

Manahan, Stanley E. "ENVIRONMENTAL AND XENOBIOTICS ANALYSIS"  
*Fundamentals of Environmental Chemistry*  
Boca Raton: CRC Press LLC,2001

## **26 ENVIRONMENTAL AND XENOBIOTICS ANALYSIS**

---

---

### **26.1 INTRODUCTION TO ENVIRONMENTAL CHEMICAL ANALYSIS**

Scientists' understanding of the environment can only be as good as their knowledge of the identities and quantities of pollutants and other chemical species in water, air, soil, and biological systems. Therefore, proven, state-of-the-art techniques of chemical analysis, properly employed, are essential to environmental chemistry. Now is a very exciting period in the evolution of analytical chemistry, characterized by the development of new and improved analysis techniques that enable detection of much lower levels of chemical species and a vastly increased data throughput. These developments pose some challenges. Because of the lower detection limits of some instruments, it is now possible to see quantities of pollutants that would have escaped detection previously, resulting in difficult questions regarding the setting of maximum allowable limits of various pollutants. The increased output of data from automated instruments has in many cases overwhelmed human capacity to assimilate and understand it.

Challenging problems still remain in developing and utilizing techniques of environmental chemical analysis. Not the least of these problems is knowing which species should be measured, or even whether an analysis should be performed at all. The quality and choice of analyses is much more important than the number of analyses performed. Indeed, a persuasive argument can be made that, given modern capabilities in analytical chemistry, too many analyses of environmental samples are performed, whereas fewer, more carefully planned analyses would yield more-useful information.

This chapter covers some of the general aspects of environmental chemical analysis. Environmental chemical analysis can be subdivided into several overlapping categories. These include analysis of water and wastewater, analysis of wastes and solids, air and gas analysis, and analysis of biological materials and xenobiotic substances, all addressed briefly in this chapter.

## 26.2 ANALYSIS OF WATER SAMPLES

### Physical Properties Measured in Water

The commonly determined physical properties of water are color, residue (solids), odor, temperature, specific conductance, and turbidity. Most of these terms are self-explanatory and will not be discussed in detail. All of these properties either influence or reflect the chemistry of the water. Solids, for example, arise from chemical substances either suspended or dissolved in the water and are classified physically as total, filterable, nonfilterable, or volatile. Specific conductance is a measure of the degree to which water conducts alternating current and reflects, therefore, the total concentration of dissolved ionic material. By necessity, some physical properties must be measured in the water without sampling (see discussion of water sampling below).

### Water Sampling

It is beyond the scope of this text to describe water sampling procedures in detail. It must be emphasized, however, that the acquisition of meaningful data demands that correct sampling and storage procedures be used. These procedures can be quite different for various species in water. In general, separate samples must be collected for chemical and biological analysis because the sampling and preservation techniques differ significantly. Usually, the shorter the time interval between sample collection and analysis, the more accurate the analysis will be. Indeed, some analyses must be performed in the field within minutes of sample collection. Others, such as the determination of temperature, must be done on the body of water itself. Within a few minutes after collection, water pH may change, dissolved gases (oxygen, carbon dioxide, hydrogen sulfide, chlorine) may be lost, or other gases (oxygen, carbon dioxide) may be absorbed from the atmosphere. Therefore, analyses of temperature, pH, and dissolved gases should always be performed in the field. Furthermore, precipitation of calcium carbonate accompanies changes in the pH-alkalinity-calcium carbonate relationship following sample collection. Analysis of a sample after standing may thus give erroneously low values for calcium and total hardness.

Oxidation-reduction reactions can cause substantial errors in analysis. For example, soluble iron(II) and manganese(II) are oxidized to insoluble iron(III) and manganese(IV) compounds when an anaerobic water sample is exposed to atmospheric oxygen. Microbial activity can decrease phenol or biological oxygen demand (BOD) values, change the nitrate-nitrite-ammonia balance, or alter the relative proportions of sulfate and sulfide. Iodide and cyanide frequently are oxidized. Chromium(VI) in solution may be reduced to insoluble chromium(III). Sodium, silicate, and boron are leached from glass container walls.

Samples can be divided into two major categories. **Grab samples** are taken at a single time and in a single place. Therefore, they are very specific with respect to time and location. **Composite samples** are collected over an extended time and may encompass different locations as well. In principle, the average results from a large number of grab samples give the same information as a composite sample. A com-

posite sample has the advantage of providing an overall picture from only one analysis. On the other hand, it may miss extreme concentrations and important variations that occur over time and space.

### *Solid-Phase Extractors*

The ease and effectiveness of various kinds of solid-phase devices for water sampling is steadily increasing their use in water analysis. Based upon size and physical configuration, at least three categories of such devices are available. One of these is the conventional solid-phase extractor (SPE) containing an extracting solid in a column. Activated carbon has been used for decades for this purpose, but synthetic materials, such as those composed of long hydrocarbon chains (C18) bound to solids have been found to be quite useful. A typical procedure uses a polymer-divinylstyrene extraction column to remove pesticides from water. The pesticide analytes are eluted from the SPE with ethyl acetate and measured by gas chromatography. A mean recovery of 85% has been reported.

Solid-phase microextraction (SPME) devices constitute a second kind of solid-phase extractor. These make use of very small-diameter devices in which analytes are bonded directly to the extractor walls, then eluted directly into a chromatograph. The use of SPME devices for the determination of haloethers in water has been described.

A third kind of device, disks composed of substances that bind with and remove analytes from water when the water is filtered through them, are available for a number of classes of substances and are gaining in popularity because of their simplicity and convenience. As an example, solid phase extraction disks can be used to remove and concentrate radionuclides from water, including  $^{99}\text{Tc}$ ,  $^{137}\text{Cs}$ ,  $^{90}\text{Sr}$ ,  $^{238}\text{Pu}$ . Organic materials sampled from water with such disks include haloacetic acids and acidic and neutral herbicides.

### **Water Sample Preservation**

It is not possible to completely protect a water sample from changes in composition. However, various additives and treatment techniques can be employed to minimize sample deterioration. These methods are summarized in [Table 26.1](#).

The most general method of sample preservation is refrigeration to 4°C. Freezing normally should be avoided because of physical changes—formation of precipitates and loss of gas—that can adversely affect sample composition. Acidification is commonly applied to metal samples to prevent their precipitation, and it also slows microbial action. In the case of metals, the samples should be filtered before adding acid to enable determination of dissolved metals. Sample holding times vary, from zero for parameters such as temperature or dissolved oxygen measured by a probe, to 6 months for metals. Many different kinds of samples, including those to be analyzed for acidity, alkalinity, and various forms of nitrogen or phosphorus, should not be held for more than 24 hours. Details on water sample preservation are to be found in standard references on water analysis, such as those listed at the end of this chapter. Instructions should be followed for each kind of sample to ensure meaningful results.

**Table 26.1 Preservatives and Preservation Methods Used with Water Samples**

Preservative or technique used	Effect on sample	Type of samples for which the method is employed
Nitric acid	Keeps metals in solution	Metal-containing samples
Sulfuric acid	Bactericide	Biodegradable samples containing organic carbon, oil, or grease
	Formation of sulfates with volatile bases	Samples containing amines or ammonia
Sodium hydroxide	Forms sodium salts from volatile acids	Samples containing volatile organic acids or cyanides
Chemical reaction	Fix a particular constituent	Samples to be analyzed for dissolved oxygen using the Winkler method

### 26.3 CLASSICAL METHODS OF WATER ANALYSIS

The most common classical methods for water analysis are titrations. Some of the titration procedures used are discussed in this section. The principles of titration analysis are discussed in Chapter 25, Section 25.6.

