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The Earth's atmosphere is a mixture of gases, water and organic vapors, and particulate matter held in suspension. The modification of the composition of the atmosphere, as a by-product of advancing technology, is of considerable concern because of the adverse effects on human health and welfare. The background and urban concentrations and sources of selected atmospheric pollutants are given in Table 1. Specific source contributions to air pollution in the United States in 1970 are shown in Figure 1. The alarming deterioration of the quality of the air we breathe has forced us in the last few years to critically examine air pollution. An intensive effort has been expended in the last decade, and especially in the last five years, to understand the causes of air pollution, its effects and the means for its control and abatement.

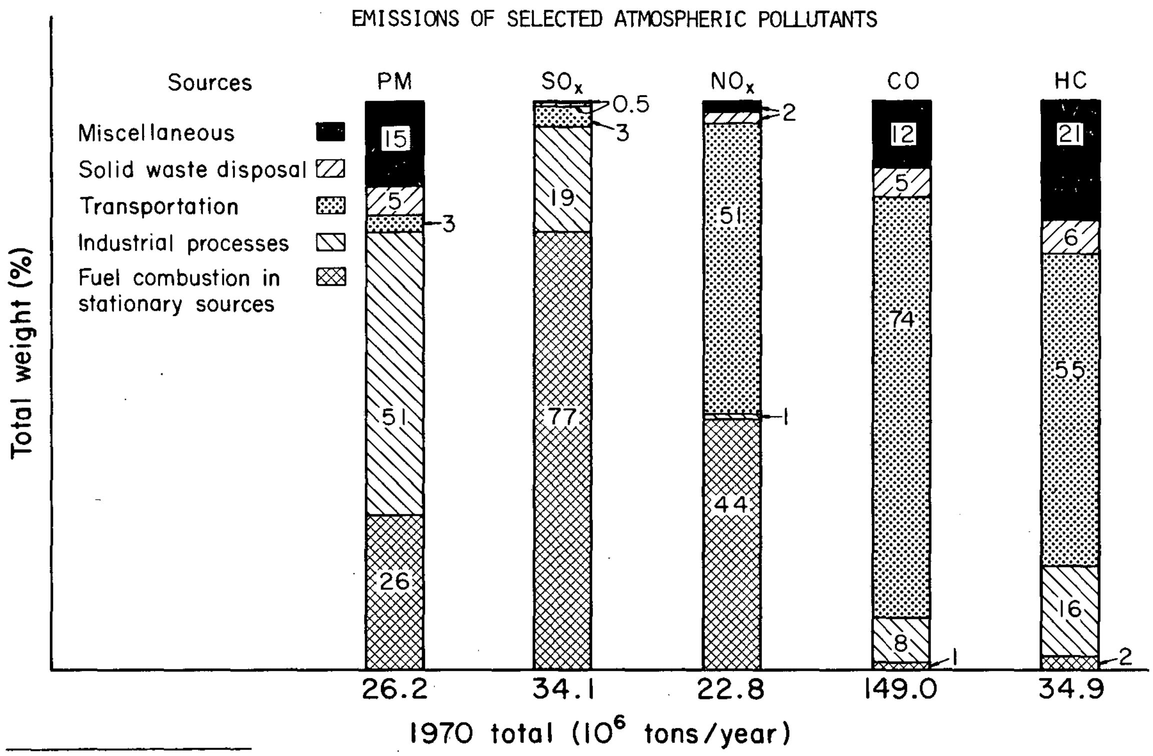
Air monitoring is the difficult task of measuring the status of the air quality and the changes and trends in the quality of the air. Air monitoring is a requisite for the control and prevention of air pollution. The data base derived from air monitoring is required to: (1) assess existing air quality, (2) study pollutant interactions, patterns and trends, (3) determine the effects of air pollution on man and his environment, (4) establish air quality standards, (5) evaluate compliance with, or progress made toward, meeting existing air quality standards, (6) develop abatement tactics and control regulations, (7) enforce control regulations, (8) activate emergency procedures to prevent air pollution episodes, and (9) guide future land use, energy systems, and transportation planning. Monitoring the nation's air quality is the responsibility of federal, state and local agencies. Development of an air quality data base requires decisions regarding the pollutants to be measured and the monitoring facilities, the number and types of monitoring sites needed, their location, choice of instrumentation, frequency and methods of sampling and calibration, etc.

The objective of this paper is to describe the current methods in air quality measurements and monitoring. Obviously only a brief discussion of this quite large and rather complex subject can be given here. More complete information on current instrumentation and principles of operation can be found in Instrumentation for Environmental Monitoring, AIR.[1]

TABLE 1.

BACKGROUND CONCENTRATIONS AND SOURCES OF SELECTED ATMOSPHERIC POLLUTANTS

POLLUTANT	MAJOR SOURCES		BACKGROUND CONCENTRATION	TYPICAL URBAN CONCENTRATION (ANNUAL MEAN)
	MAN MADE	NATURAL		
PARTICULATE MATTER	COMBUSTION	VOLCANOES, SOIL, SEA SALT	1-30 $\mu g/m^3$	100 $\mu g/m^3$
SO_2	COMBUSTION OF COAL & OIL	VOLCANOES	0.0002-0.0004 PPM	0.03 PPM
NO_2	COMBUSTION	BACTERIAL ACTION	0.001-0.003 PPM	0.05 PPM
OZONE	PHOTOCHEMICAL REACTIONS	ATMOSPHERIC ELECTRICAL DISCHARGE	0.01 PPM	0.03 PPM
CO	AUTO EXHAUST AND OTHER COMBUSTION	FOREST FIRES	0.1 PPM	4 PPM
HYDROCARBONS:	COMBUSTION, EXHAUST, CHEMICAL PROCESSES	BIOLOGICAL PROCESSES		
NON-CH_4			< 0.001 PPM	0.5 PPM
CH_4			1-1.5 PPM	2 PPM



PM = PARTICULATE MATTER
SO_X = TOTAL OXIDES OF SULFUR
NO_X = TOTAL OXIDES OF NITROGEN
CO = CARBON MONOXIDE
HC = HYDROCARBONS

FIGURE 1.

National Air Pollution Standards

In order to put the various monitoring requirements in perspective, a brief review of the current national air quality and emission standards is appropriate. 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 within areas as shown in Table 2.

National Primary and Secondary Air Quality Standards were promulgated on April 30, 1971.[2] Primary standards to protect public health and secondary standards to protect public welfare (against effects on, e.g., vegetation, animals, materials) were promulgated for particulate matter, sulfur dioxide, nitrogen dioxide, photochemical oxidants, carbon monoxide, and hydrocarbons. The regulations also include reference methods for measuring the six pollutants. Primary ambient air standards are listed in Table 3.

