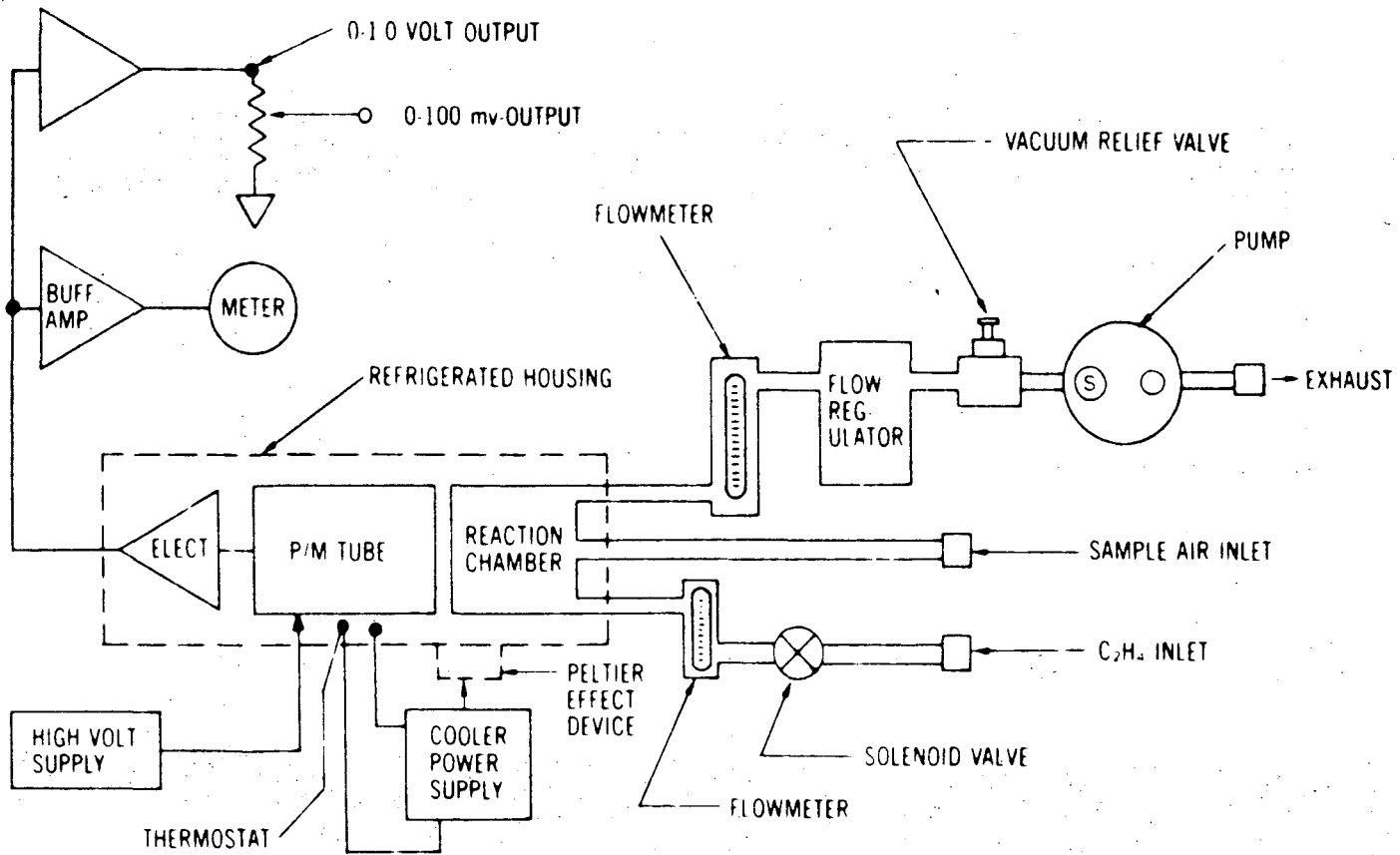


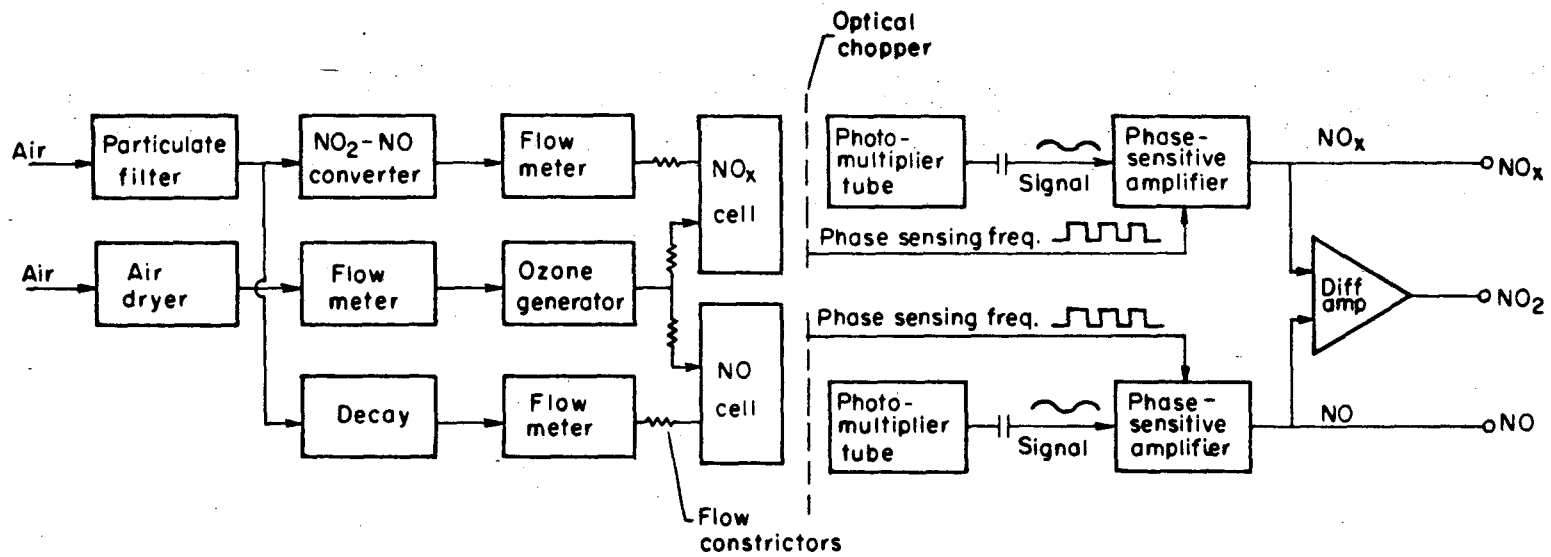
Fig. 2 Simplified Schematic of Electrochemical Cell

