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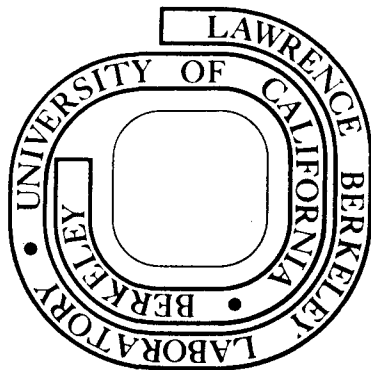
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ENVIRONMENTAL MEASUREMENTS OF AIR AND WATER QUALITY*

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Summary

New energy conversion processes may aggravate the problem of maintaining a high quality of our environment. Central to the concept of maintaining high quality is the need to measure those parameters which contribute to environmental degradation. There is thus an obvious requirement for use of accurate and effective instrumentation.

This paper will list the most prevalent air and water pollutants, note typical levels encountered in background and urban concentrations and examine the methods presently employed in their analysis.

Introduction

Good management of our natural resources and their conversion to usable products includes the maintenance of a high quality of our environment. This maintenance of high environmental quality in turn requires that we measure those environmental parameters in the three media: air, water and land. The most important, and the focus of this paper are air and water. Thus, there is an obvious necessity for effective and accurate instrumentation to perform this measurement and monitoring.

During the past 5 years an increasing number of us in nuclear physics, chemistry and engineering have enlarged our focus to include environmental problems together with our nuclear science activities. See Ref. 1, for example. In the U. S. and elsewhere a number of agencies are devoting a large portion of their efforts to an investigation of the environmental effects of energy conversion. With the transition last January 19 of the U.S. Atomic Energy Commission to the U. S. Energy Research and Development Administration (ERDA) an increasing number of instrumentation specialists are asking: Does nuclear instrumentation have a role in the measurement and monitoring of air- and water-quality parameters? The answer is an emphatic "YES".

The direction of modern analysis is away from wet-chemical procedures and toward physical techniques. There are several reasons for this:

These procedures are quite often time-consuming and require skilled operators, and they require reagents that may vary in purity with time and from batch to batch.

Physical methods, such as those used in nuclear research, on the other hand, are usually rapid; they quite often simplify the sample handling by being performed in situ and in a few cases allow simultaneous multi-parameter analysis.²

Air Quality

Let us begin by identifying the contaminants of major concern in air and then discuss their means of analysis. Our atmosphere is an exceedingly complicated reaction vessel. Numerous constituents such as the oxides of carbon occur naturally in very low concentrations. Others called primary pollutants are the result of man's activities; still others react photochemically or catalytically to produce secondary pollutants. Gaseous air pollutants include sulfur oxides; nitrogen oxides; photochemical oxidants, primarily ozone and other compounds (such as peroxyacetyl nitrate [PAN]); carbon monoxide; hydrocarbons; halogens and halogenated compounds; ammonium compounds and oxygenated compounds (such as aldehydes).

Organic or inorganic particles in the atmosphere constitute particulate air pollutants. Suspended particulate matter includes metals (such as Pb and Cd), nitrates, sulfates, fluorides, polycyclic organics, oxygenated compounds, pesticides and aeroallergens.

Table I lists the major air pollutants of concern in the U.S.; it is these we will discuss here.^{3,4,5}

It will be noted that levels are given in increasing order of their effect upon humans. While taste and smell are not known for their quantitative properties, it will be noted that for most gases (except for a few such as CO) adequate warning is given by these senses before serious injury is incurred. When a range of sensitivities has been given in the literature, the lowest level of perception is shown here. The effects of some pollutants (e.g., lead) are known to be cumulative while others may not be. Likewise, exposures may be of short duration (e.g., minutes) or prolonged (e.g., months). Except for carbon monoxide which is well establish-

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TABLE I HUMAN RESPONSE TO INCREASING CONCENTRATIONS OF AIR POLLUTANTS

AIR POLLUTANT	HUMAN RESPONSE TO INCREASING CONCENTRATIONS			
	THRESHOLD DETECTION BY TASTE OR SMELL	IRRITATING	CAUSES ILLNESS	LETHAL
SULFUR DIOXIDE	0.3 ppm, TASTE	> 3 ppm (A) PUNGENT ODOR	5 ppm (A)	400 ppm (A)
NITROGEN DIOXIDE	0.2 ppm, ODOR (A)		0.06 ppm (C)	> 100 ppm
OZONE	0.015 ppm, ODOR	0.3 ppm, (C) (NASAL & THROAT)	1 ppm FATIGUE (A)	
CARBON MONOXIDE	ODORLESS	600 ppm (A)	1000 ppm (A)	> 4000 ppm (A)
HYDROCARBONS	DEPENDS UPON COMPOUND			
LEAD	ODORLESS		6 µG/m ³ /DAY (C)	
MERCURY	ODORLESS	0.01 Mg/m ³ (C)	{ 1.2 Mg/m ³ (A) 0.1 Mg/m ³ (C)	
CADMIUM	ODORLESS			