The EPA is responsible for promulgating regulations on stationary source emissions for facilities built after the regulations take effect for the purpose of controlling emissions which may contribute significantly to air pollution covered under the ambient air quality standards. Standards of Performance for New Stationary Sources were promulgated on December 23, 1971,[3] for five types (referred to as

TABLE 2.

CATEGORIES OF
NATIONAL AIR POLLUTION STANDARDS

AMBIENT AIR STANDARDS
NATIONAL PRIMARY AND SECONDARY AIR QUALITY STANDARDS
STATIONARY SOURCE EMISSION STANDARDS
STANDARDS OF PERFORMANCE FOR NEW STATIONARY SOURCES
NATIONAL EMISSIONS STANDARDS FOR HAZARDOUS AIR POLLUTANTS
MOBILE SOURCE EMISSION STANDARDS
CONTROL OF AIR POLLUTION FROM NEW MOTOR VEHICLES AND NEW MOTOR VEHICLE ENGINES
CONTROL OF AIR POLLUTION FROM AIRCRAFT AND AIRCRAFT ENGINES

TABLE 3.

NATIONAL PRIMARY AMBIENT AIR QUALITY STANDARDS*

POLLUTANT	AVERAGING TIME	CONCENTRATION		REFERENCE METHOD
		μG/M³	PPM	
PARTICULATE MATTER	24 HR	260	–	HIGH VOLUME SAMPLING METHOD
	ANNUAL GEOMETRIC MEAN	75	–	
SULFUR DIOXIDE	24 HR	365	0.14	PARAROSANILINE METHOD
	ANNUAL ARITHMETIC MEAN	80	0.03	
NITROGEN DIOXIDE	ANNUAL ARITHMETIC MEAN	100	0.05	NEW REFERENCE METHOD UNDER STUDY
PHOTOCHEMICAL OXIDANTS (CORRECTED FOR NO_2 & SO_2)	1 HR	160	0.08	GAS PHASE CHEMILUMINESCENT METHOD
CARBON MONOXIDE	1 HR	40,000	35	NON-DISPERSIVE INFRARED SPECTROSCOPY
	8 HR	10,000	9	
HYDROCARBONS (NONMETHANE)	3 HR (6 TO 9 A.M.)	160	0.24	FLAME IONIZATION DETECTION USING GAS CHROMATOGRAPHY

* NATIONAL STANDARDS OTHER THAN THOSE BASED ON ANNUAL ARITHMETIC MEANS OR ANNUAL GEOMETRIC MEANS ARE NOT TO BE EXCEEDED MORE THAN ONCE PER YEAR.

Category I) of new and modified stationary sources (Table 4). On March 8, 1974,[4] the EPA published standards of performance of seven additional types (Category II) of stationary sources (see Table 5). In October, 1974,[5,6,7,8,9,10] standards of performance for additional sources (Category III) were proposed (Table 6).

The stationary source regulations include measurement methods for determining emissions. Two types of measurements are prescribed in the regulations: compliance test methods and continuous methods. The compliance test method (reference method) is a discrete measurement to verify that the emissions from the industry are in compliance with the emission standards. Compliance test measurement requirements for Categories I, II and III industries are given in Tables 4, 5, and 6, respectively. The actual compliance test measurement methods for the specific pollutants are given in Table 7. Continuous methods are required mainly in support of regulations requiring industry to maintain proper operation. Specific instrumentation for continuous monitoring is not specified in the regulations.

Hazardous air pollutants are defined as those materials discharged into the atmosphere to which no ambient air quality applies and which may cause, or contribute to, an increase in mortality or an increase in serious irreversible or incapacitating reversible illness. They are so serious that there are direct federal controls on their emissions into the air from existing plants. The EPA has identified and promulgated on April 6, 1973,[11] national emission standards for three hazardous air pollutants:

Asbestos	No visible emissions
Beryllium	10 g/day or 10 ng/m³
Mercury	20 μg/day or 1 μg/m³

The particular operations and facilities affected and the reference methods of measurement are given in Table 8.

The EPA is also charged with promulgating mobile source emission standards. Mobile sources for which emission standards have been established and the reference methods of measurements are given in Table 9.[12,13,14]

Air Monitoring Systems

Air pollution analysis has been traditionally carried out by wet chemical manual methods. Due to the time consumption in analysis, the care required in handling reagents and the need for highly trained personnel, many of these methods have been superseded

TABLE 4.

STANDARDS OF PERFORMANCE FOR NEW AND MODIFIED STATIONARY SOURCES (CATEGORY I - PROMULGATED)

POLLUTANT	MEASUREMENT REQUIREMENTS FOR INDICATED SOURCES				
	POWER PLANTS	CEMENT PLANTS	INCINERATORS	SULFURIC ACID PLANTS	NITRIC ACID PLANTS
PARTICULATES (MASS)	X	X	X		
SULFUR DIOXIDE (MANUAL)	X			X	
NITROGEN OXIDES	X				X
SULFURIC ACID & OXIDES OF SULFUR				X	
VISIBLE EMISSIONS	X	X		X	X
CARBON MONOXIDE					
HYDROGEN SULFIDE IN FUEL					
SULFUR DIOXIDE (CONTINUOUS)					
FLUORIDES					

TABLE 5.

STANDARDS OF PERFORMANCE FOR NEW AND MODIFIED STATIONARY SOURCES (CATEGORY II - PROMULGATED)

POLLUTANT	MEASUREMENT REQUIREMENTS FOR INDICATED SOURCES						
	ASPHALT CONCRETE PLANTS	PETROLEUM REFINERIES	PETROLEUM STORAGE VESSELS*	BRASS & BRONZE MILLS	IRON & STEEL MILLS (BOF)	SEWAGE TREATMENT PLANTS	SECONDARY LEAD SMELTERS & REFINERIES
PARTICULATES (MASS)	X	X		X	X	X	X
SULFUR DIOXIDE (MANUAL)		X					
NITROGEN OXIDES							
SULFURIC ACID AND OXIDES OF SULFUR							
VISIBLE EMISSIONS	X	X		X	X	X	X
CARBON MONOXIDE		X					
HYDROGEN SULFIDE IN FUEL		X					
SULFUR DIOXIDE (CONTINUOUS)							
FLUORIDES							

* STANDARDS FOR PETROLEUM STORAGE VESSEL SPECIFY APPROPRIATE TYPES OF VESSELS FOR VARIOUS STROAGE PRESSURES; EMISSIONS MEASUREMENTS ARE NOT REQUIRED.

by automated instrumental methods. Of course, manual wet chemical methods are still employed as standard reference methods in many cases. In this paper we will discuss only instrumental methods and not the wet chemical manual methods.