(Dynasciences Corporation)



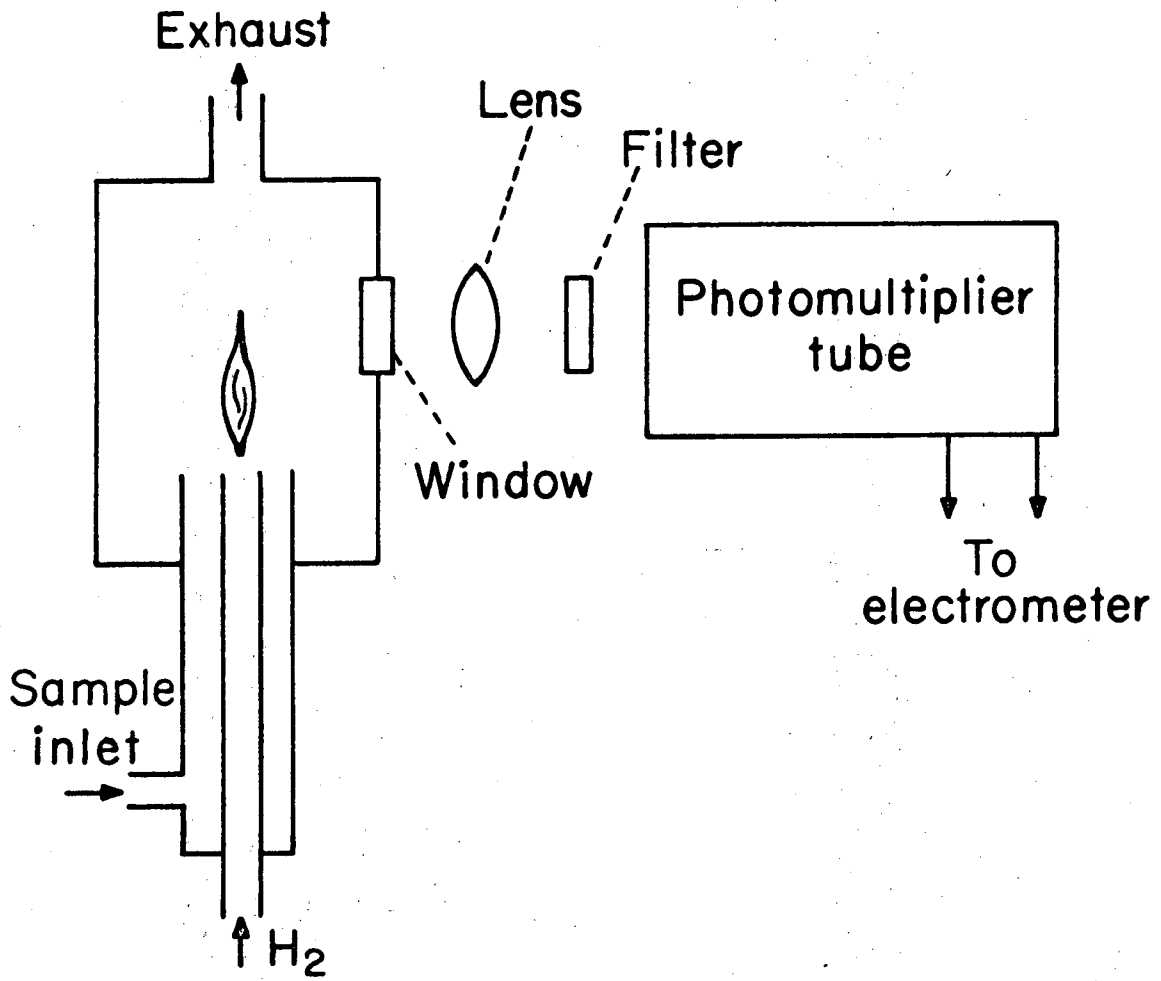
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Fig. 3 Ozone Chemiluminescent Analyzer (McMillan Electronics Corporation)