(A) = ACUTE
(C) = CHRONIC

(Ref. 3,4,5)

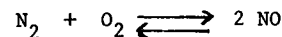
ed, the levels causing disease and death for other air pollutants depend upon many factors and are not well understood. Goldwater defines an acute exposure or dose as a single occurrence whose duration is measured in seconds, minutes or hours; a chronic exposure or dose is defined as a prolonged or repeated exposure or dose extending over a period of days, months or even years.³ For discussion of other pollutants the reader is referred to the current literature.^{2,4,6,7} It is obvious that a great deal of work needs to be undertaken to accurately determine the biological effects of air pollutants.

Gaseous Air Pollutants

Sulfur dioxide is one of the most serious atmospheric pollutants. A non-flammable, colorless gas, its presence arises primarily from burning fossil fuels containing sulfur. SO₂ undergoes oxidation in the atmosphere to sulfuric acid and particulate sulfates. These species have been shown recently to be greater health hazards than SO₂. The effects of sulfur oxides on man are increased respiratory problems especially among those suffering from chronic respiratory diseases.

Nitrogen oxides are atmospheric pollutants produced principally from high temperature combustion processes (e.g., fossil fuel combustion) followed by rapid cooling. Of the several oxides of nitrogen only nitric oxide (NO) and nitrogen dioxide (NO₂) are serious atmospheric pollutants; they are often referred to collectively as the oxides of nitrogen (NO_x).

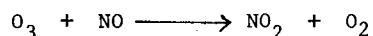
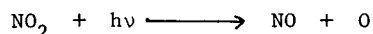
Nitric oxide is a colorless, odorless gas, the primary product of high temperature combustion processes between atmospheric nitrogen and oxygen as indicated below:



When rapid cooling follows combustion, equilibrium is not attained, and NO persists. There is no evidence that nitric oxide is a significant health hazard; however, NO may be oxidized photochemically to form the irritating and toxic nitrogen dioxide.

NO₂ is an orange-brown gas with a pungent odor; it is corrosive and highly oxidizing. Oxidation of NO to NO₂ is normally very slow; however, under certain conditions when sunlight and

hydrocarbons are present, NO is oxidized very rapidly to NO₂. The photolytic reactions are usually expressed as follows:



M is a third collisional molecule which removes energy and allows the formation of stable O₃.

Ozone is a colorless gas with a pungent odor. It is highly oxidizing and irritating to the nose and throat.

The above cycle explains the initial formation of ozone (O₃), but does not account for the levels occurring in the atmosphere. If no additional processes were involved, NO and O₃ would be in equilibrium. Experiments have shown that hydrocarbons in the atmosphere explain the mechanism which allows the buildup of O₃ and NO₂.

Carbon monoxide is the most prevalent pollutant in urban air. It is the result of incomplete combustion of any fuel containing carbon. It is interesting to note that when a global inventory was made of CO, man-made sources contributed less than 10% of the total carbon monoxide found in our atmosphere. The main toxic reaction of CO is that with hemoglobin in the blood; hemoglobin has

more than 200 times affinity for CO than oxygen and preferentially reacts with CO to deprive the blood of O₂.

Hydrocarbons, as described here, are a group of hydrogen and carbon compounds arising from combustion processes, the greater part being from vehicles. The main concern over hydrocarbons is that they react with nitrogen oxides to produce photochemical oxidants. Reacting hydrocarbons include alkanes (single bond), olefins (double bond), alkynes (triple bond), aromatics (benzene ring structure compounds) and oxygenated hydrocarbons (aldehydes and ketones). Methane it should be noted is not an important pollutant since it is not highly reactive chemically.

Legislation

Substantial legislation to protect and improve the quality of the atmosphere in the U.S. came in 1970 as amendments to the Clean Air Act. The Environmental Protection Agency (EPA) was set up and given the responsibility of setting national air quality standards which are listed in Table II.^{6,8} These National Primary and Secondary Air Quality Standards were established on April 30, 1971. The Primary Standards are to protect the public health; the Secondary Standards concern the effects on animals, vegetation and materials which are an important part of the public welfare.