**Acidity** (see Chapter 11, Section 11.6) is determined simply by titrating hydrogen ion with base. Titration to the methyl orange endpoint (pH 4.5) yields the “free acidity” due to strong acids (HCl, H<sub>2</sub>SO<sub>4</sub>). Carbon dioxide does not, of course, appear in this category. Titration to the phenolphthalein endpoint, pH 8.3, yields total acidity and accounts for all acids except those weaker than HCO<sub>3</sub><sup>-</sup>.

**Alkalinity** can be determined by titration with H<sub>2</sub>SO<sub>4</sub> to pH 8.3 to neutralize bases as strong as, or stronger than, carbonate ion,



or by titration to pH 4.5 to neutralize bases weaker than CO<sub>3</sub><sup>2-</sup>, but as strong as, or stronger than, HCO<sub>3</sub><sup>-</sup>:



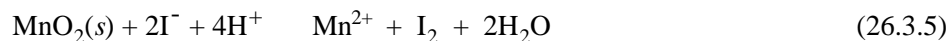
Titration to the lower pH yields total alkalinity.

The ions involved in water hardness, a measure of the total concentration of calcium and magnesium in water, are readily titrated at pH 10 with a solution of EDTA, a chelating agent mentioned as a titrant for metals in Chapter 25, Section 25.6. The titration reaction is



where H<sub>2</sub>Y<sup>2-</sup> is the partially ionized EDTA chelating agent. Eriochrome Black T is used as an indicator, and it requires the presence of magnesium, with which it forms a wine-red complex.

Several oxidation-reduction titrations can be used for environmental chemical analysis. Oxygen is determined in water by the Winkler titration. The first reaction in the Winkler method is the oxidation of manganese(II) to manganese(IV) by the oxygen analyte in a basic medium; this reaction is followed by acidification of the brown hydrated  $\text{MnO}_2$  in the presence of  $\text{I}^-$  ion to release free  $\text{I}_2$ , then titration of the liberated iodine with standard thiosulfate, using starch as an endpoint indicator:



A back calculation from the amount of thiosulfate required yields the original quantity of dissolved oxygen (DO) present. Biochemical oxygen demand, BOD (see Chapter 12, Section 12.9), is determined by adding a microbial “seed” to the diluted sample, saturating with air, incubating for 5 days, and determining the oxygen remaining. The results are calculated to show BOD as mg/L of  $\text{O}_2$ . A BOD of 80 mg/L, for example, means that biodegradation of the organic matter in a liter of the sample would consume 80 mg of oxygen.

## 26.4 INSTRUMENTAL METHODS OF WATER ANALYSIS

### Absorption Spectrophotometry

Absorption spectrophotometry of light-absorbing species in solution, an instrumental technique discussed in Chapter 25, Section 25.7, is useful for a number of common analytes measured in water. Recall that absorption spectrophotometry consists of measuring the percent transmittance (%T) of monochromatic light passing through a light-absorbing solution as compared with the amount passing through a blank solution containing everything in the medium but the sought-for constituent (100%). The absorbance (A) is defined as  $\log(100/\%T)$  and the relationship between A and the concentration (C) of the absorbing substance is given by Beer’s law:

$$A = abC \quad (26.4.1)$$

where a is the absorptivity, a wavelength-dependent parameter characteristic of the absorbing substance; b is the path length of the light through the absorbing solution; and C is the concentration of the absorbing substance.

A number of solution spectrophotometric methods have been developed and used for the determination of water pollutants. Some of these are summarized in [Table 26.2](#).

### Atomic Spectrophotometric Analysis of Water

Discussed in Section 25.7, atomic spectrometric methods are favored for the determination of most metals in water. Atomic absorption analysis has been widely employed for water analysis. Flame atomic absorption is useful for a variety of

metals whose concentrations are not too low. Much lower detection limits can be obtained with flameless (graphite furnace) atomic absorption, a technique that, fortunately, is particularly useful for some of the more troublesome metal pollutants in water, including cadmium, lead, and chromium. Another water pollutant metal of great concern is mercury, which is measurable at very low levels by cold vapor atomic absorption from atomic mercury generated by reduction in solution.

**Table 26.2 Solution Spectrophotometric Methods of Analysis for Water**

Analyte	Reagent and Method
Arsenic	Reaction of arsine, $\text{AsH}_3$ , with silver diethylthiocarbamate in pyridine, forming a red complex
Boron	Reaction with curcumin, forming red rosocyanine
Bromide	Reaction of hypobromite with phenol red to form bromphenol blue-type indicator
Cyanide	Formation of a blue dye from reaction of cyanogen chloride, $\text{CNCl}$ , with pyridine-pyrazolone reagent, measured at 620 nm
Fluoride	Decolorization of a zirconium-dye colloidal precipitate ("lake") by formation of colorless zirconium fluoride and free dye
Nitrate and nitrite	Nitrate is reduced to nitrite, which is diazotized with sulfanilamide and coupled with N-(1-naphthyl)-ethylenediamine dihydrochloride to produce a highly colored azo dye measured at 540 nm
Phenols	Reaction with 4-aminoantipyrine at pH 10 in the presence of potassium ferricyanide, forming an antipyrine dye that is extracted into pyridine and measured at 460 nm
Phosphate	Reaction with molybdate ion to form a phosphomolybdate, which is selectively reduced to intensely colored molybdenum blue
Selenium	Reaction with diaminobenzidine, forming colored species absorbing at 420 nm
Silica	Formation of molybdosilicic acid with molybdate, followed by reduction to a heteropoly blue measured at 650 nm or 815 nm
Sulfide	Formation of methylene blue
Surfactants	Reaction with methylene blue to form blue salt
Tannin and lignin	Blue color from tungstophosphoric and molybdophosphoric acids

Atomic emission is useful for the determination of a number of metals and, in some respects, complementary to atomic absorption. Flame atomic emission can be performed with the same instrument used for atomic absorption. Inductively coupled

plasma atomic emission analysis greatly extends the scope and speed of elemental analysis by atomic spectrometric means. A major advantage of inductively coupled plasma atomic emission analysis is its multielement capability, in which up to 30 elements can be measured at once. It can also measure some nonmetals.

## **Chromatographic Analysis of Water**

The principles and types of chromatographic analysis are discussed in Chapter 25, Section 25.9. The versatility, the sensitivity, and, especially with mass spectrometric detection, the specificity of chromatographic analysis, have made various chromatographic methods favored techniques for a variety of organic analytes in water. In addition, the development of ion chromatography, discussed later in this section, has made chromatography a feasible method for measuring some important ions, particularly anions, in water.

The U.S. Environmental Protection Agency and other agencies have developed a wide array of chromatographic analysis techniques for solutes in water. These are listed according to method numbers. These techniques have been adapted to other kinds of samples as well, particularly hazardous-waste materials. Some of the major standard chromatographic techniques for the determination of analytes in water are listed in [Table 26.3](#).

### **Ion Chromatography**

The liquid chromatographic determination of ions, particularly anions, has enabled the measurement of species that, despite their widespread occurrence in water, used to pose special challenges for water chemists to determine. This technique has come to be known as **ion chromatography**, and its development has been facilitated by special detection techniques using so-called suppressors to enable detection of analyte ions in the chromatographic effluent. Ion chromatography has been developed for the determination of most of the common anions, including arsenate, arsenite, borate, carbonate, chlorate, chlorite, cyanide, the halides, hypochlorite, hypophosphite, nitrate, nitrite, phosphate, phosphite, pyrophosphate, selenate, selenite, sulfate, sulfite, sulfide, trimetaphosphate, and tripolyphosphate. Cations, including the common metal ions, can also be determined by ion chromatography, although they are relatively easy to determine by other means.