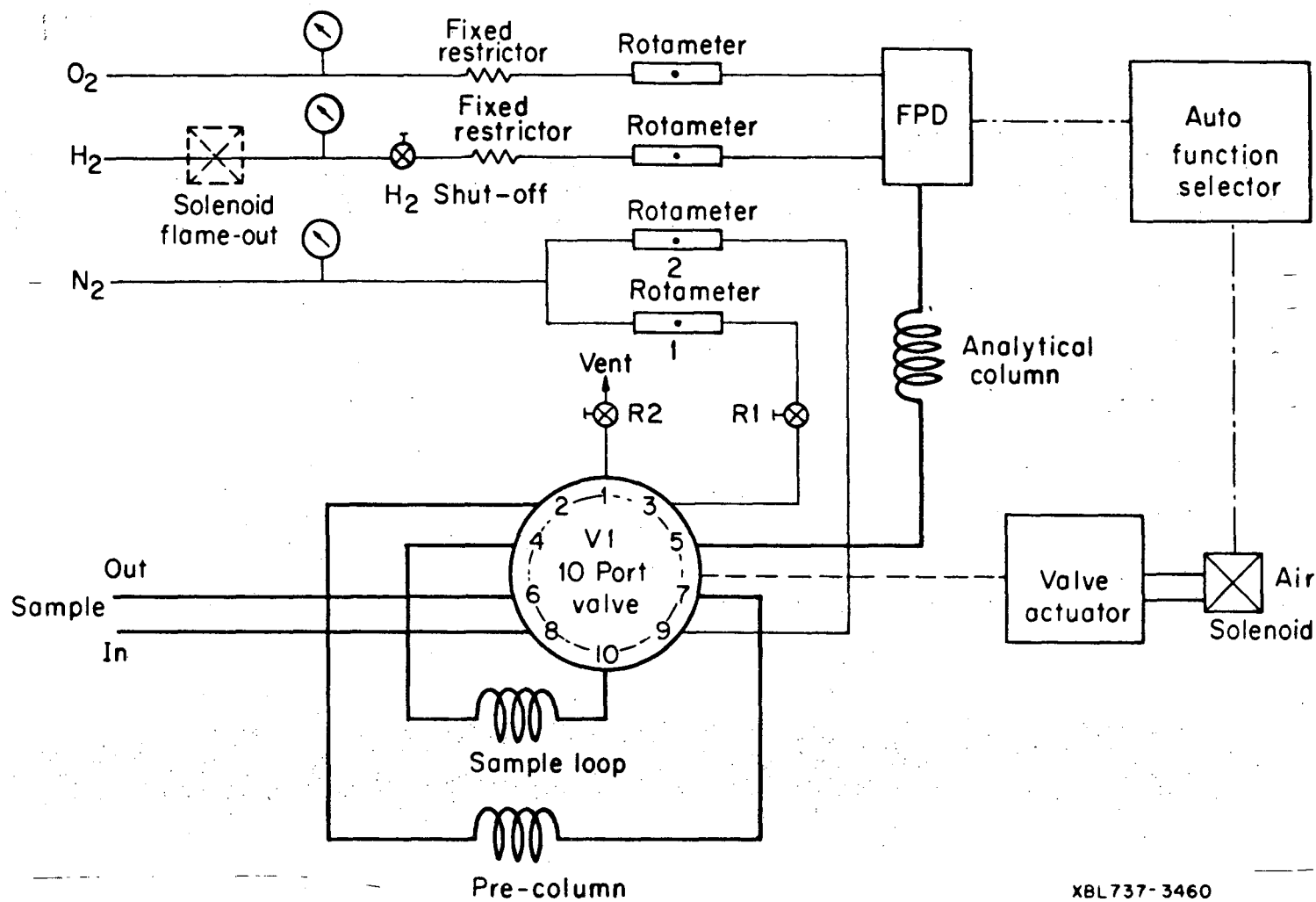
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Fig. 4 Oxides of Nitrogen Chemiluminescent Analyzer (Monitor Labs, Incorporated)



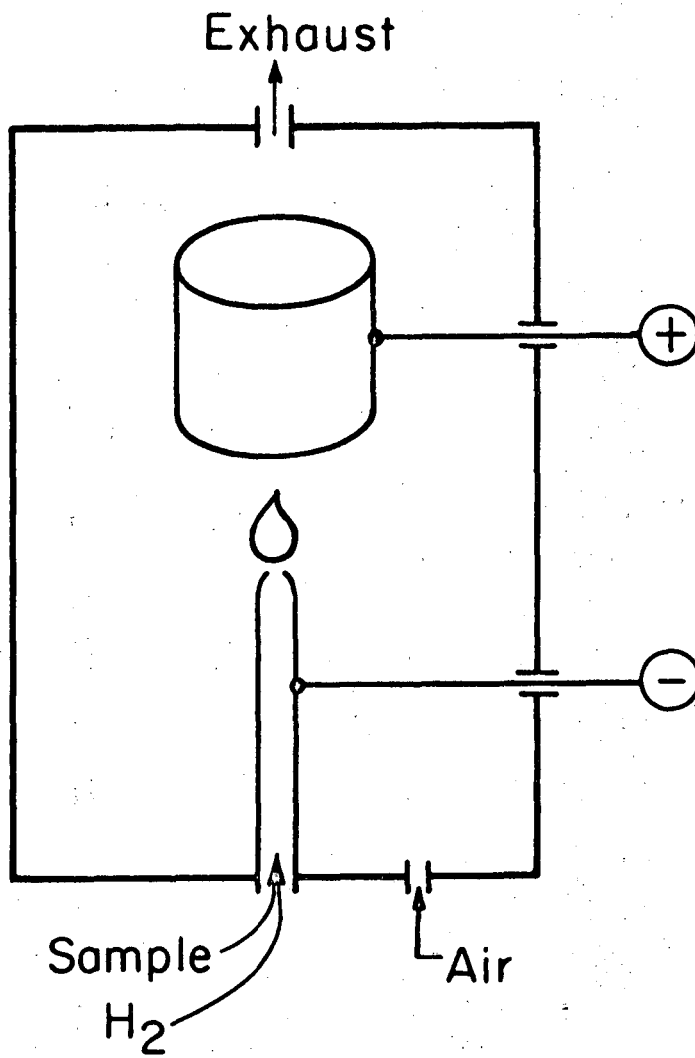
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Fig. 5 Flame Photometric Detector