Air quality standards were established for particulate matter, sulfur dioxide, nitrogen

TABLE II U.S. NATIONAL AIR QUALITY STANDARDS, BACKGROUND AND TYPICAL URBAN ANNUAL MEAN CONCENTRATIONS OF AIR POLLUTANTS

AIR POLLUTION	U.S. NATIONAL AIR QUALITY STANDARDS*		AVERAGING TIME	BACKGROUND CONCENTRATION	TYPICAL URBAN ANNUAL MEAN CONCENTRATIONS
	CONCENTRATION				
	μG/m ³	ppm			
PARTICULATE MATTER	260		24 HR	1-30 μG/m ³	100μG/m ³
	75		ANNUAL GEOMETRIC MEAN		
SULFUR DIOXIDE	365	0.14	24 HR	0.0002-0.0004 ppm	0.03 ppm
	80	0.03	ANNUAL ARITHMETIC MEAN		
NITROGEN DIOXIDE	100	0.05	ANNUAL ARITHMETIC MEAN	0.001-0.003 ppm	0.05 ppm
PHOTOCHEMICAL OXIDANTS (CORRECTED FOR NO ₂ & SO ₂)	160	0.08	1 HR	0.01 ppm	0.03 ppm
CARBON MONOXIDE	40,000	35	1 HR	0.1 ppm	4 ppm
	10,000	9	8 HR		
HYDROCARBONS (NONMETHANE)	160	0.24	3 HR (6-9 AM)	< 0.001 ppm	0.5 ppm

*National Standards other than those based on annual arithmetic means or annual geometric means are not to be exceeded more than once per year.

dioxide, photochemical oxidants, carbon monoxide and hydrocarbons.

Also listed in Table II are both background concentrations usually encountered and concentrations typically found in cities in the U.S.

Instrumentation

To introduce the problem of physical instrumentation let us first consider the phenomena that are available for characterizing the various contaminants discussed above. Most of them involve electromagnetic radiation. The range to be considered extends from 10^8 to 10^{20} Hz (i.e., 3 meters to 3×10^{-3} nanometers). This spectral region and the principle phenomena involved are shown in Fig. 1. Physical measurements are generally limited to some observation of these phenomena. In addition to instruments involving electromagnetic radiation there are also some which involve acoustic effects, gas flow, particle motion and the mechanical effects. Finally, there is a group of instruments which are based on the electrical properties of liquids, such as conductivity, electromotive force and electrolysis.

Table III from Hollowell⁶ lists the commonly employed chemical and physical methods for analyzing gaseous air pollutants. Techniques shown are suitable for three types of monitoring employed today; ambient air monitoring, stationary source monitoring and mobile source or vehicular emissions monitoring. The EPA has issued regulations indicating reference methods for the analysis of a number of the air pollutants. By reference method EPA means a particular analytical procedure whereby all measurements may be "referenced" for intercomparison and interpretation. An

equivalent method means any method of sampling and analysis which can be demonstrated to have a consistent relationship to the reference method. Obviously there are a number of methods for analyzing each pollutant; however, the equivalency of one method compared with another is the cause for a great deal of laboratory measurement and concern.

The reference method for the determination of sulfur dioxide is the pararosaniline method. SO_2 is bubbled into a reagent to form a chemically stable complex. This complex in turn is reacted with a pararosaniline and formaldehyde complex to form a highly colored solution. The absorbance of the solution, a function of the sulfur dioxide concentration, is measured spectrophotometrically.

The Jacobs-Hochheiser procedure developed in 1958 has been the reference method for the determination of NO_2 . An air sample containing NO_2 is drawn through a solution of sodium hydroxide for sampling periods of several hours. The resulting solution is reacted with a reagent to form a deeply colored azo dye. The light absorption in the solution (measured at 540 nanometers) is proportional to the integrated concentration of nitrogen dioxide.

In 1971, however, several important questions were raised concerning the accuracy of the measurement. It was shown that the method overestimates the NO_2 concentration at low levels and underestimates the concentration at high levels. Furthermore, the presence of nitric oxide gives a positive interference. (An interference is the presence of another pollutant interfering with the measurement.) As a result the Jacobs-Hochheiser procedure was withdrawn as a reference method in June 1973.