### **Total Organic Carbon in Water**

The importance and possible detrimental effects of dissolved organic compounds in water were discussed in Chapter 12. Dissolved organic carbon exerts an oxygen demand in water, often is in the form of toxic substances, and is a general indicator of water pollution. Therefore, its measurement is quite important. The measurement of total organic carbon, TOC, is now recognized as the best means of assessing the organic content of a water sample. The measurement of this parameter has been facilitated by the development of methods which, for the most part, totally oxidize the dissolved organic material to produce carbon dioxide. The amount of carbon dioxide evolved is taken as a measure of TOC.



**Table 26.3 Chromatography-based EPA Methods for Organic Compounds in Water**

Class of compounds	Method Number			Example analytes
	GC <sup>1</sup>	GC/MS <sup>2</sup>	HPLC <sup>3</sup>	
Purgeable halocarbons	601			Carbon tetrachloride
Purgeable aromatics	602			Toluene
Acrolein and acrylonitrile	603			Acrolein
Phenols	604			Phenol and chlorophenols
Benzidines			605	Benzidine
Phthalate esters	606			Bis(2-ethylhexylphthalate)
Nitrosamines	607			N-nitroso-N-dimethylamine
Organochlorine pesticides and PCBs	608			Heptachlor, PCB 1016
Nitroaromatics and isophorone	609			Nitrobenzene
Polycyclic aromatic hydrocarbons	610		610	Benzo[a]pyrene
Haloethers	611			Bis(2-chloroethyl) ether
Chlorinated hydrocarbons	612			1,3-Dichlorobenzene
2,3,7,8-Tetrachlorodibenzo-p-dioxin		613		2,3,7,8-TCDD
Organophosphorus pesticides	614			Malathion
Chlorinated Herbicides	615			Dinoseb
Triazine Pesticides	619			Atrazine
Purgeable organics		624		Ethylbenzene
Base/neutrals and acids		625		More than 70 organic compounds
Dinitro aromatic pesticides		646		Basalin (Fluchloralin)
Volatile organic compounds		1624		Vinyl chloride

<sup>1</sup> GC: Gas chromatography

<sup>2</sup> GC/MS: Gas chromatography with mass spectrometric detection

<sup>3</sup> HPLC: High performance liquid chromatography

TOC can be determined by a technique that uses a dissolved oxidizing agent promoted by ultraviolet light. Potassium peroxydisulfate,  $K_2S_2O_8$ , can be used as an oxidizing agent to be added to the sample. Phosphoric acid is also added to the sample, which is sparged with air or nitrogen to drive off  $CO_2$  formed from  $HCO_3^-$

and  $\text{CO}_3^{2-}$  in solution. After sparging, the sample is pumped to a chamber containing a lamp emitting ultraviolet radiation of 184.9 nm. This radiation produces reactive free radical species such as the hydroxyl radical,  $\text{HO}\cdot$ , discussed extensively as a photochemical reaction intermediate in Chapters 14, 15, and 16. These active species bring about the rapid oxidation of dissolved organic compounds as shown in the following general reaction:



After oxidation is complete, the  $\text{CO}_2$  is sparged from the system and measured with a gas chromatographic detector or by absorption in ultrapure water followed by a conductivity measurement. Figure 26.1 is a schematic of a TOC analyzer showing the major components of this instrument.

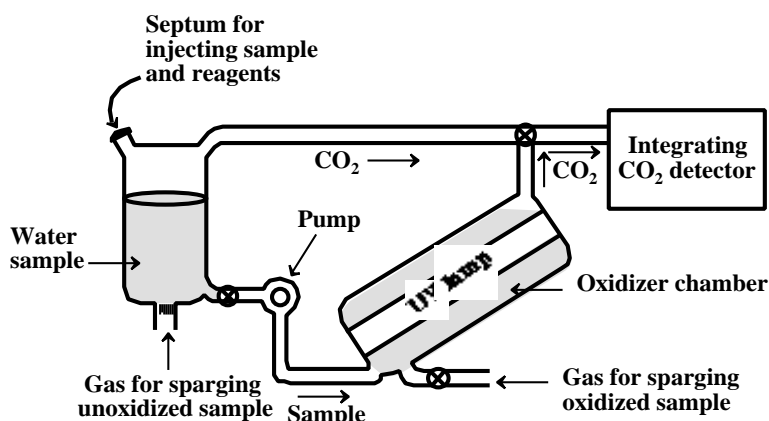


Figure 26.1 TOC analyzer employing UV-promoted sample oxidation.

## Measurement of Radioactivity in Water

There are several potential sources of radioactive materials that can contaminate water (see Chapter 12, Section 12.13). Radioactive contamination of water is normally detected by measurements of gross beta and gross alpha activity, a procedure that is simpler than detecting individual isotopes. The measurement is made from a sample formed by evaporating water to a very thin layer on a small pan, which is then inserted inside an internal proportional counter. This setup is necessary because beta particles can penetrate only very thin detector windows, and alpha particles have essentially no penetrating power. More detailed information can be obtained for radionuclides that emit gamma rays by the use of gamma spectrum analysis. This technique employs solid state detectors to resolve rather closely spaced gamma peaks in the sample's spectra. In conjunction with multichannel spectrometric data analysis, it is possible to determine a number of radionuclides in the same sample without chemical separation. This method requires minimal sample preparation.

## Biological Toxins

Toxic substances produced by microorganisms are of some concern in water. Photosynthetic cyanobacteria and some kinds of algae growing in water produce potentially troublesome toxic substances. An immunoassay method of analysis (see Chapter 25, Section 25.12) for such toxins has been described.<sup>1</sup>

## Summary of Water Analysis Procedures

The main chemical parameters commonly determined in water are summarized in Table 26.4. In addition to these, a number of other solutes, especially specific organic pollutants, may be determined in connection with specific health hazards or incidents of pollution.

## 26.5 ANALYSIS OF WASTES AND SOLIDS

The analysis of hazardous wastes of various kinds for a variety of potentially dangerous substances is one of the most important aspects of hazardous waste management. These analyses are performed for a number of reasons including tracing the sources of wastes, assessing the hazards posed by the wastes to surroundings and to waste remediation personnel, and determining the best means of waste treatment. Here is presented a brief overview of several of the main considerations applied to the analysis of wastes. For purposes of this discussion, wastes are broadly defined to include all kinds of solids, semisolids, sludges, liquids, contaminated soils, sediments, and other kinds of materials that are either wastes themselves or are contaminated by wastes.

For the most part, the substances determined as part of waste analysis, the *analytes*, are measured by techniques that are used for the determination of the same analytes in water and, to a lesser extent, in air. However, the preparation techniques that must be employed for waste analysis are usually more complex than those used for the same analytes in water. That is because the matrices in which the waste analytes are contained are usually relatively complicated, which makes it difficult to recover all the analytes from the waste and which introduces interfering substances. As a result, the lower limits at which substances can be measured in wastes (a parameter known as the practical quantitation limit) are usually significantly higher than in water.

There are several distinct steps in the analysis of a waste. Compared with water, wastes are often highly heterogeneous, making the collection of representative samples difficult. Whereas water samples can often be introduced into an analytical instrument with minimal preparation, the processing of hazardous wastes to get a sample that can be introduced into an instrument is often relatively complicated. Such processing can consist of dilution of oily samples with an organic solvent, extraction of organic analytes into an organic solvent, evolution and collection of volatile organic carbon analytes, or digestion of solids with strong acids and oxidants to extract metals for analysis. The products of these processes must often be subjected to relatively complicated sample cleanup procedures to remove contaminants that might interfere with the analysis or damage the analytical instrument.