Although the instrumental method is necessary for the actual pollutant measurement, it is never sufficient by itself. The concept of the complete monitoring system should also be appreciated. The term "system" here may refer to a physically integrated collection of instruments that performs all steps in the monitoring operation, or it may refer to an organized sequence of procedures intended to accomplish the monitoring operation. Depending upon the specific application, systems vary widely in requirements and complexities. Nevertheless, there are basic building blocks which serve for sampling, analysis, calibration and data acquisition, reduction and interpretation. Each is equally important, and the entire monitoring system must be fully understood to define its capabilities and limitations.

Air monitoring systems may be divided into two classes: manual and automatic. Manual operation

TABLE 6.

STANDARDS OF PERFORMANCE FOR NEW AND MODIFIED STATIONARY SOURCES (CATEGORY III - PROPOSED)

POLLUTANT	MEASUREMENT REQUIREMENTS FOR INDICATED SOURCES							
	PRIMARY COPPER SMELTERS	PRIMARY ZINC SMELTERS	PRIMARY LEAD SMELTERS	PRIMARY ALUMINUM REDUCTION PLANTS	PHOSPHATE FERTILIZER INDUSTRIES (5 CATEGORIES)	COAL PREPARATION PLANTS	STEEL PLANTS: ELECTRIC ARC FURNACES	FERROALLOY PRODUCTION FACILITIES
PARTICULATES (MASS)	X	X	X			X	X	X
SULFUR DIOXIDE (MANUAL)								
NITROGEN OXIDES								
SULFURIC ACID & OXIDES OF SULFUR								
VISIBLE EMISSIONS	X	X	X	X	X	X	X	X
CARBON MONOXIDE								X
HYDROGEN SULFIDE IN FUEL								
SULFUR DIOXIDE (CONTINUOUS)	X	X	X					
FLUORIDES				X	X			

implies human involvement in order to progress from one step in the system to another; automatic operation implies that essentially all 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 and techniques will not be discussed in detail in this paper.

TABLE 7.

COMPLIANCE TEST METHODS FOR STATIONARY SOURCE MONITORING (REFERENCE METHODS)

POLLUTANT	SAMPLING AND ANALYSIS TECHNIQUES
PARTICULATES (MASS)	FILTER, SAMPLING TRAIN; GRAVIMETRIC ANALYSIS
SULFUR DIOXIDE (MANUAL)	IMPINGERS, BARIUM REAGENT; THORIN TITRATION
NITROGEN OXIDES	EVACUATED FLASK, PHENOLDISULFONIC ACID REAGENT; COLORIMETRIC ANALYSIS
SULFURIC ACID & OXIDES OF SULFUR	IMPINGERS, BARIUM REAGENT; THORIN TITRATION
VISIBLE EMISSIONS	HUMAN OBSERVER
CARBON MONOXIDE	NONDISPERSIVE INFRARED (NDIR)
HYDROGEN SULFIDE IN FUEL	IMPINGERS, REAGENT; TITRATION FOR IODINE
SULFUR DIOXIDE (CONTINUOUS)	EXTRACTIVE OR IN SITU SAMPLING; CONTINUOUS INSTRUMENTAL ANALYSIS*
FLUORIDES	IMPINGERS, FILTER, SPADNS MIXED REAGENT; COLORIMETRIC ANALYSIS* OR IMPINGERS, FILTER; SPECIFIC ION ELECTRODE ANALYSIS*

*PROPOSED METHODS

In continuous analyzing systems 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 electronic processing delays may be involved. A nondispersive spectrophotometer is an example of an instrument which operates on a continuous basis.

Semi-continuous analyzing systems are those where a representative fraction (sample) of the unknown is taken and analyzed and the process automatically repeated on a regular basis. Ideally the analyzing period is sufficiently short so that only small changes take place before another sample is measured. A gas chromatograph operating in a cyclic mode and combined with a detector may be considered an instrument which operates on a semi-continuous basis.

Monitoring systems can be designated as those suitable for three types of monitoring: ambient air monitoring, stationary source monitoring, and mobile

TABLE 8.

NATIONAL EMISSIONS STANDARDS FOR HAZARDOUS AIR POLLUTANTS

POLLUTANT	SOURCES	REFERENCE METHOD
BERYLLIUM	BERYLLIUM EXTRACTION PLANTS BERYLLIUM METAL & ALLOY MACHINE SHOPS BERYLLIUM FOUNDRIES BERYLLIUM CERAMIC PLANTS ROCKET MOTOR FIRING FACILITIES	FILTER, SAMPLING TRAIN; ATOMIC ABSORPTION
MERCURY	MERCURY ORE PROCESSING FACILITIES MERCURY CHLOR-ALKALI CELL PLANTS	IMPINGER, REAGENT; SPECTROPHOTOMETRIC ANALYSIS
ASBESTOS	ASBESTOS MILLS ROADWAYS MANUFACTURING PLANTS DEMOLITION OPERATIONS SRAYING OPERATIONS	EMISSION STANDARD BASED ON EQUIPMENT

TABLE 9.

MOBILE SOURCE EXHAUST EMISSION STANDARDS

POLLUTANT	MOBILE SOURCE						
	MOTORCYCLES*	GASOLINE-FUELED AND DIESEL POWERED PASSENGER CARS AND LIGHT DUTY TRUCKS	GASOLINE-FUELED HEAVY DUTY ENGINES	DIESEL-POWERED HEAVY DUTY ENGINES	TURBINE AIRCRAFT ENGINES	PISTON AIRCRAFT ENGINES	REFERENCE METHOD
CARBON MONOXIDE	X	X	X	X	X	X	NONDISPERSIVE INFRARED ABSORPTION ANALYSIS
HYDROCARBONS	X	X	X**	X	X	X	FLAME IONIZATION DETECTION
NITROGEN OXIDES	X	X	X**	X**	X	X	CHEMILUMINESCENCE ANALYSIS
SMOKE				X	X		LIGHT EXTINCTION METER (TRUCKS); FILTER, REFLECTOMETER ANALYSIS (AIRCRAFT)

*PROPOSED STANDARDS.

**NDIR IS REFERENCE METHOD.

source monitoring. Typical gaseous pollutant monitoring system configurations for ambient air, stationary source and mobile source applications are illustrated in Figures 2, 3, and 4, respectively. The discussion below applies specifically to gaseous pollutant monitoring systems, however, the general concepts apply to particulate monitoring systems also.

Manual ambient air monitoring systems involve ambient sampling by mechanical devices followed by laboratory analysis; examples of mechanical sampling devices are gas bubblers and colorimetric length-of-stain indicators.