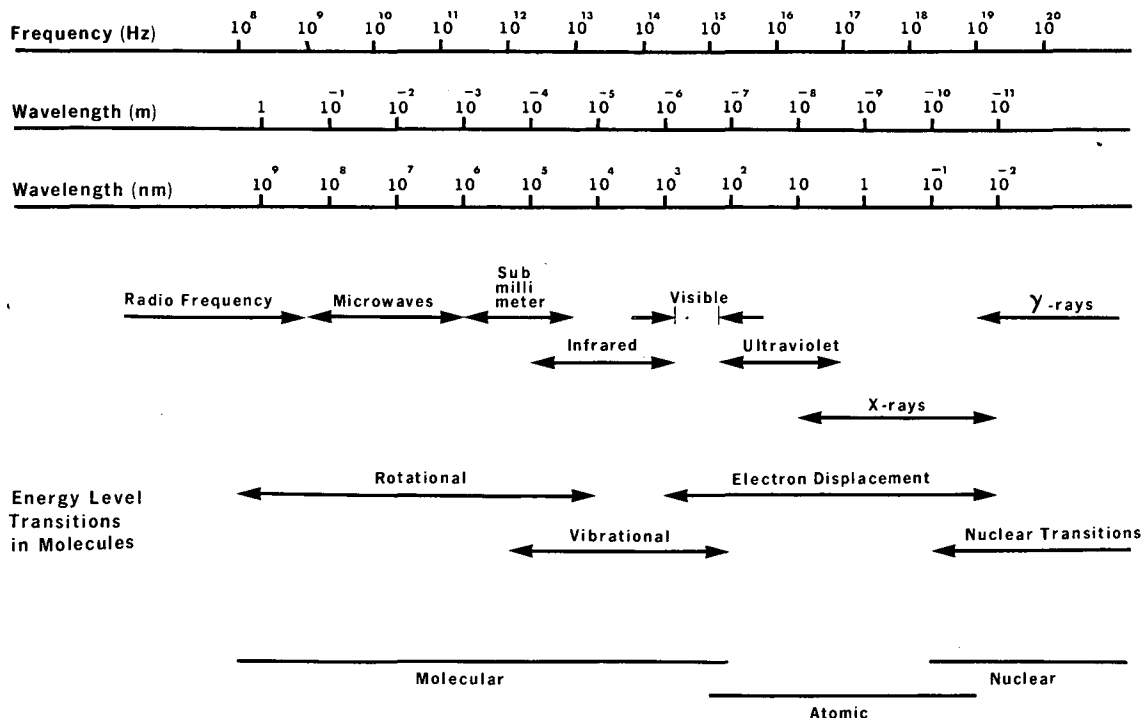


Fig. 1 ELECTROMAGNETIC SPECTRUM

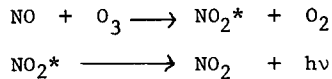
TABLE III GASEOUS POLLUTANT MONITORING INSTRUMENTATION

MEASUREMENT PRINCIPLE	MONITORING APPLICATION		
	AMBIENT AIR	STATIONARY SOURCE	MOBILE SOURCE
<u>SO₂ 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/NO₂ 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

Three alternative reference methods for the determination of NO₂ are now under evaluation: The continuous Saltzman method, a chemiluminescent method and the Christie (arsenite) method.

In the continuous Saltzman method NO₂ reacts with sulfanilic acid to form a colored solution. This method is less subject to interferences normally encountered in air monitoring; however, the color of the dye fades if the sampling periods are longer than one hour.

Chemiluminescence is the emission of radiant energy in the reaction between two molecular species. Chemiluminescent nitrogen oxides analyzers make use of the reaction between nitric oxide and ozone



This radiation in the region of 600 to 3000 nm is measured with a photomultiplier. To detect NO₂ the gas must first be converted to NO.

The Christie (arsenite) method is similar to the original Jacobs-Hochheiser method except that sodium hydroxide-sodium arsenite is substituted as the absorbing solution.

The reference method for ozone prescribed by the EPA is based on gas-phase chemiluminescence between ozone and ethylene. The emission which peaks at 435 nm is detected with a photomultiplier. No interferences have been found due to other gas pollutants. Photochemical oxidants (primarily ozone) may also be measured colorimetrically, electrochemically or by UV absorption.