**Table 26.4 Chemical Parameters Commonly Determined in Water**

Chemical species	Significance in water	Methods of analysis
Acidity	Indicative of industrial pollution or acid mine drainage	Titration
Alkalinity	Water treatment, buffering, algal productivity	Titration
Aluminum	Water treatment, buffering	AA, <sup>1</sup> ICP <sup>2</sup>
Ammonia	Algal productivity, pollutant	Spectrophotometry
Arsenic	Toxic pollutant	Spectrophotometry, AA, ICP
Barium	Toxic pollutant	AA, ICP
Beryllium	Toxic pollutant	AA, ICP, fluorimetry
Boron	Toxic to plants	Spectrophotometry, ICP
Bromide	Seawater intrusion, industrial waste	Spectrophotometry, potentiometry, ion chromatography
Cadmium	Toxic pollutant	AA, ICP
Calcium	Hardness, productivity, treatment	AA, ICP, titration
Carbon dioxide	Bacterial action, corrosion	Titration, calculation
Chloride	Saline water contamination	Titration, electrochemical, ion chromatography
Chlorine	Water treatment	Spectrophotometry
Chromium	Toxic pollutant (hexavalent Cr)	AA, ICP, colorimetry
Copper	Plant growth	AA, ICP
Cyanide	Toxic pollutant	Spectrophotometry, potentiometry, ion chromatography
Fluoride	Water treatment, toxic at high levels	Spectrophotometry, potentiometry, ion chromatography
Hardness	Water quality, water treatment	AA, titration
Iodide	Seawater intrusion, industrial waste	Catalytic effect, potentiometry, ion chromatography
Iron	Water quality, water treatment	AA, ICP, colorimetry
Lead	Toxic pollutant	AA, ICP, voltammetry

**Table 26.4 (Cont.)**

Lithium	May indicate some pollution	AA, ICP, flame photometry
Magnesium	Hardness	AA, ICP
Manganese	Water quality (staining)	AA, ICP
Mercury	Toxic pollutant	Flameless atomic absorption
Methane	Anaerobic bacterial action	Combustible-gas indicator
Nitrate	Algal productivity, toxicity	Spectrophotometry, ion chromatography
Nitrite	Toxic pollutant	Spectrophotometry, ion chromatography
Nitrogen (albuminoid) (organic)	Proteinaceous material Organic pollution indicator	Spectrophotometry Spectrophotometry
Oil and grease	Industrial pollution	Gravimetry
Organic carbon	Organic pollution indicator	Oxidation-CO <sub>2</sub> measurement
Organic contaminants	Organic pollution indicator	Activated carbon adsorption
Oxygen	Water quality	Titration, electrochemical
Oxygen demand (biochemical) (chemical)	Water quality and pollution Water quality and pollution	Microbiological-titration Chemical oxidation-titration
Ozone	Water treatment	Titration
Pesticides	Water pollution	Gas chromatography
pH	Water quality and pollution	Potentiometry
Phenols	Water pollution	Distillation-colorimetry
Phosphate	Productivity, pollution	Spectrophotometry
Phosphorus (hydrolyzable)	Water quality and pollution	Spectrophotometry
Potassium	Productivity, pollution	AA, ICP, flame photometry
Selenium	Toxic pollutant	Spectrophotometry, ICP, neutron activation
Silica	Water quality	Spectrophotometry, ICP
Silver	Water pollution	AA, ICP

**Table 26.4 (Cont.)**

Sodium	Water quality, saltwater intrusion	AA, ICP, flame photometry
Strontium	Water quality	AA, ICP, flame photometry
Sulfate	Water quality, water pollution	Ion chromatography
Sulfide	Water quality, water pollution	Spectrophotometry, titration, chromatography
Sulfite	Water pollution, oxygen scavenger	Titration, ion chromatography
Surfactants	Water pollution	Spectrophotometry
Tannin, Lignin	Water quality, water pollution	Spectrophotometry
Vanadium	Water quality, water pollution	ICP
Zinc	Water quality, water pollution	AA, ICP

<sup>1</sup> AA denotes atomic absorption

<sup>2</sup> ICP stands for inductively coupled plasma techniques, including atomic emission and detection of plasma-atomized atoms by mass spectrometry.

Over a number of years, the U.S. Environmental Protection Agency has developed specialized methods for the characterization of wastes. These methods are given in the publication entitled *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods* ("SW-846"), which is periodically updated to keep it current<sup>2</sup> and is available on CD-ROM.<sup>3</sup> Because of the difficult and exacting nature of many of the procedures in this work and because of the hazards associated with the use of reagents such as strong acids and oxidants employed for sample digestion and solvents used to extract organic analytes, anyone attempting analyses of hazardous-waste materials should use this resource and follow procedures carefully with special attention to precautions.

### Sample Digestion

To analyze a solid waste sample by flame atomic absorption spectroscopy, graphite furnace absorption spectroscopy, inductively coupled argon plasma spectroscopy, or inductively coupled argon plasma mass spectrometry, the sample must first be digested to get the analyte metals in solution. Digestion dissolves only those fractions of metals that can be put into solution under relatively extreme conditions and therefore enables measurement of available metals. It should be noted that sample digestion procedures generally use highly corrosive, dangerous reagents that are strong acids and strong oxidants and demand expert personnel using the proper equipment, including fume hoods and adequate personnel protection.

EPA Method 3050 is a procedure for acid digestion of sediments, sludges, and soils. A sample of up to 2 g is treated with a mixture of nitric acid and hydrogen peroxide; the sample is then refluxed with either con. HNO<sub>3</sub> or con. HCl, then refluxed with dilute HCl, filtered, and the filtrate analyzed for metals.

Microwave heating can be used to assist the digestion of samples. The procedure for the digestion of aqueous liquids consists of mixing a 45 mL sample with 5 mL of concentrated nitric acid, placing it in a fluorocarbon (Teflon) digestion vessel, and heating for 20 minutes. After digestion is complete, the sample is cooled, solids are separated by filtration or centrifugation, and the liquid remaining is analyzed by the appropriate atomic spectrometric technique.

Method 3052 is a procedure for microwave-assisted acid digestion of siliceous and organically based matrices. It can be used on a variety of kinds of samples including biological tissues, oils, oil-contaminated soils, sediments, sludges, and soil. This method is not appropriate for analyses of leachable metals, but is used for measurement of total metals. A sample of up to 0.5 g is digested with microwave heating for 15 minutes in a chemically resistant fluorocarbon polymer container in an appropriate acid mixture. Commonly, the reagents employed are a mixture of 9 mL of con. nitric acid and 3 mL hydrofluoric acid, although other acid mixtures employing reagents such as con. HCl and hydrogen peroxide can be used. The sample is heated in the microwave oven to 180°C and held at that temperature for at least 9.5 minutes. After heating, the residual solids are filtered off and the filtrate analyzed for metals.

Many kinds of hazardous waste samples contain metals dissolved or suspended in viscous petroleum products, including oils, oil sludges, tars, waxes, paints, paint sludges, and other hydrocarbon materials. Method 3031 can be used to dissolve these metals—including antimony, arsenic, barium, beryllium, cadmium, chromium, cobalt, copper, lead molybdenum, nickel, selenium, silver, thallium, vanadium, and zinc—in a form suitable for atomic spectrometric analysis. The procedure involves mixing 0.5 g of sample with 0.5 g of finely ground  $\text{KMnO}_4$  and 1.0 mL of con.  $\text{H}_2\text{SO}_4$ , which causes a strongly exothermic reaction to occur as the hydrocarbon matrix is oxidized. After the reaction has subsided, 2 mL of con.  $\text{HNO}_3$  and 2 mL of con. HCl are added, the sample is filtered with filter paper, the filter paper is digested with con. HCl, and the sample is diluted and analyzed for metals.