Automatic ambient air monitoring systems may be: (1) of the point sampling type in which a discrete sample is extracted from the ambient air and analyzed on-site with an automatic analyzer (e.g., spectrophotometric instrument); or (2) long-path monitoring in which analysis is by double-ended optical methods (e.g., laser resonance absorption).

Manual stationary source monitoring systems involve sampling with devices of the mechanical type such as gas bubblers. The analysis is performed in a laboratory usually removed from the sampling site.

Automatic stationary source monitoring systems may be: (1) the extractive type in which a sample is extracted from the stack and analyzed on-site, usually with an automatic analyzer; (2) the in-situ type in which analysis is by across-the-stack optical methods; (3) the remote monitoring type in which analysis is by single-ended optical methods, and monitoring is of a remote point such as a stack plume; or (4) the long-path monitoring type in which analysis is by double-ended optical methods, and monitoring is between two points such as across the envelope of a plume.

Mobile source emissions monitoring systems are those suitable for analyzing the exhaust from, for example, automobiles operating in the field or brought

MONITORING APPROACHES FOR AMBIENT AIR

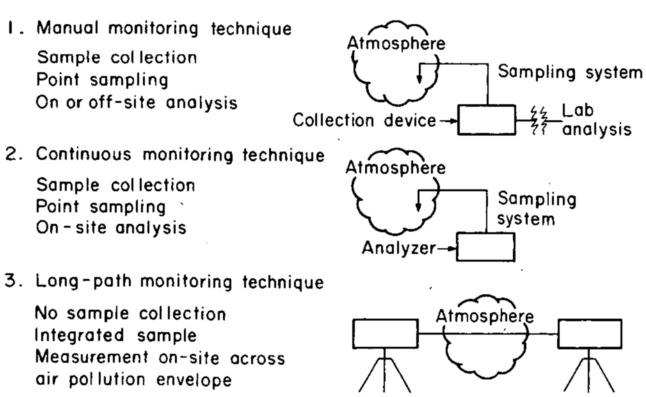


FIGURE 2.

MONITORING APPROACHES FOR STATIONARY SOURCES

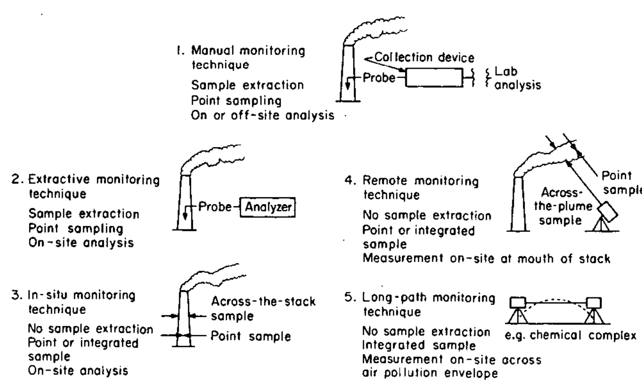


FIGURE 3.

to a laboratory. Manual systems are most often used in certification testing (bag sampling with subsequent automated analysis by a laboratory). Automatic systems are typically of the type used for diagnostic purposes in automotive maintenance and surveillance (usually with exhaust probe sampling). Recently, however, automatic certification testing systems (with bag sampling) have appeared on the market. Automatic remote systems are under development.

MONITORING APPROACHES FOR MOBILE SOURCES

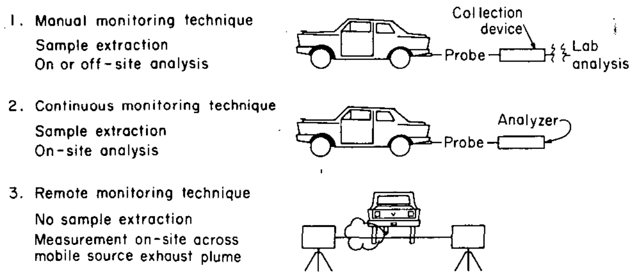


FIGURE 4.

Instrumentation for Air Pollution Measurements

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. We will now focus our attention on the various types of continuous and semi-continuous instrumentation currently commercially available for air pollution monitoring. We shall restrict our discussion to those major pollutants for which national air quality standards have been established.

The measuring instrument (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; sampling lines; conditioning units to dry, heat, cool, or otherwise pretreat the sample before analysis; selective filters to remove gases or particulate matter 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.

Of primary concern are the performance and durability of the complete system. The performance is governed by such factors as lower detectable limit, interferences, and accuracy. It will usually be necessary to settle for less than maximum performance because of financial limitations in manpower available for operation, 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. Many factors must be considered in the selection of instrumentation for air pollution monitoring. The most important are listed in Table 10.

Tables 11 through 15 list the types of monitoring instrumentation that are currently available for air pollution analysis. The measurement principles range from automated wet chemical analyses to sophisticated spectroscopic techniques. Only those methods commonly

TABLE 10.

FACTORS AFFECTING CHOICE OF MONITORING INSTRUMENTATION

RANGE	POWER REQUIREMENTS
LOWER DETECTABLE LIMIT	SPACE AND WEIGHT REQUIREMENTS
ACCURACY	TEMPERATURE AND HUMIDITY REQUIREMENTS
PRECISION	SET-UP TIME
ZERO AND SPAN DRIFT	SERVICEABILITY
LAG TIME	RUGGEDNESS IN MONITORING ENVIRONMENT
RISE AND FALL TIME	SPECIAL OPERATOR TRAINING REQUIRED
INTERFERENCES	LEASING AND SERVICE CONTRACTS AVAILABLE
COST	SAFETY OF EQUIPMENT AND REAGENTS
PORTABILITY	
CALIBRATION METHOD	
SIGNAL OUTPUT	
INTERFACING SYSTEM NEEDS	

in use today and their principle applications (ambient, stationary source, mobile source) are given here. Methods listed in Tables 14 and 15 are used in all three types of monitoring applications.

The most frequently used monitoring instrumentation for the major gaseous pollutants and physical characterization of particulates are highlighted in the discussion below. The pollutants (either SO_2, NO_x, oxidants, CO, hydrocarbons -- abbreviated as HC, or particulates) which can be monitored by a specific technique are indicated. NO_x refers to total oxides of nitrogen; however, analyzers may be specific for NO, NO_2, or both. Oxidant measurements when corrected for NO_2 and SO_2, are primarily an indication of ozone.

Colorimetric analyzers measure a solution's optical absorbance spectrophotometricaly to obtain an indication of the pollutant (SO_2, NO_x, oxidants) concentration in the sampled air (see Figure 5). The pollutant is dissolved in an aqueous solution by bubbling the sample through the reagent and then chemically complexed to form a highly colored compound. Within limitations, the absorbance is linearly proportional to the concentration of the colored species.