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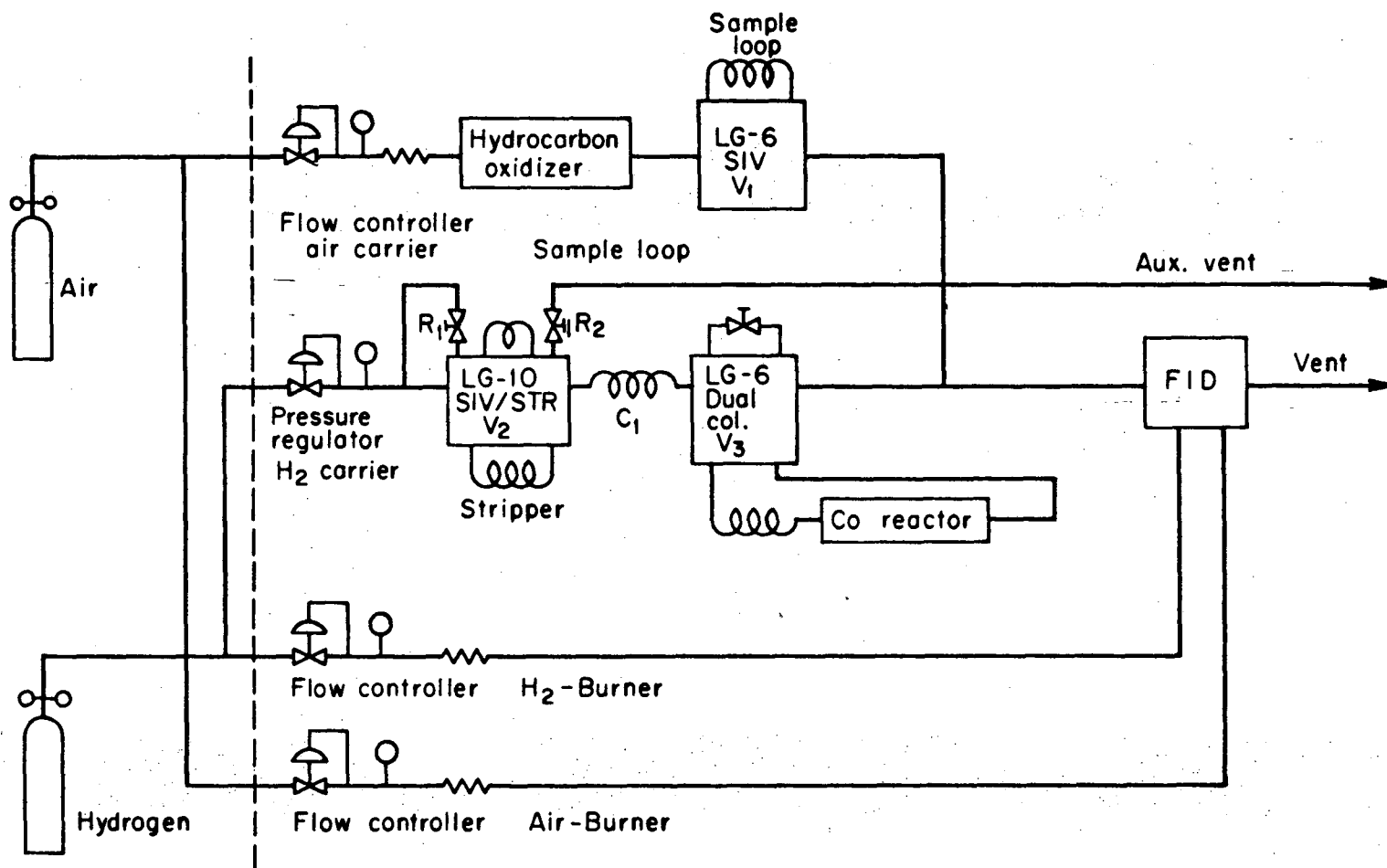
Fig. 6 Gas Chromatography-Flame Photometric Detector Analyzer (Tracor, Incorporated)