Nondispersive infrared (NDIR) spectrometry is the reference method for the ambient air monitor-

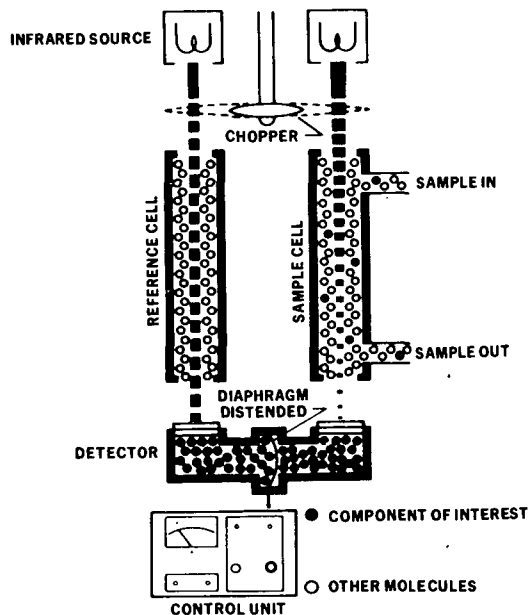


Fig. 2 AN EXAMPLE OF A NONDISPERSIVE INFRARED ABSORPTION ANALYZER

(Ref. 6)

ing of carbon monoxide. It is the broadband spectral absorption of IR radiation by the gas under examination. Practical instruments usually employ a double beam arrangement whereby the absorption characteristics of two sample gas cells are compared; one cell contains the sample, the other a non-absorbing gas. The difference in pressure between the two chambers is noted as a change in capacitance between a diaphragm and a fixed plate.⁶ See Fig. 2.

Total hydrocarbons may be readily detected by a number of methods shown in Table III. However, when it is desired to remove the non-reactive methane component from the analysis, gas chromatography (GC) is one of the few methods applicable. In principle GC is a technique for physically separating a gaseous mixture into its components by passing it through a column with a high surface-to-volume ratio. The surface area may be either a solid material or a liquid dispersed on a solid. The segregation of the various gaseous components depends upon their temporary selective absorption by the material in the column. An inert carrier gas moves the sample through the column; if the sample contains different hydrocarbons, the various components will emerge from the column at different times, the weakly absorbing components emerging first. In the reference method flame ionization detection (FID) is employed to detect the various hydrocarbons emerging from the column. In FID the sample is introduced into a hydrogen flame. The combustion of even a few parts per billion of a hydrocarbon produces measurable ionization, the ion current being proportional to the number of carbon ions present.

Particulates

The measurement and analysis of particulate emissions is vital to an understanding of a number of energy conversion systems, e.g., fossil fuel burning power plants and motor vehicles. Table IV lists the various categories of particulate instrumentation.⁶

Particulate monitoring for mass and chemical analysis has traditionally been performed with a high volume (hi-vol) air sampler. Hi-vol samplers use a blower with flow rates of 0.9 to 1.4 m³/min to collect particulates on an air filter. After a collection period of 24 hours or more the increase in filter weight is recorded. Chemical analysis is described below.

Opacity measurements determine the fraction of light absorbed or scattered by airborne particulates. This in turn measures the concentration of the particulates.

Size monitoring is of interest in determining the initial source and history of the particulates.

One example of a monitor which separates particles by their size is a dichotomous sampler developed by Goulding and Jaklevic at our Laboratory. This sampler separates particulates into two size ranges: less than and greater than 2 μm. It has been established that particles smaller than 3.5 μm can penetrate into the human lungs while larger diameter particles are trapped in the human respiratory system. Submicron particles are

TABLE IV PARTICULATE MONITORING INSTRUMENTATION

TYPE OF MONITORING AND MEASUREMENT PRINCIPLE	MONITORING APPLICATION	
	AMBIENT AIR	SOURCE
<u>MASS MONITORING</u>		
FILTER COLLECTION, GRAVIMETRIC ANALYSIS	X	X
BETA RADIATION ATTENUATION	X	X
PIEZOELECTRIC MICROBALANCE	X	X
NEPHELOMETRY	X	
<u>OPACITY MONITORING</u>		
VISUAL OBSERVATION		X
PAPER TAPE METHOD	X	
LIGHT TRANSMISSION		X
NEPHELOMETRY	X	
<u>SIZE MONITORING</u>		
SEDIMENTATION	X	X
CENTRIFUGATION	X	X
IMPACTION	X	X
SINGLE PARTICLE OPTICAL COUNTING	X	
ELECTRICAL MOBILITY ANALYSIS	X	
MICROSCOPY (OPTICAL AND ELECTRON)	X	X
<u>CHEMICAL COMPOSITION</u>		
INORGANIC PARTICULATES		
COLORIMETRIC (UV-VIS SPECTROPHOTOMETRY)	X	X
ION-SELECTIVE ELECTRODE	X	X
ATOMIC ABSORPTION AND EMISSION SPECTROPHOTOMETRY	X	X
NEUTRON ACTIVATION ANALYSIS	X	X
X-RAY FLUORESCENCE ANALYSIS	X	X
ELECTRON SPECTROSCOPY FOR CHEMICAL ANALYSIS (ESCA)	X	X
ORGANIC PARTICULATES		
UV ABSORPTION AND FLUORESCENCE SPECTROSCOPY	X	X
GAS CHROMATOGRAPHY	X	X
GAS CHROMATOGRAPHY-MASS SPECTROMETRY	X	X