### **Analyte Isolation for Organics Analysis**

The determination of organic analytes requires that they be isolated from the sample matrix. Since organic analytes are generally soluble in organic solvents, they can usually be extracted from samples with a suitable solvent. Although extraction works well for nonvolatile and semivolatile analytes, it is not so suitable for volatile organic compounds, which are readily vaporized during sample processing. The volatile materials are commonly isolated by techniques that take advantage of their high vapor pressures.

### **Solvent Extraction**

Method 3500 is a procedure for extracting nonvolatile or semivolatile compounds from a liquid or solid sample. The sample is extracted with an appropriate solvent, dried, and concentrated in a Kuderna-Danish apparatus prior to further processing for analysis.

A number of methods more complicated than Method 3500 have been devised

for extracting nonvolatile and semivolatile analytes from waste samples. Method 3540 uses extraction with a Soxhlet extractor. This device, illustrated in Chapter 10, [Figure 10.6](#), for the extraction of lipids from biological tissue, provides for recirculation of continuously redistilled fresh solvent over a sample of soils, sludges, and wastes. The sample is first mixed with anhydrous  $\text{Na}_2\text{SO}_4$  to dry it, then placed inside an extraction thimble in the Soxhlet apparatus, which redistills a relatively small volume of extraction solvent over the sample. After extraction, the sample can be dried, concentrated, and exchanged into another solvent prior to analysis.

Method 3545 uses pressurized fluid extraction at  $100^\circ\text{C}$  and a pressure up to 2000 psi to remove organophilic analyte species from dried solid samples including soils, clays, sediments, sludges, and waste solids. Used for the extraction of semivolatile organic compounds, organophosphorus pesticides, organochlorine pesticides, chlorinated herbicides, and PCBs, it requires less solvent and takes less time than the Soxhlet extraction described above.

Method 3550 uses sonication with ultrasound to expedite the extraction of nonvolatile and semivolatile organic compounds from solids including soils, sludges, and wastes. The procedure calls for subjecting the finely divided dried sample mixed with solvent to ultrasound for a brief period of time. Low-concentration samples can be subjected to multiple extractions with additional fresh solvent.

Although the requirement for specialized high pressure equipment has limited its application, extraction with supercritical carbon dioxide maintained at temperatures and pressures above the critical point where separate liquid and vapor phases do not exist is a very effective means of extracting some organic analytes. Method 3561 is used to extract polycyclic aromatic hydrocarbons such as acenaphthene, benzo(a)pyrene, fluorene, and pyrene from solid samples using a relatively complicated three-step procedure.

## Sample Preparation for Volatile Organic Compounds

Several approaches are used to isolate and concentrate volatile analytes from waste samples for subsequent measurement. Some of these based on **headspace analysis** involve evaporation of volatile substances into the space above the sample (headspace) in a closed container. Method 5021, "Volatile Organic Compounds in Soils and Other Solid Matrices Using Equilibrium Headspace Analysis," is used to isolate volatile organic compounds, such as benzene, bromomethane, chloroform, 1,4-dichlorobenzene, dichloromethane, styrene, toluene, vinyl chloride, and the xylene isomers, from soil, sediment, or solid waste samples for determination by gas chromatography or gas chromatography/mass spectrometry.

In addition to headspace analysis, purge-and-trap procedures can be employed that drive volatile analytes from a sample and collect them on an adsorbent column for subsequent analysis. Distillation techniques, including azeotropic distillation and vacuum distillation are also used to isolate volatile analytes.

## Sample Cleanup

Most waste, soil, and sediment samples result in extraction of extraneous substances that can result in the observation of extraneous peaks, be detrimental to



peak resolution and column efficiency, and be damaging to expensive columns and detectors. As shown in Table 26.5, **sample cleanup** refers to a number of measures that can be taken to remove these constituents from sample extracts by several procedures. Sample cleanup may involve distillation, partitioning with immiscible solvents, adsorption chromatography, gel permeation chromatography, or the chemical destruction of interfering substances with acid, alkali, or oxidizing agents; two or more of these techniques may be used in combination. The most widely applicable cleanup technique is gel permeation chromatography, which can be used to separate substances with high molecular weights from the analytes of interest. Treatment by adsorption column chromatography with alumina, Florisil, or silica gel can be used to isolate a relatively narrow polarity range of analytes away from interfering substances. Acid-base partitioning can be used in the determination of materials such as chlorophenoxy herbicides and phenols to separate acidic, basic, and neutral organics.

**Table 26.5 Sample Cleanup Techniques and Their Applications**

Number	Type	Applications
3610	Alumina column	Phthalate esters, nitrosamines
3611	Alumina column cleanup and separation of petroleum wastes	Polycyclic aromatic hydrocarbons, petroleum wastes
3620	Florisil column	Phthalate esters, nitrosamines, organochlorine pesticides, PCBs, chlorinated hydrocarbons, organophosphorus pesticides
3630	Silica gel	Polycyclic aromatic hydrocarbons
3630(b)	Silica gel	Phenols
3640	Gel permeation chromatography	Phenols, phthalate esters, nitrosamines, organochlorine pesticides, PCBs, nitroaromatics, cyclic ketones, polycyclic aromatic hydrocarbons, chlorinated hydrocarbons, organophosphorus pesticides, priority pollutant semivolatiles
3650	Acid-base liquid/liquid partition	Phenols, priority pollutant semivolatiles
3660	Sulfur cleanup	Organochlorine pesticides, PCBs, Priority pollutant semivolatiles

Alumina column cleanup makes use of highly porous granular aluminum oxide. Available in acidic, neutral, and basic pH ranges, this solid is packed into a column topped with a water-absorbing substance over which the sample is eluted with a suitable solvent, which leaves interferences on the column. After elution, the sample is concentrated, exchanged with another solvent if necessary, then analyzed. Florisil

is an acidic magnesium silicate and a registered trade name of Floridin Co. It is used in a column cleanup procedure in a manner similar to alumina. Silica gel is a weakly acidic amorphous silicon oxide. It can be activated by heating for several hours at 150–160°C and used for the separation of hydrocarbons. Deactivated silica gel containing 10–20% water acts as an adsorbent for compounds with ionic and nonionic functionalities such as dyes, alkali metal cations, terpenoids, and plasticizers. It is used in a column as described for alumina above. Gel-permeation chromatography separates solutes by size carried over a hydrophobic gel by organic solvents. A gel must be chosen that will separate the appropriate size range of analytes and interferences. The gel is preswelled before loading onto a column and flushed extensively with solvent before the sample is introduced for separation.

## 26.6 TOXICITY CHARACTERISTIC LEACHING PROCEDURE

The **Toxicity Characteristic Leaching Procedure (TCLP)** is specified to determine the potential toxicity hazard of various kinds of wastes.<sup>4</sup> The test was designed to estimate the availability to organisms of both inorganic and organic species in hazardous materials present as liquids, solids, or multiple phase mixtures by producing a leachate, the TCLP extract, which is analyzed for the specific toxicants listed in [Table 26.6](#).

The procedure for conducting the TCLP is rather involved. The procedure need not be run at all if a total analysis of the sample reveals that none of the pollutants specified in the procedure could exceed regulatory levels. At the opposite end of the scale, analysis of any of the liquid fractions of the sample showing that any regulated species would exceed regulatory levels even after the dilutions involved in the TCLP measurement have been carried out designate the sample as hazardous, and the TCLP measurement is not required.