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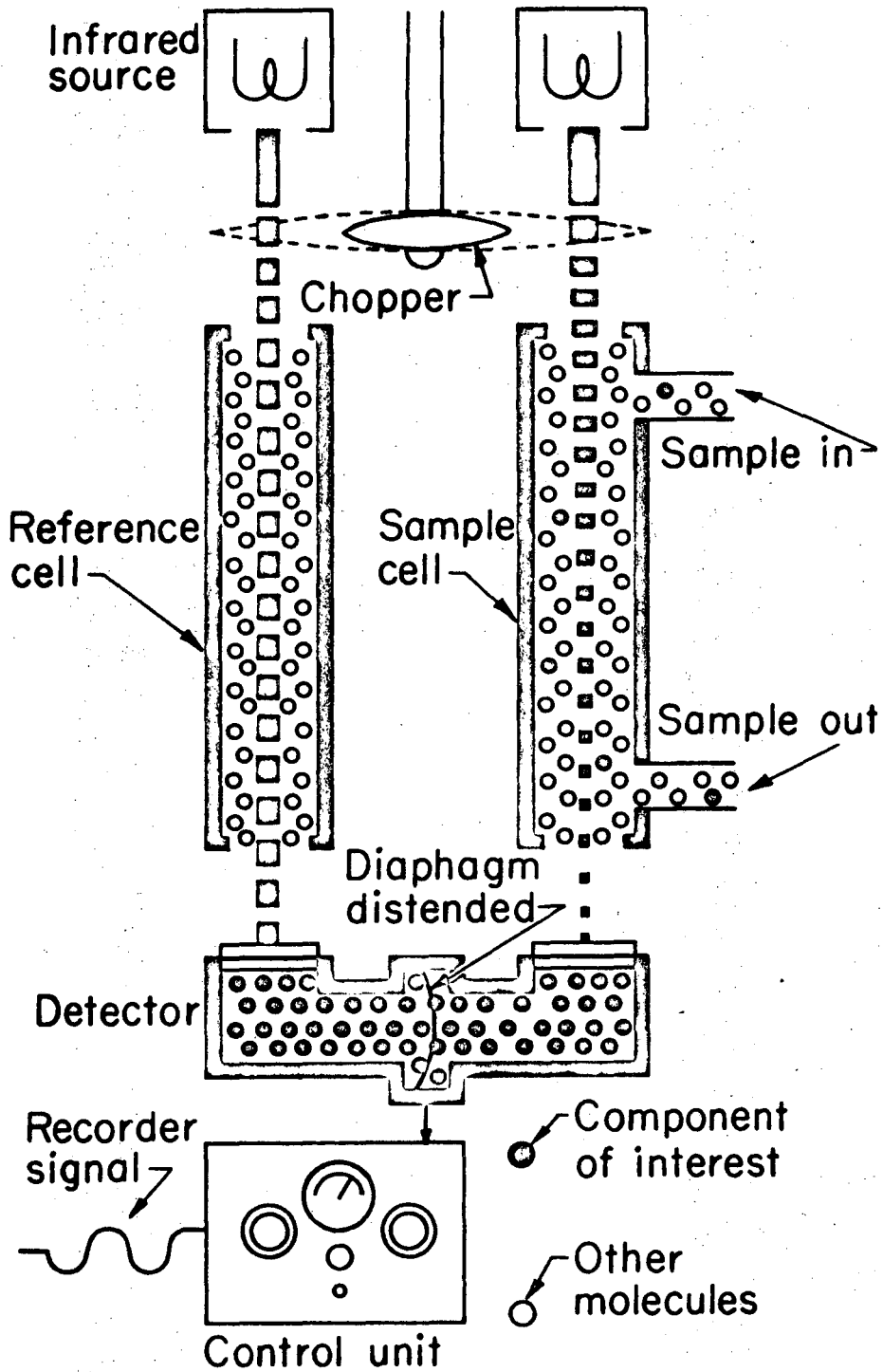
Fig. 7 Flame Ionization Detector





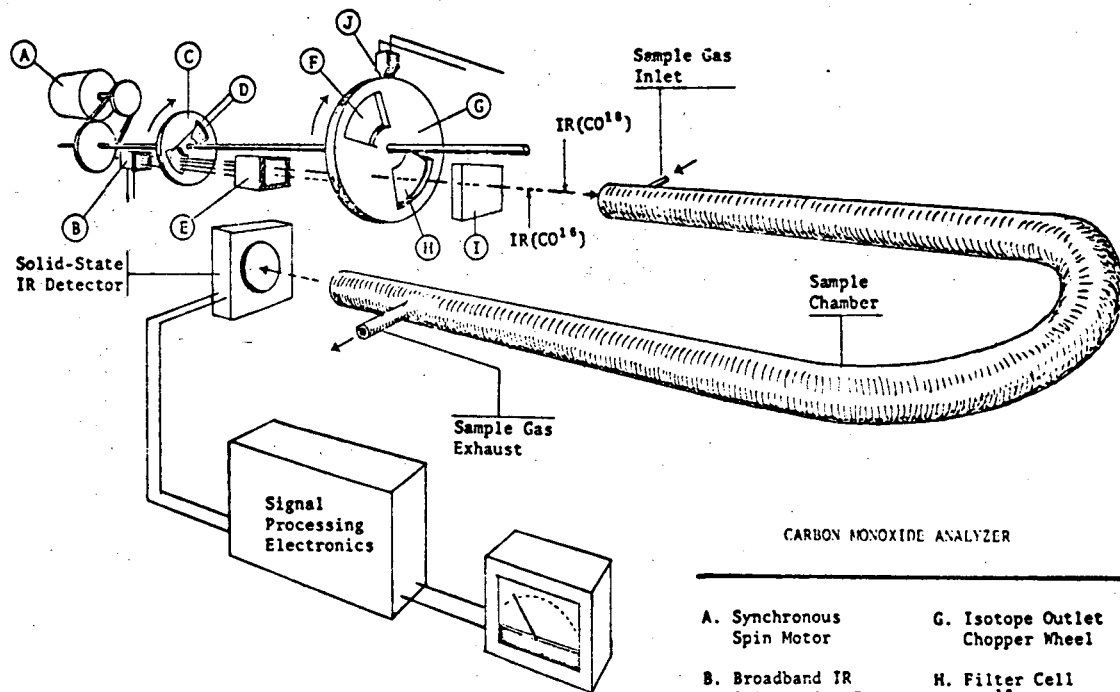
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Fig. 8 Gas Chromatography-Flame Ionization Detector for the Analysis of HC, THC and CO  
(Beckman Instrument Incorporated)