primarily from combustion processes of man-made origin; particles larger than 2 μ m are usually dust from the earth's crust.²

The chemical composition of particulates is of obvious interest in that they may give a clue to their origin. An x-ray fluorescence analyzer has been developed in connection with the dichotomous sampler mentioned above.⁶ It automatically analyzes air filter samples for more than 15 elements with atomic numbers greater than 13 (aluminum) at a rate of 4 filters per hour and with elemental concentrations of 1 ppm or less.

Hazardous air pollutants, such as mercury, cadmium and lead, are usually analyzed spectrophotometrically. This method will be discussed in more detail under water analysis.

Future Trends in Air Monitoring Instrumentation

The methods described above have become the standard procedures whereby air pollutants may be analyzed. However, each month some new or refined physical principle is described; for example, Fourier interferometry, a dispersive technique whereby a radiation interference is generated in an optical system. The interferogram is Fourier transformed into a conventional wavelength spectrum. In this method all wavelengths are scanned at the same time and converted into a frequency spectrum. High resolution is now obtainable in the infrared. Also, lasers show promise for remote monitoring of a number of air pollutants. Laser induced fluorescence is presently under investigation at several laboratories; it promises to ease the identification of molecular species of many gaseous air pollutants.

Water Quality

When discussing the parameters that affect its quality, water may be classified in a number of different ways. Water is frequently divided into two categories; water and waste water;¹⁰ while in other cases it is subdivided into five general areas of use: public water supplies; industry; agriculture; aquatic life and wildlife; and recreation and aesthetics.¹¹ In this paper discussion will center around drinking water whose parameters are listed in the EPA 1975 Interim Primary Drinking Water Standards.¹² For consideration of other contaminants the reader is referred to the recent literature.^{13,14,15}

Table V lists the response to increasing concentrations of water pollutants.^{11,13} These values taken from the published literature give the levels applicable to humans; however, in the case of some pesticides the only published levels apply to studies on dogs or rats. Since the levels are expressed in mg of water per kg of body weight per day, the values may be extrapolated to human levels of toxicity. (In these cases an average man is assumed to weigh 70 kg; a dog, 10 kg; and a rat, 0.3 kg. Where the total daily intake might occur through both food and water, it is assumed that a person drinks 2 liters of water daily.)¹¹ The danger of extrapolating toxicity levels from rats to man is understandable; however, when more definitive data are not known, there is no alternative but to use animal toxic-

ity levels multiplied by an appropriate safety factor and apply them to man.

Inorganic Chemicals

Toxic effects of inorganic chemicals on mammals vary according to the particular element, its oxidation state and its excretion rate from the body. For example, Cr^{+6} is found to be considerably more toxic than Cr^{+3} , and methylmercury is very much more toxic than most inorganic mercury compounds. Also the more lethal methylmercury is retained in the body longer than less toxic inorganic forms.

Fluoride is often intentionally introduced into water supplies because of its property of reducing dental cavities in children; an excessive concentration, on the other hand, causes dental fluorosis (e.g., mottled enamel on human teeth). Sulfate is not listed in the Interim Standards, but is expected to be reinstated at 250 Mg/l in the future.

Pesticides

Pesticides are a class of chemical compounds which are used to limit, control or eradicate certain insects and life forms that are considered to be undesirable.^{13,15} The most dramatic advance in the use of pesticides came in 1939 with the introduction of DDT. The toxicity of DDT to insects and its comparative safety to plants, animals and man, provided almost miraculous properties toward insect control. However, soon resistant strains of insects survived that required ever increasing doses to be effective. Because of the large amounts used and the persistence of DDT and the whole family of chlorinated hydrocarbons, they have become worldwide pollutants. Almost all uses of DDT in the U.S. were stopped in 1971. Happily alternative insecticides have been developed that are readily degradable.