In conducting the TCLP test, if the waste is a liquid containing less than 0.5% solids, it is filtered through a 0.6–0.8 µm glass fiber filter and the filtrate is designated as the TCLP extract. At solids levels exceeding 0.5%, any liquid present is filtered off for separate analysis and the solid is extracted to provide a TCLP extract (after size reduction, if the particles exceed certain size limitations). The choice of the extraction fluid is determined by the pH of the aqueous solution produced from shaking a mixture of 5 g of solids and 96.5 mL of water. If the pH is less than 5.0, a pH 4.93 acetic acid/sodium acetate buffer is used for extraction; otherwise, the extraction fluid used is a pH of 2.88±0.05 solution of dilute acetic acid. Extractions are carried out in a sealed container rotated end-over-end for 18 hours. The liquid portion is then separated and analyzed for the specific substances given in [Table 26.6](#). If values exceed the regulatory limits, the waste is designated as “toxic.”

## 26.7 ATMOSPHERIC MONITORING

The atmosphere is a particularly difficult analytical system because of the very low levels of substances to be analyzed; sharp variations in pollutant level with time and location; differences in temperature and humidity; and difficulties encountered in reaching desired sampling points, particularly those substantially above the earth's surface. These conditions make the acquisition of representative atmospheric samples

**Table 26.6 Contaminants Determined in TCLP Procedure**

EPA hazard- ous-waste number	Contaminant	Regulatory level, mg/L	EPA hazard- ous-waste number	Contaminant	Regulatory level, mg/L
<i>Heavy metals (metalloids)</i>					
D004	Arsenic	5.0	D033	Hexachloro- butadiene	0.5
D005	Barium	100.0			
D006	Cadmium	1.0	D034	Hexachloro- ethane	3.0
D007	Chromium	5.0			
D008	Lead	5.0	D035	Methylethyl ketone	200.0
D009	Mercury	0.2			
D010	Selenium	1.0	D036	Nitrobenzene	2.0 <sup>2</sup>
D011	Silver	5.0	D037	Pentachloro- phenol	100.0
<i>Organics</i>					
			D038	Pyridine	5.0 <sup>2</sup>
			D039	Tetrachloro- ethylene	0.7
D018	Benzene	0.5			
D019	Carbon tetrachloride	0.5	D040	Trichloroethylene	0.5
			D041	2,4,5-Trichloro- phenol	400.0
D021	Chloro- benzene	100.0	D042	2,4,6-Trichloro- phenol	2.0
D022	Chloroform	6.0			
D023	<i>o</i> -Cresol	200.0 <sup>1</sup>	D043	Vinyl chloride	0.2
D024	<i>m</i> -Cresol	200.0 <sup>1</sup>	<i>Pesticides</i>		
D025	<i>p</i> -Cresol	200.0 <sup>1</sup>	D012	Endrin	0.02
D026	Cresol	200.0 <sup>1</sup>	D013	Lindane	0.4
D027	1,4-Dichloro- obenzene	7.5	D014	Methoxychlor	10.0
D028	1,2-Dichloro- oethane	0.5	D015	Toxaphene	0.5
D029	1,1-Dichloro- oethylene	0.7	D016	2,4-D	10.0
D030	2,4-Dinitro- toluene	0.13 <sup>2</sup>	D017	2,4,5-TP (Silvex)	1.0
			D020	Chlordane	0.03
D032	Hexachloro- benzene	0.13 <sup>2</sup>	D031	Heptachlor (and its epoxide)	0.008

<sup>1</sup> If *o*-, *m*-, and *p*-Cresol concentrations cannot be differentiated, the total cresol (D026) concentration is used. The regulatory level of total cresol is 200 mg/L.

<sup>2</sup> Quantitation limit is greater than the calculated regulatory level. The quantitation limit therefore becomes the regulatory level.

particularly challenging. The ideal atmospheric analysis techniques are those that work successfully without sampling, such as long-path laser resonance absorption monitoring. For most analyses, however, various types of sampling are required. In some very sophisticated monitoring systems, samples are collected and analyzed automatically and the results are transmitted to a central receiving station. Often, however, a batch sample is collected for later chemical analysis. Figure 26.2 illustrates the effect of duration of sampling upon observed values of air pollutant levels.

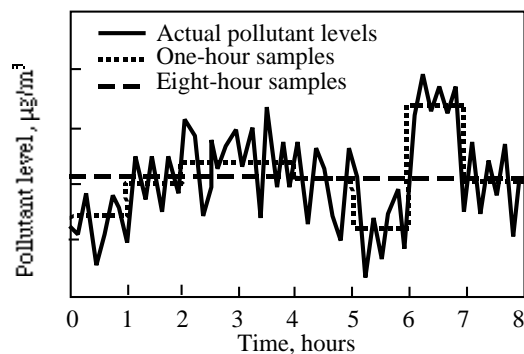


Figure 26.2 Effect of duration of sampling upon observed values of air pollutant levels.

The most straightforward technique for the collection of particles is sedimentation. A sedimentation collector may be as simple as a glass jar equipped with a funnel. Liquid is sometimes added to the collector to prevent the solids from being blown out. Filtration is the most common technique for sampling particulate matter. Filters composed of fritted (porous) glass, porous ceramics, paper fibers, cellulose fibers, fiberglass, asbestos, mineral wool, or plastic can be used. A special type of filter is the membrane filter, which yields high flow rates with small, moderately uniform pores. Impingers, as the name implies, collect particles from a relatively high-velocity air stream directed at a surface.

Sampling for vapors and gases may range from methods designed to collect only one specific pollutant to those designed to collect all pollutants. Essentially all pollutants can be removed from an air sample cryogenically by freezing or by liquifying the air in collectors maintained at a low temperature. Absorption in a solvent, such as by bubbling the gas through a liquid, can be used for the collection of gaseous pollutants. Adsorption, in which a gas collects on the surface of a solid, is particularly useful for the collection of samples to be analyzed by gas chromatography.

## Methods of Air Pollutant Analysis

A very large number of different analytical techniques are used for atmospheric pollutant analysis. A summary of some of the main instrumental techniques for air monitoring is presented in Table 26.7.

The U.S. Environmental Protection Agency specifies reference methods of analysis for selected air pollutants to determine compliance with the primary and secondary national ambient air quality standards for those pollutants. These methods are

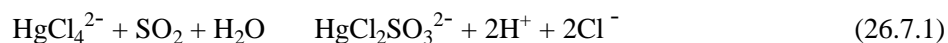
published annually in the *Code of Federal Regulations*.<sup>5</sup> These methods are not necessarily state-of-the-art, and, in some cases, are outdated and cumbersome. However, they provide proven reliable measurements for regulatory and legal purposes.