COLORIMETRIC ANALYZER

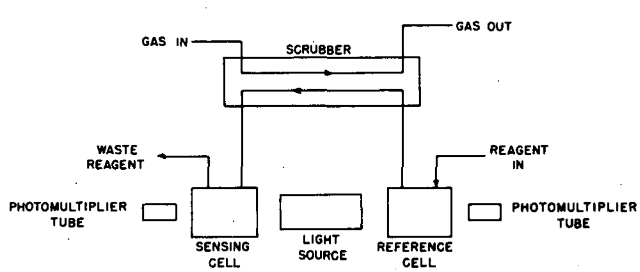


FIGURE 5.

TABLE 11.

GASEOUS POLLUTANT MONITORING INSTRUMENTATION

MEASUREMENT PRINCIPLE	MONITORING APPLICATION		
	AMBIENT AIR	STATIONARY SOURCE	MOBILE SOURCE
<u>SO_2 MONITORING INSTRUMENTATION</u>			
COLORIMETRIC METHOD (UV-VIS SPECTROPHOTOMETRY)	X		
CONDUCTIMETRIC METHOD	X		
ELECTROCHEMICAL METHOD	X	X	
FLAME PHOTOMETRIC DETECTION (FPD)	X		
GAS-CHROMATOGRAPHY - FLAME PHOTOMETRIC DETECTION (GC-FPD)	X		
NONDISPERSIVE INFRARED ABSORPTION (NDIR)		X	
DISPERSIVE INFRARED ABSORPTION (DIR)		X	
UV ABSORPTION SPECTROPHOTOMETRY		X	
UV FLUORESCENCE SPECTROPHOTOMETRY		X	
<u>NO/NO_2 MONITORING INSTRUMENTATION</u>			
COLORIMETRIC METHOD (UV-VIS SPECTROPHOTOMETRY)	X		
ELECTROCHEMICAL METHOD	X	X	
CHEMILUMINESCENCE	X	X	X
NONDISPERSIVE INFRARED ABSORPTION (NDIR)		X	X
UV-VIS ABSORPTION SPECTROPHOTOMETRY		X	
<u>PHOTOCHEMICAL OXIDANTS MONITORING INSTRUMENTATION</u>			
COLORIMETRIC METHOD (UV-VIS SPECTROPHOTOMETRY)	X		
ELECTROCHEMICAL METHOD	X		
CHEMILUMINESCENCE	X		
UV ABSORPTION SPECTROPHOTOMETRY	X		
<u>CO MONITORING INSTRUMENTATION</u>			
ELECTROCHEMICAL METHOD	X		
CATALYTIC OXIDATION - THERMAL DETECTION	X		X
GAS CHROMATOGRAPHY-FLAME IONIZATION DETECTION (GC-FID)	X		
NONDISPERSIVE INFRARED ABSORPTION (NDIR)	X	X	X
DISPERSIVE INFRARED ABSORPTION (DIR)		X	X
<u>HYDROCARBON MONITORING INSTRUMENTATION</u>			
FLAME IONIZATION DETECTION (FID)	X	X	X
CATALYTIC OXIDATION - FLAME IONIZATION DETECTION	X		
GAS CHROMATOGRAPHY-FLAME IONIZATION DETECTION (GC-FID)	X	X	X
NONDISPERSIVE INFRARED ABSORPTION (NDIR)		X	X
DISPERSIVE INFRARED ABSORPTION (DIR)			X

Chemiluminescent analyzers are based on the emission characteristics of a molecular species formed in the reaction between the gas pollutant (NO_x, or oxidants measured as ozone) being monitored and a gas or solid species (see Figure 6). Ozone, when allowed to react on a surface (e.g., organic dye on silica gel), with NO or ethylene gas, produces chemiluminescence which is measured with a photomultiplier tube. This reaction is specific for ozone. To monitor NO, the sample is reacted with ozone to give excited NO_2 which proceeds to the ground state with the emission of radiant energy, measured with a photomultiplier tube.

Flame photometric detection (FPD) analyzers measure the emissions from sulfur compounds introduced into hydrogen-rich flame (Figure 7). A narrow-band optical filter selects the 394 nanometer S_2 emission band. For SO_2 monitoring, FPD analyzers are susceptible to interference from other sulfur compounds.

TABLE 12.

PARTICULATE MASS MONITORING INSTRUMENTATION

MEASUREMENT PRINCIPLE	MONITORING APPLICATION	
	AMBIENT AIR	STATIONARY SOURCE
FILTER COLLECTION/GRAVIMETRIC ANALYSIS	X	X
BETA RADIATION ATTENUATION	X	X
PIEZOELECTRIC MICROBALANCE	X	X
NEPHELOMETRY	X	

TABLE 13.

OPACITY MONITORING INSTRUMENTATION

MEASUREMENT PRINCIPLE	MONITORING APPLICATION	
	AMBIENT AIR	STATIONARY SOURCE
VISUAL OBSERVATION		X
PAPER TAPE METHOD	X	
LIGHT TRANSMISSION		X
NEPHELOMETRY	X	

TABLE 14.

PARTICULATE SIZE MONITORING INSTRUMENTATION

MEASUREMENT PRINCIPLE
SEDIMENTATION
CENTRIFUGATION
IMPACTION
SINGLE PARTICLE OPTICAL COUNTING
ELECTRICAL MOBILITY ANALYSIS
MICROSCOPY (OPTICAL AND ELECTRON)

TABLE 15.

PARTICULATE CHEMICAL COMPOSITION INSTRUMENTATION

MEASUREMENT PRINCIPLE
INORGANICS
COLORIMETRIC METHOD (UV-VIS SPECTROPHOTOMETRY)
ION-SELECTIVE ELECTRODE METHOD
ATOMIC ABSORPTION AND EMISSION SPECTROPHOTOMETRY
NEUTRON ACTIVATION ANALYSIS
X-RAY FLUORESCENCE ANALYSIS
ELECTRON SPECTROSCOPY FOR CHEMICAL ANALYSIS
ORGANICS
UV ABSORPTION AND FLUORESCENCE SPECTROSCOPY
GAS CHROMATOGRAPHY
GAS CHROMATOGRAPHY - MASS SPECTROMETRY

Although H_2S, H_2SO_4, and mercaptans are commonly found in the atmosphere, their contribution to the total sulfur content is usually 5% or less and can thus usually be neglected. However, if sulfur compounds other than SO_2 are present in appreciable concentrations, gas chromatography-flame photometric detection (GC-FPD) analyzers can be used to distinguish the sulfur compounds.