Chlorophenoxy's are a family of herbicides whose acute toxicity is primarily limited to plants. Although readily biodegradable, one of the metabolites imparts an undesirable taste and odor to water.

Other Contaminants

Turbidity or cloudiness in water is due to suspended finely divided organic or inorganic matter, such as clay or silt. Excessive turbidity is objectionable in drinking water for aesthetic reasons; it also interferes with disinfection efficiency and often signals the onset of other health hazards.

The analytical procedures for the direct identification of disease-causing bacteria, viruses, protozoa, worms and fungi are not well enough developed for widespread application. However, coliform bacteria have been used many years as indicators of microbiological contamination; the number present in a water supply provides a good measure of the sanitary quality of the water.

TABLE V RESPONSE TO INCREASING CONCENTRATIONS OF WATER POLLUTANTS

WATER POLLUTANT	HUMAN RESPONSE TO INCREASING CONCENTRATIONS		
	SAFE LEVEL	CAUSES ILLNESS	LETHAL
INORGANIC CHEMICALS			
ARSENIC	0.1 Mg/L (C)	100 Mg (A), 0.3 Mg/L (C)	130 Mg (A)
BARIUM	2 Mg/L (C)	-	550 Mg (A)
CADMIUM	-	13 Mg/L (A), 600 UG/DAY (C)	8.9 G (A)
CHROMIUM	0.45 Mg/L (C)	-	-
CYANIDE	2.9 Mg/DAY (C), 10 Mg (A)	-	50 Mg (A)
FLUORIDE	-	> RECOMMENDED VALUE CAUSES DENTAL FLUOROSIS	-
LEAD	0.6 Mg/DAY (C)	-	-
MERCURY	-	0.3 Mg/DAY (C)	20 Mg (A)
NITRATE	10 Mg/L (C)	20.4 Mg/L (C)	-
SELENIUM	-	-	9 Mg/L (C)
SILVER	-	1 G (A)	-
ORGANIC CHEMICALS			
PESTICIDES			
CHLORINATED HYDROCARBONS			
CHLORDANE	.42 Mg/Kg/DAY (RAT) (C)	> .003 Mg/L (C)	6-60 G EST (A)
ENDRIN	.06 Mg/Kg/DAY (DOG) (C)	-	3.5 Mg/Kg CHICKS (FOOD) (C)
HEPTACHLOR	.08 Mg/Kg/DAY (DOG) (C)	-	-
HEPTACHLOR EPOXIDE	0.01 Mg/Kg/DAY (DOG) (C)	-	-
LINDANE	0.3 Mg/Kg/DAY (DOG) (C)	45 Mg (A)	-
METHOXYCHLOR	140 Mg/DAY (C)	-	-
TOXAPHENE	8 Mg/Kg/DAY (DOG) (C)	> .005 Mg/L (C)	2-7 G EST (A) 35 Mg/Kg CATTLE (FOOD) (C)
CHLOROPHENOXY			
2,4-D	500 Mg/DAY (C)	-	500 Mg/Kg (RAT) (A)
2,4,5-TP SILVEX	0.9 Mg/Kg/DAY (DOG) (C)	-	500 Mg/Kg (RAT) (A)

(A) = ACUTE
(C) = CHRONIC

(Ref. 11,13)

Drinking Water Standards

Table VI lists the 1975 Interim Primary Drinking Water Standards which will become effective in the U.S. in December 1976.¹² In the meantime, the U.S. Public Health Service Drinking Water Standards of 1962 are in force.¹³ The new standards have very nearly the same maximum levels for inorganic chemicals as the present standards; however, the standards for pesticides and microbiological contaminants have been substantially revised.

It is expected that the EPA will soon issue additional regulations on maximum permissible concentrations for Aldrin (0.001 mg/l), DDT (0.05

mg/l) and Dieldrin (0.001 mg/l) although the use of each of these pesticides has now been prohibited.

No standards for radioactivity are included in the new standards; however, the EPA has stated that maximum contaminant levels and analytical and sampling requirements may be expected in the near future.

Reference analytical methods required by the EPA are listed in Column 3 of Table V. These methods will be discussed in more detail below.

Kopp and Kroner¹⁶ made a five year study of trace metals in rivers and lakes of the United

TABLE VI

U.S. EPA INTERIM PRIMARY DRINKING WATER STANDARDS 1975; OBSERVED MEAN VALUES AND FREQUENCY OF DETECTION OF SOME WATER POLLUTANTS.