**Table 26.7 The Main Techniques Used for Air Pollutant Analysis**

Pollutant	Method	Potential interferences
SO <sub>2</sub> (total S)	Flame photometric (FPD)	H <sub>2</sub> S, CO
SO <sub>2</sub>	Gas chromatography (FPD)	H <sub>2</sub> S, CO
SO <sub>2</sub>	Spectrophotometric (pararosaniline wet chemical)	H <sub>2</sub> S, HCl, NH <sub>3</sub> , NO <sub>2</sub> , O <sub>3</sub>
SO <sub>2</sub>	Electrochemical	H <sub>2</sub> S, HCl, NH <sub>3</sub> , NO, NO <sub>2</sub> , O <sub>3</sub> , C <sub>2</sub> H <sub>4</sub> ,
SO <sub>2</sub>	Conductivity	HCl, NH <sub>3</sub> , NO <sub>2</sub>
SO <sub>2</sub>	Gas-phase spectrophotometric	NO, NO <sub>2</sub> , O <sub>3</sub> ,
O <sub>3</sub>	Chemiluminescent	H <sub>2</sub> S
O <sub>3</sub>	Electrochemical	NH <sub>3</sub> , NO <sub>2</sub> , SO <sub>2</sub>
O <sub>3</sub>	Spectrophotometric (potassium iodide reaction, wet chemical)	NH <sub>3</sub> , NO <sub>2</sub> , NO, SO <sub>2</sub>
O <sub>3</sub>	Gas-phase spectrophotometric	NO <sub>2</sub> , NO, SO <sub>2</sub>
CO	Infrared	CO <sub>2</sub> (at high levels)
CO	Gas chromatography	---
CO	Electrochemical	NO, C <sub>2</sub> H <sub>4</sub>
CO	Catalytic combustion-thermal detection	NH <sub>3</sub>
CO	Infrared fluorescence	---
CO	Mercury replacement ultraviolet photometric	C <sub>2</sub> H <sub>4</sub>
NO <sub>2</sub>	Chemiluminescent	NH <sub>3</sub> , NO, NO <sub>2</sub> , SO <sub>2</sub>
NO <sub>2</sub>	Spectrophotometric (azo-dye reaction, wet chemical)	NO, SO <sub>2</sub> , NO <sub>2</sub> , O <sub>3</sub>
NO <sub>2</sub>	Electrochemical	HCl, NH <sub>3</sub> , NO, NO <sub>2</sub> , SO <sub>2</sub> , O <sub>3</sub> , CO
NO <sub>2</sub>	Gas-phase spectrophotometric	NH <sub>3</sub> , NO, NO <sub>2</sub> , SO <sub>2</sub> , CO
NO <sub>2</sub>	Conductivity	HCl, NH <sub>3</sub> , NO, NO <sub>2</sub> , SO <sub>2</sub>

### Determination of Sulfur Dioxide

The reference method for the analysis of sulfur dioxide is the spectrophotometric West-Gaeke pararosaniline method. It uses a collecting solution of 0.04 M potassium tetrachloromercurate to collect sulfur dioxide according to the following reaction:



The  $\text{HgCl}_2\text{SO}_3^{2-}$  complex stabilizes readily oxidized sulfur dioxide from reaction with oxidants such as ozone and nitrogen oxides. For analysis, sulfur dioxide in the scrubbing medium is reacted with formaldehyde:



The adduct formed is then reacted with uncolored organic pararosaniline hydrochloride to produce a red-violet dye that is measured spectrophotometrically.

Performed manually, the West-Gaeke method for sulfur dioxide analysis is cumbersome and complicated. However, the method has been refined to the point that it can be done automatically with continuous-monitoring equipment. A block diagram of such an analyzer is shown in Figure 26.3.

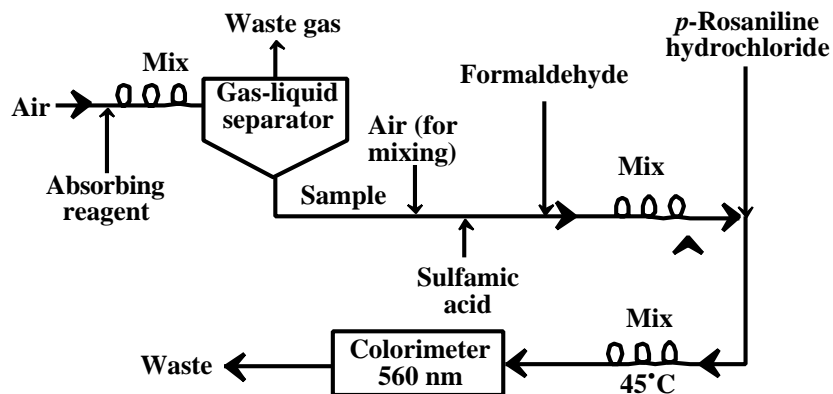


Figure 26.3 Block diagram of an automated system for the determination of sulfur dioxide by the pararosaniline method.

Several types of sulfur dioxide monitors are based on amperometry, in which an electrical current is measured that is proportional to the  $\text{SO}_2$  in a collecting solution. Sulfur dioxide can be determined using ion chromatography by bubbling  $\text{SO}_2$  through hydrogen peroxide solution to produce  $\text{SO}_4^{2-}$ , followed by analysis of the sulfate by ion chromatography, a method that separates ions on a chromatography column and detects them very sensitively by conductivity measurement. Flame photometry, sometimes in combination with gas chromatography, is used for the detection of sulfur dioxide and other gaseous sulfur compounds. The gas is burned in a hydrogen flame, and the sulfur emission line at 394 nm is measured.

Several direct spectrophotometric methods are used for sulfur dioxide measurement, including nondispersive infrared absorption, Fourier transform infrared analysis (FTIR), ultraviolet absorption, molecular resonance fluorescence, and second-derivative spectrophotometry. The principles of these methods are the same for any gas measured.

## Nitrogen Oxides

Gas-phase chemiluminescence is the favored method of  $\text{NO}_x$  analysis. The general phenomenon of chemiluminescence was defined in Chapter 14, Section 14.8. It results from the emission of light from electronically excited species formed by a

chemical reaction. In the case of NO, ozone is used to bring about the reaction, producing electronically excited nitrogen dioxide:



The species loses energy and returns to the ground state through emission of light in the 600–3000 nm range. The emitted light is measured by a photomultiplier; its intensity is proportional to the concentration of NO. A schematic diagram of the device used is shown in Figure 26.4.

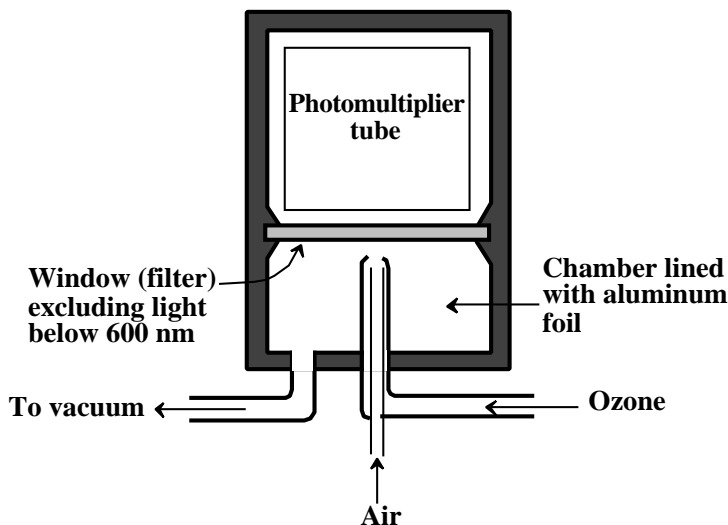


Figure 26.4 Chemiluminescence detector for  $\text{NO}_x$ .

Since the chemiluminescence detector system depends upon the reaction of  $\text{O}_3$  with NO, it is necessary to convert  $\text{NO}_2$  to NO in the sample prior to analysis. This is accomplished by passing the air sample over a thermal converter, which brings about the desired conversion. Analysis of such a sample gives  $\text{NO}_x$ , the sum of NO and  $\text{NO}_2$ . Chemiluminescence analysis of a sample that has not been passed over the thermal converter gives NO. The difference between these two results is  $\text{NO}_2$ .

This analysis technique is illustrative of chemiluminescence analysis in general. Chemiluminescence is an inherently desirable technique for the analysis of atmospheric pollutants because it avoids wet chemistry, is basically simple, and lends itself well to continuous monitoring and instrumental methods. Another chemiluminescence method, that employed for the analysis of ozone, is described below.