The sensor which is involved in over 90% of the hydrocarbon monitoring systems in use today is the flame ionization detector (FID). In some cases, it is used in a system which makes no attempt to separate the various hydrocarbons. These systems

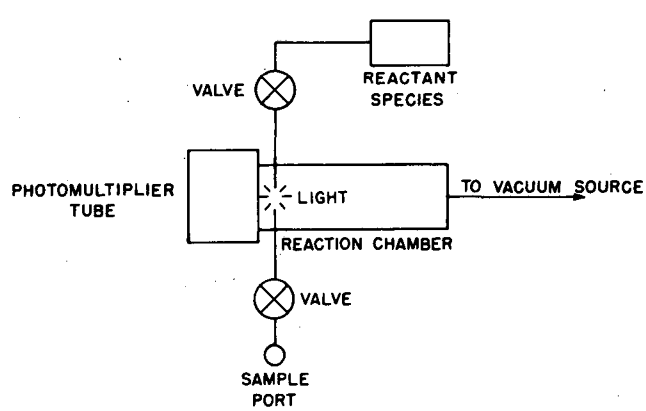


FIGURE 6.

FLAME PHOTOMETRIC DETECTOR.

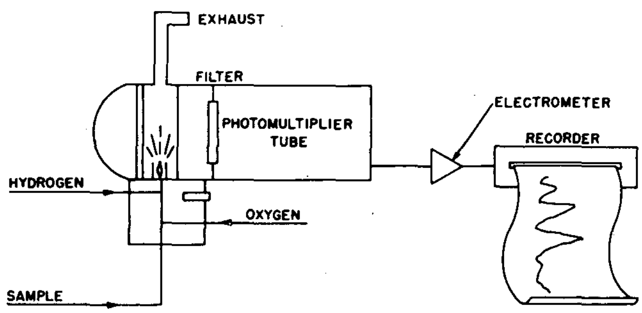


FIGURE 7.

are referred to as total HC monitors. In about an equal number of cases, this detector is used as the sensor following gas chromatographic separation. In addition, this sensor has been used as a CO detector by first converting the CO to CH_4.

In the FID analyzer, the sample is introduced into a combustion region created by the reaction of hydrogen with a surplus of oxygen (see Figure 8). The combustion occurs between electrodes which have a voltage drop of a few hundred volts between them (polarization voltage). Negatively ionized combustion fragments are attracted to the anode which results in an electrical current whose magnitude is related to the concentration of hydrocarbons introduced into the sensor. Catalytic oxidation-flame ionization detection analyzers have been developed to separate methane

FLAME IONIZATION DETECTOR

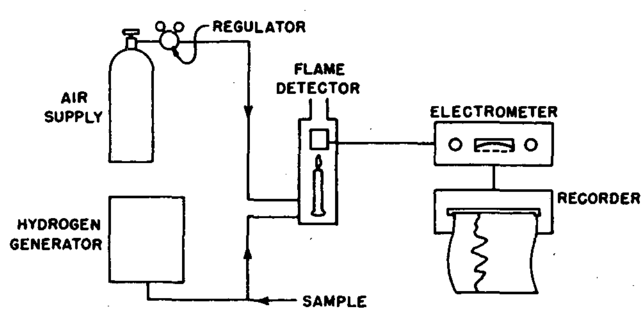


FIGURE 8.

from total hydrocarbons. A dual flame design permits measurements of two flow streams, one containing total hydrocarbons and the other containing only methane following catalytic oxidation of all other hydrocarbons to CO_2.

Gas chromatography-flame ionization detection (GC-FID) is another approach in instrumentation to separate methane from total hydrocarbons. The GC column is packed with an inert solid support upon which is distributed a thin layer of 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 the differing affinities for the liquid solvent. This method of operation requires intermittent sampling, since a few minutes is required for passage through the column.

A nondispersive absorption spectrometer is an instrument which is based on broad-band spectral absorption and which is sensitized for a particular gas -- SO_2, NO_x, CO, HC -- 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.

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 (SO_2, NO_x, CO or HC) 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.

Typical nondispersive infrared (NDIR) analyzers use infrared radiation from filaments directed onto two cells: a reference cell filled with a noninfrared absorbing gas, such as nitrogen or argon, and a sample cell through which the sample air is continuously drawn (see Figure 9).

Several instruments designed for ultraviolet and visible nondispersive absorption employ a double-beam arrangement through two cells (reference and sample) and a photomultiplier tube for detection of SO_2, NO_x, or oxidants. Some instruments base their operation on the measurement of the difference in absorption

NONDISPERSIVE INFRARED ABSORPTION ANALYZER

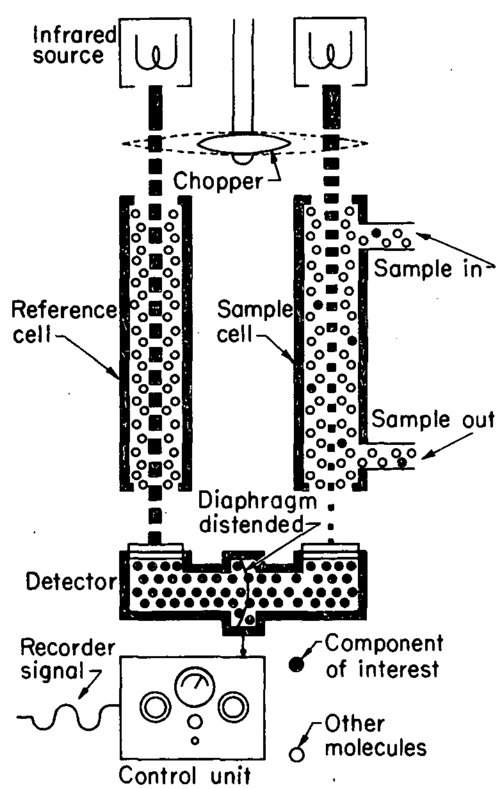


FIGURE 9.

by the sample at two separate wavelengths, the absorbing wavelength of the pollutant and a nonabsorbing wavelength (see Figure 10).

NONDISPERSIVE ULTRAVIOLET AND VISIBLE ABSORPTION ANALYZER

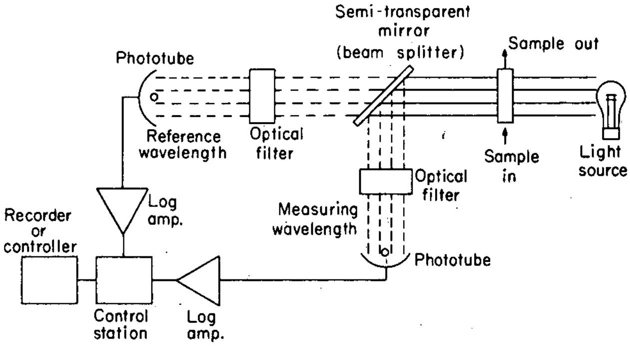


FIGURE 10.