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Fig. 9 Nondispersive Infrared Analyzer  
(Beckman Instruments Incorporated)



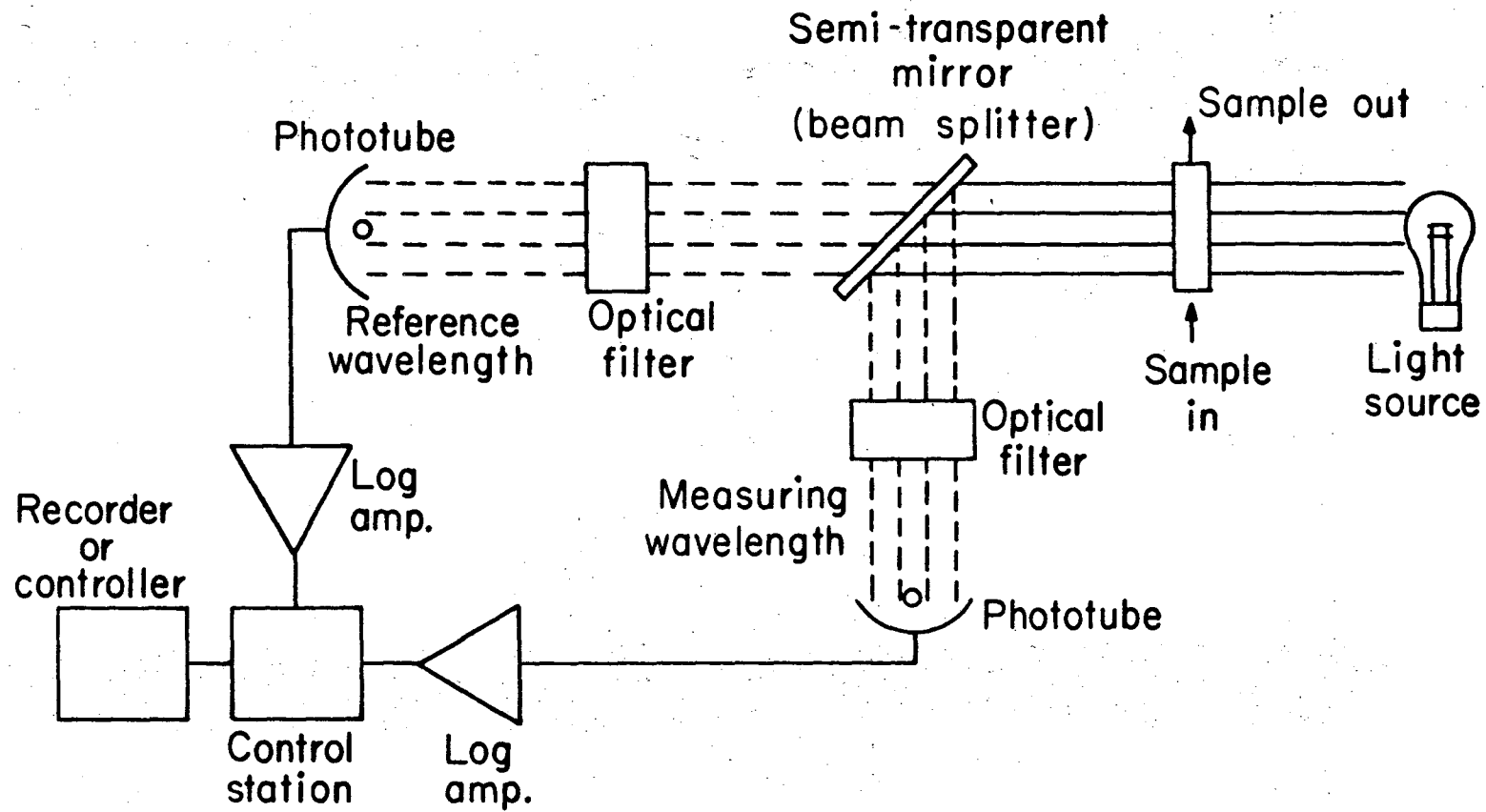
CARBON MONOXIDE ANALYZER

- |                                     |                                    |
|-------------------------------------|------------------------------------|
| A. Synchronous Spin Motor           | G. Isotope Outlet Chopper Wheel    |
| B. Broadband IR Stimulation Source  | H. Filter Cell (CO <sup>18</sup> ) |
| C. Broadband IR Inlet Chopper Wheel | I. IR Outlet Window                |
| D. Inlet Windows                    | J. Magnet Pickup For Sync Pulses   |
| E. Dual-Isotope-Fluorescent Cell    |                                    |
| F. Filter Cell (CO <sup>16</sup> )  |                                    |