WATER POLLUTANT	U.S. EPA INTERIM PRIMARY DRINKING WATER STANDARDS 1975		OBSERVED MEAN VALUES IN U.S. WATERS Mg/L	FREQUENCY OF DETECTION % IN 1577 SAMPLES
	MAXIMUM LEVELS Mg/L	ANALYSIS METHODS		
INORGANIC CHEMICALS				
ARSENIC	.05	AA	.064	5.5
BARIUM	1.	AA	.043	99.4
CADMIUM	0.010	AA	.0095	2.5
CHROMIUM	0.05	AA	.0097	24.5
CYANIDE	0.2	TITRATION OR COLORIMETRIC		
FLUORIDE	1.4 TO 2.4*	{ ELECTRODE OR COLORIMETRIC WITH PRELIMINARY DISTILLATION		
LEAD	0.05	AA	.023	19.3
MERCURY	0.002	FLAMELESS AA	<.0005	IN 93% OF STREAMS
NITRATE (AS N)	10.	BRUCINE COLORIMETRIC		
SELENIUM	0.01	AA		
SILVER	0.05	AA	.0026	6.6
ORGANIC CHEMICALS	0.7	ACTIVATED CARBON ABSORPTION AND SOLVENT EXTRACTION		
PESTICIDES				
CHLORINATED HYDROCARBONS				
CHLORDANE	0.003	} GAS CHROMATOGRAPHIC		
ENDRIN	0.0002			
HEPTACHLOR	0.0001			
HEPTACHLOR EPOXIDE	0.0001			
LINDANE	0.004			
METHOXYCHLOR	0.1			
TOXAPHENE	0.005			
CHLOROPHENOXY				
2,4-D	0.1			
2,4,5-TP SILVEX	0.01			
TURBIDITY	1 TURB. UNIT	NEPHELOMETRIC		
MICROBIOLOGICAL CONTAMINANTS				
COLIFORM BACTERIA	SEE REF.	{ COLIFORM COUNT. CHLORINE RESIDUAL		

*DEPENDING UPON AIR TEMPERATURE

(Ref. 12,16)

States. Selected values and the frequency in which they occurred in 1577 samples are listed in Columns 4 and 5 of Table VI.

Water Quality Instrumentation

The methods of analysis discussed here will deal primarily with the measurement of inorganic chemicals, chiefly metals and organic chemicals, mainly pesticides. For other water measurements,

such as biochemical oxygen demand and dissolved oxygen, the reader is referred to the literature.^{10,13,17}

Metals Analysis

Atomic absorption spectrophotometry is the chief method for measuring the metal content of water samples. In principle monochromatic light is excited with a spectral content characteristic

of the metal being analyzed. Light is absorbed on passing through a chamber, usually a flame or furnace, which atomizes the metal. The attenuation in light intensity is proportional to the number of atomized ions. For all metals except Hg, a furnace is used. In the furnace the liquid sample is evaporated, ashed if necessary, and then heated to incandescence to atomize the metal. A cold vapor atomizing method is employed for the analysis of mercury. In cases where the concentration is below the instrumental sensitivity a premeasurement concentration step is required. By using various chelating and extraction techniques lower detection limits are now in the $\mu\text{g/l}$ range for many metals.

Fluoride may be detected with an ion selective electrode. In the ion selective electrode, fluoride ions change the potential of an electrode in a manner which is proportional to the logarithm of the ion concentration in the sample.

Pesticide Analysis

Gas chromatography, described previously, is routinely employed in pesticide analysis. When coupled with an appropriate detector GC is the most sensitive and selective method for both the qualitative and quantitative analysis of organic compounds. These detectors include electron capture, microcoulometric, electrolytic conductivity and flame photometric.¹⁵ Although these detectors may have a high degree of selectivity, it is still possible that two organic compounds may emerge from the GC column at the same time. Coupling a mass spectrometer to the outlet of the gas chromatograph has solved this problem - the specific identification of organic compounds. Under computer control much of the tediousness of comparing GS-MS spectra with catalogs of known constituents is eliminated.

Future Water Instrumentation

Several categories for improved water monitoring are currently under development: These include improved ion-selective and gas membrane electrodes for a number of ions and gases. Development is proceeding on better detectors for gas chromatography. Other laboratories are developing atomic absorption spectrophotometers with improved furnace techniques. The use of an inductively coupled plasma in emission spectroscopy may allow multi-element capability at ambient levels. In addition, a great deal of effort is presently being expended on increasing sensitivity and selectivity in general and automating existing techniques now performed manually. Especial emphasis is being given to point source monitors.

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