High volume (Hi-Vol) air samplers are designed for the collection of suspended particulates in outdoor environments (see Figure 11). Their importance lies in the fact that they have been the workhorse of particulate mass and chemical composition determinations. The samplers normally operate for 24-hour periods (or longer), with flow rates ranging from 30 to 50 CFM, and collect particles on filter media. The particulates collected on the filter are analyzed gravimetrically for particulate mass and occasionally analyzed for their chemical composition.

HIGH-VOLUME PARTICULATE SAMPLER

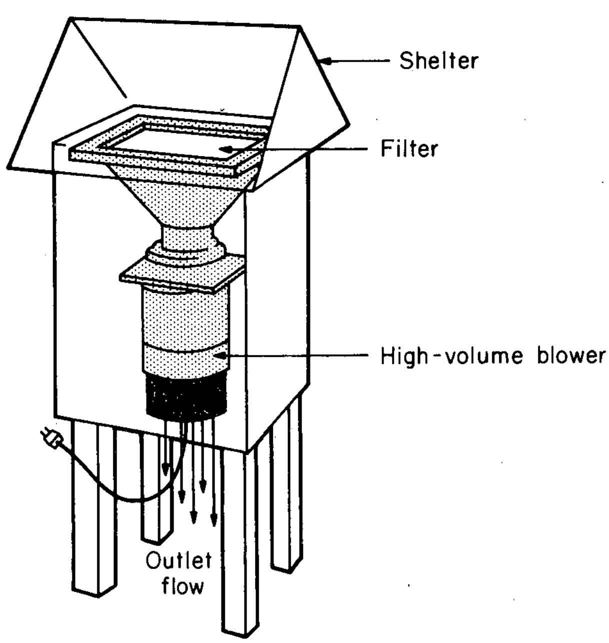


FIGURE 11.

Until very recently, innovative trends in instrumentation for the measurement of particulate matter have not kept pace with the advances made in gaseous air pollutant monitoring. Two types of instruments developed within the last few years have the necessary sensitivity to measure directly mass concentrations in real time. These use the beta radiation absorption and piezoelectric microbalance techniques.

The beta radiation absorption instrumental technique is based on the measurement of the attenuation of beta radiation as it traverses a layer of deposited particulate matter (Figure 12). The beta-attenuation or absorption process has the property that the penetration of low-energy beta radiation (e.g., carbon-14 and promethium-147 are good sources for this purpose) depends almost exclusively on the area density of the absorbing material and on the maximum energy of the impinging electrons, but is independent of the chemical composition of the absorbing substances.

BETA RADIATION ATTENUATION PARTICULATE MASS ANALYZER

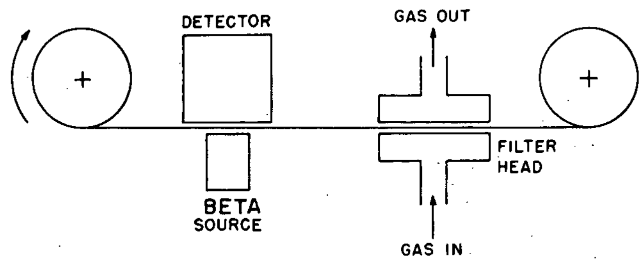


FIGURE 12.

In a piezoelectric microbalance instrument, particles are deposited on a peizoelectric quartz crystal (Figure 13). The crystal forms part of a resonant circuit, whose frequency is controlled by the mechanical resonant frequency of the crystal, which is in turn a function of the deposited mass on the crystal surface. The resonant frequency is inversely proportional to the deposited mass for small mass variations. In practice, the change in resonant

PIEZOELECTRIC MICROBALANCE PARTICULATE MASS ANALYZER

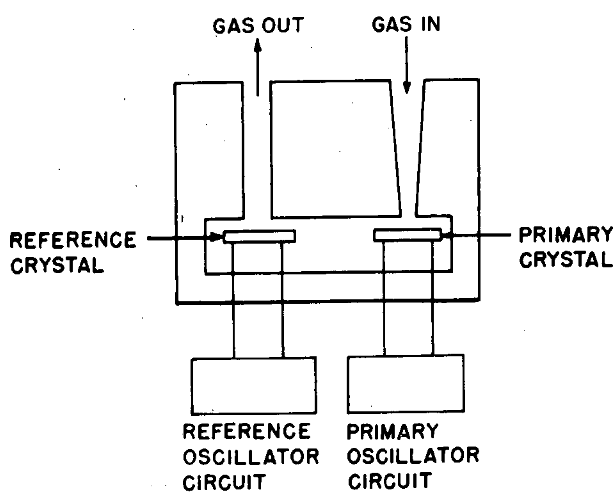


FIGURE 13.

frequency is detected by the change in the beat frequency, created by mixing the sensing crystal signal with that from a reference crystal with a slightly higher frequency. An increase in mass, therefore, results in an increase in the beat frequency.

There is considerable interest in particulate sizing instrumentation in order to ascertain the size distribution of particulates. Particulates found in ambient air exhibit a bimodal distribution: those above 2 microns originate from natural sources and those below 2 microns are from man-made combustion sources and represent also the respirable fraction of total particulates. It is therefore desirable to determine the size distribution for health reasons and for source identification studies.

The most highly developed and frequently used device for particulate size distribution determinations is the impactor. There are several different designs commercially available; two types often used are the Anderson cascade impactor head for Hi-Vol samplers and the Lundgren impactor. The Anderson unit uses multijet impaction stages (Figures 14 and 15) and operates at a sampling rate of 20 CFM. The Lundgren impactor uses rotating, drum-shaped collection surfaces (Figure 16), which increase the available areas of the various stages for particle impaction and permit the evaluation of collected particles as a function of sampling time.

Opacity meters, usually referred to as transmissometers, continuously measure the relative opacity of stack gas streams (Figure 17). The optical system normally has an optical head assembly and a retroreflector assembly or detection unit that is mounted directly opposite the head in a stack. Opacity measurements are made by means of a modulated light beam, and are displayed as a direct percentage (0-100%) with a typical accuracy of 3%.