Block Diagram  
Figure 3-1

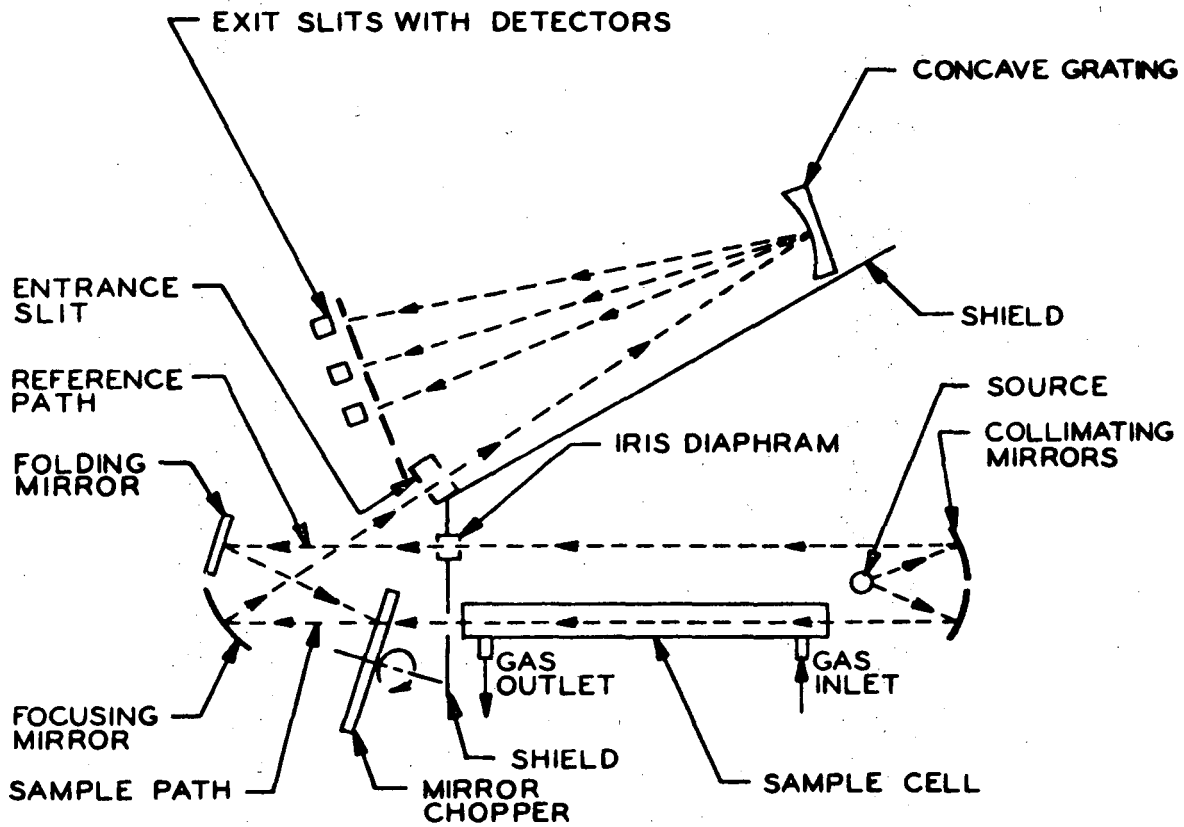
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Fig. 10 Fluorescent Nondispersive Infrared Analyzer (Andros Incorporated)



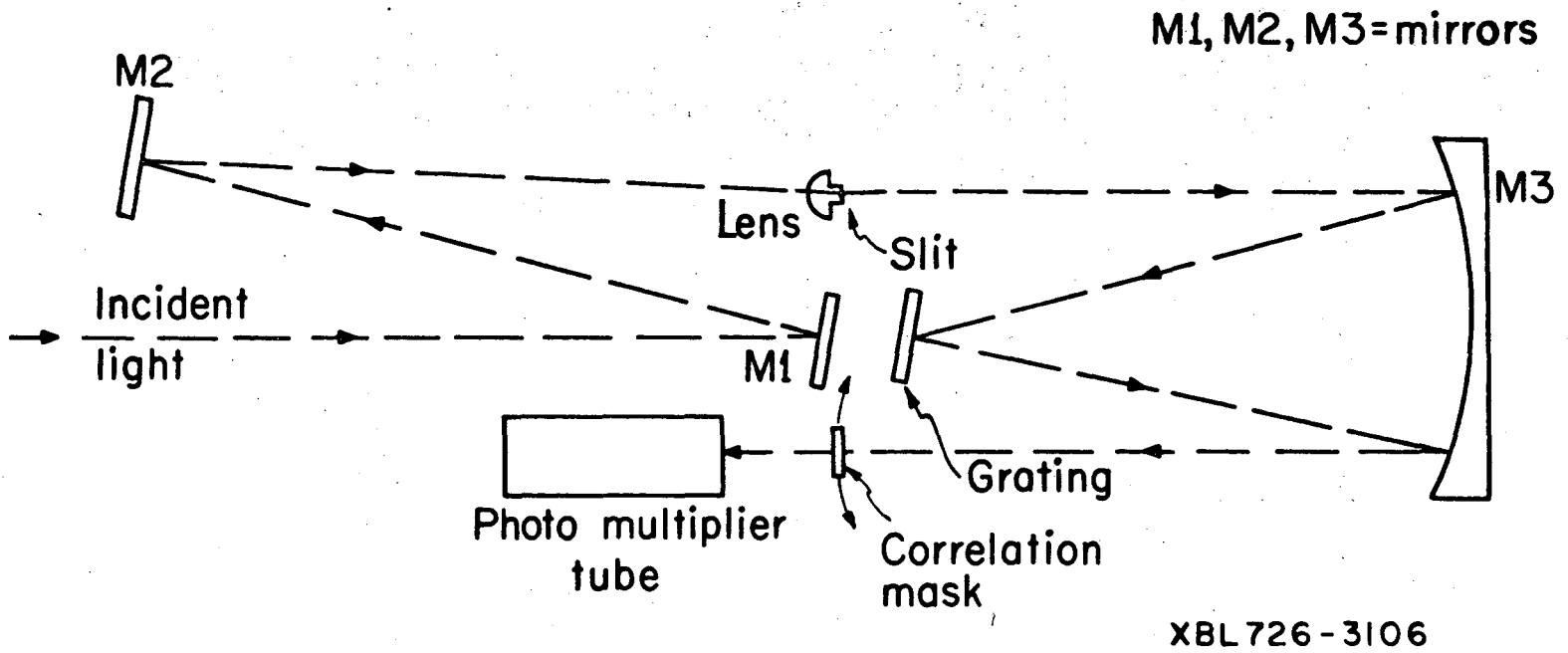
XBL726-3105

Fig. 11 Nondispersive Ultraviolet and Invisible Absorption Analyzer (E.I. du Pont de Nemours and Company Incorporated)



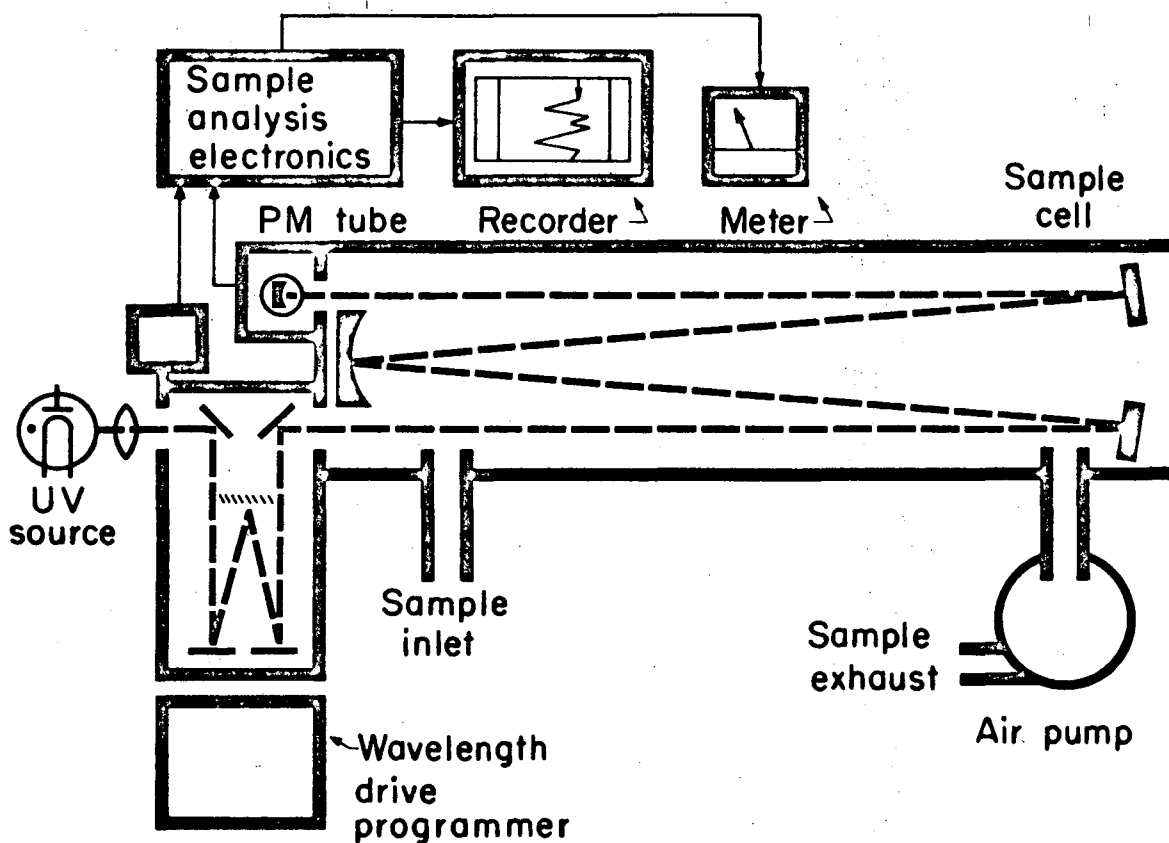
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Fig. 12 Dispersive Infrared Absorption Spectrometer (Chrysler Corporation)



XBL726-3106

Fig. 13 Correlation Spectrometer (Barringer Research Limited)



XBL726-3107

Fig. 14 Second Derivative Spectrometer (Spectrometrics, Lear Siegler Incorporated)

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