It is obvious from the above discussion that a multitude of instrumental techniques have been applied

HIGH-VOLUME CASCADE IMPACTOR WITH BACKUP FILTER FOR SAMPLING ATMOSPHERIC PARTICULATES

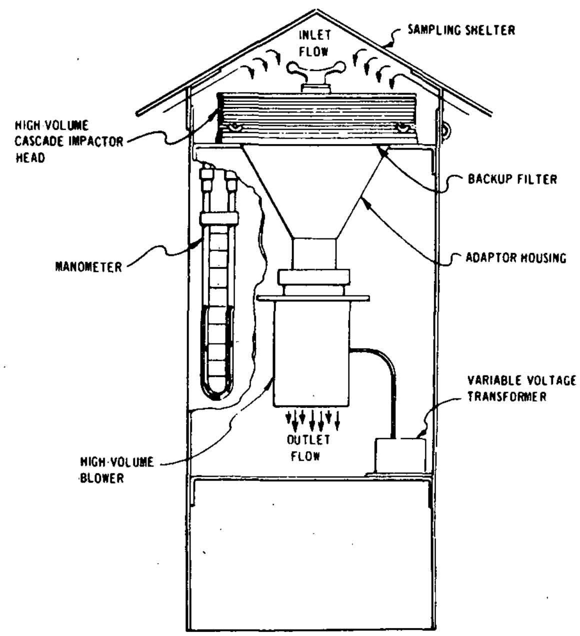


FIGURE 14.

HIGH-VOLUME CASCADE IMPACTOR HEAD

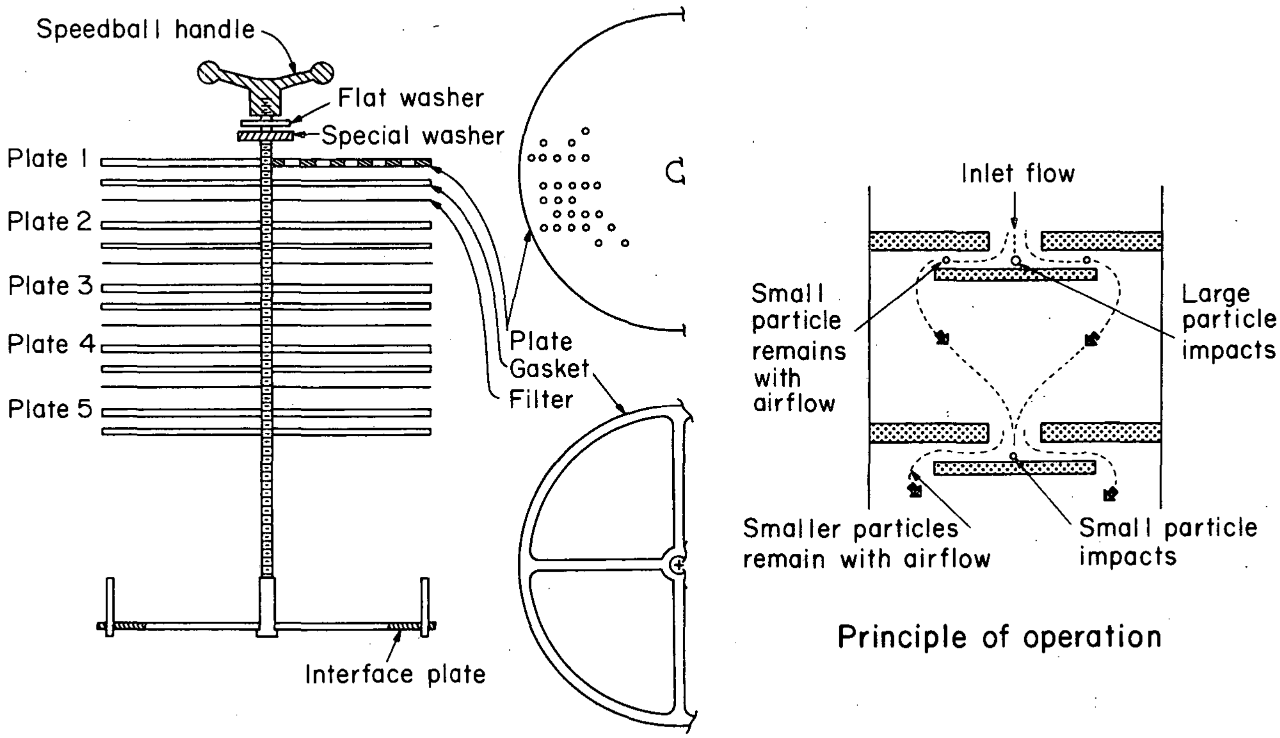


FIGURE 15.

LUNDGREN IMPACTOR

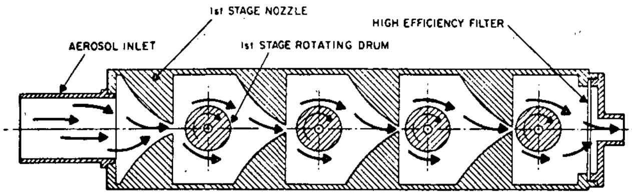


FIGURE 16.

TRANSMISSOMETER OPACITY METER

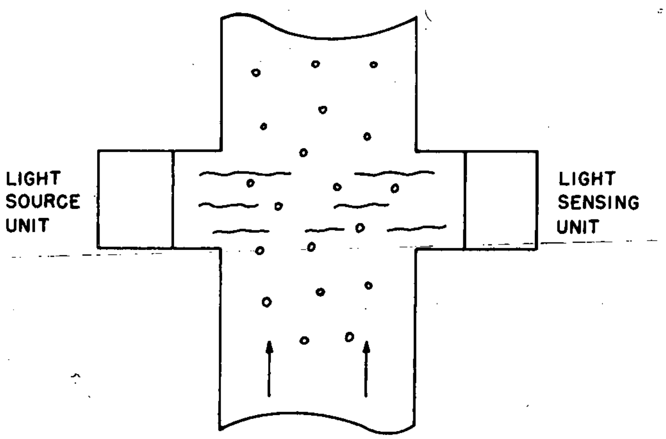


FIGURE 17.

to and developed for air pollution monitoring. The trend in the last few years has been towards the development of sophisticated, continuous monitoring, automated equipment. This is especially true for gaseous air pollutant monitoring instrumentation where the shift has been from manual and automated wet-chemical methods to the more reliable and less troublesome physical and physicochemical, real-time systems. While current instrumentation may be adequate in many respects there are still numerous improvements which need to be considered. The most promising developments are with those instruments that possess the following characteristics:

1. Specific for the pollutant of interest, i.e., the analyzer sensitivity to interferences should be at a minimum.
2. Measuring principle based on physical rather than chemical methods.
3. Automatic, unattended operation.
4. Minimum of sampling system requirements.
5. Reliability and ease of calibration method.
6. Ruggedness and ease of maintenance.
7. Adaptability to specific monitoring application, e.g., stack monitoring, personnel dosimetry monitoring.
8. Competitive price.

Multiparameter capability also appears to be an obvious advantage; however, one must consider the marketing acceptability of multiparameter instruments. Except when one is equipping a brand new laboratory, obsolescence of existing equipment is an important factor. Several adequate single-parameter analyzers cannot be written off early and replaced by a multiparameter analyzer in most labs.

Acknowledgment

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