### **Analysis of Oxidants**

The atmospheric oxidants that are commonly determined include ozone, hydrogen peroxide, organic peroxides, and chlorine. The classic manual method for the analysis of oxidants is based upon their oxidation of  $\text{I}^-$  ion followed by spectrophotometric measurement of the product. The sample is collected in 1% KI buffered at pH 6.8. Oxidants react with  $\text{I}^-$  ion as shown by the following reaction of ozone:



The absorbance of the colored  $\text{I}_3^-$  product is measured spectrophotometrically at 352 nm. Generally, the level of oxidant is expressed in terms of ozone, although it should be noted that not all oxidants—PAN, for example—react with the same efficiency as  $\text{O}_3$ . Oxidation of  $\text{I}^-$  as shown in the above reaction can be used to determine oxidants in a concentration range of several hundredths of a part per million to approximately 10 ppm. Nitrogen dioxide gives a limited response to the method, and reducing substances interfere seriously.

The currently favored method for oxidant analysis uses the chemiluminescent reaction between ozone and ethylene. This reaction emits light at a maximum intensity at 435 nm. The intensity of emitted light is directly proportional to the level of ozone.

### Analysis of Carbon Monoxide

Carbon monoxide is analyzed in the atmosphere by nondispersive infrared spectrometry. This technique depends upon the fact that carbon monoxide absorbs infrared radiation strongly at certain wavelengths. Therefore, when such radiation is passed through a long (typically 100 cm) cell containing trace levels of carbon monoxide, more of the infrared radiant energy is absorbed.

A nondispersive infrared spectrometer differs from standard infrared spectrometers in that the infrared radiation from the source is not dispersed according to wavelength by a prism or grating. The nondispersive infrared spectrometer is made very specific for a given compound, or type of compound, by using the sought-for material as part of the detector, or by placing it in a filter cell in the optical path. A diagram of a nondispersive infrared spectrometer selective for CO is shown in [Figure 26.5](#). Radiation from an infrared source is “chopped” by a rotating device so that it alternately passes through a sample cell and a reference cell. In this particular instrument, both beams of light fall on a detector filled with CO gas and separated into two compartments by a flexible diaphragm. The relative amounts of infrared radiation absorbed by the CO in the two sections of the detector depend upon the level of CO in the sample. The difference in the amount of infrared radiation absorbed in the two compartments causes slight differences in heating, so that the diaphragm bulges slightly toward one side. Very slight movement of the diaphragm can be detected and recorded. By means of this device, carbon monoxide can be measured from 0–150 ppm, with a relative accuracy of  $\pm 5\%$  in the optimum concentration range.

Flame-ionization gas chromatography detection can also be used for the analysis of carbon monoxide. This detector system is selective for hydrocarbons, and conversion of CO to methane in the sample is required. This is accomplished by reaction with hydrogen over a nickel catalyst at 360 °C:



A major advantage of this approach is that the same basic instrumentation can be used to measure hydrocarbons.



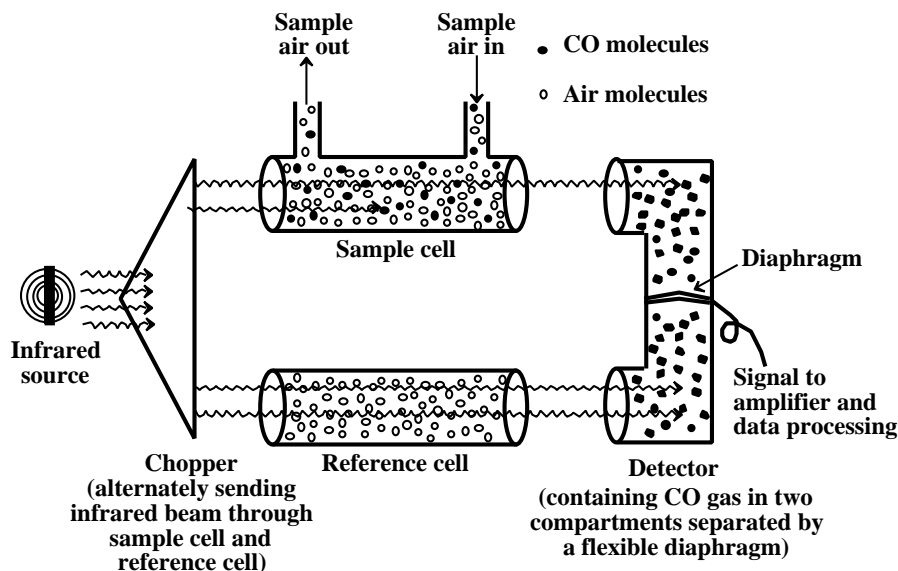


Figure 26.5 Nondispersive infrared spectrometer for the determination of carbon monoxide in the atmosphere.

## Determination of Hydrocarbons and Organics

Monitoring of hydrocarbons in atmospheric samples takes advantage of the very high sensitivity of the hydrogen flame ionization detector to measure this class of compounds. Known quantities of air are run through the flame ionization detector 4 to 12 times per hour to provide a measure of total hydrocarbon content.

In some cases, it is important to have a method to determine individual organics because of their toxicities, ability to form photochemical smog, as indicators of photochemical smog, and as a means of tracing sources of pollution. Numerous techniques have been published for the determination of organic compounds in the atmosphere. For example, whole-air samples can be collected in Tedlar bags, and the organic analytes concentrated cryogenically at  $-180^{\circ}\text{C}$ , then thermally desorbed and measured with high-resolution capillary column gas chromatography.

## Analysis of Particulate Matter

Particles are almost always removed from air or gas (such as exhaust flue gas) prior to analysis. The two main approaches to particle isolation are filtration and removal by methods that cause the gas stream to undergo a sharp bend such that particles are collected on a surface.

The method commonly used for determining the quantity of total suspended particulate matter in the atmosphere draws air over filters that remove the particles. This device, called a **Hi-Vol sampler** (Figure 26.6), is essentially a glorified vacuum cleaner that draws air through a filter. The samplers are usually placed under a shelter that excludes precipitation and particles larger than about 0.1 mm in

diameter, favoring collection of particles up to 25–50  $\mu\text{m}$  diameter. These devices efficiently collect particles from a large volume of air, typically 2000  $\text{m}^3$ , and typically over a 24-hour period.

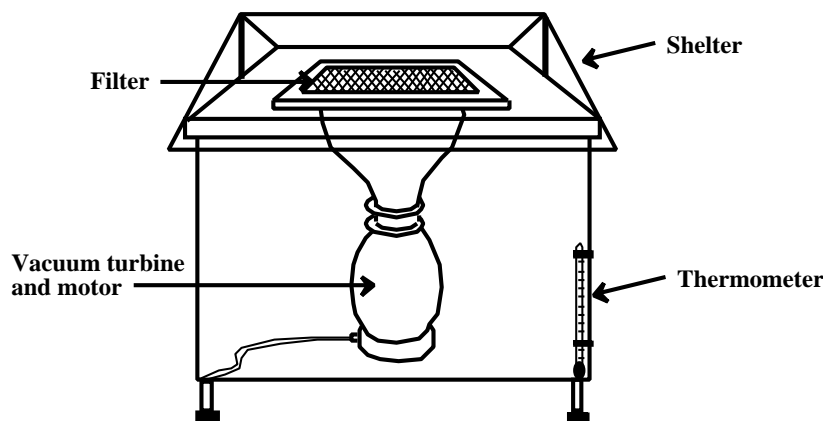


Figure 26.6 Hi-Vol sampler for the collection of particulate matter from the atmosphere for analysis.

The filters used in a Hi-Vol sampler are usually composed of glass fibers and have a collection efficiency that is at least 99% for particles with 0.3  $\mu\text{m}$  diameter. Particles with diameters exceeding 100  $\mu\text{m}$  remain on the filter surface, whereas particles with diameters down to approximately 0.1  $\mu\text{m}$  are collected on the glass fibers in the filters. Efficient collection is achieved by using very small-diameter fibers (less than 1  $\mu\text{m}$ ) for the filter material.

The technique described here is most useful for determining total levels of particulate matter. Prior to taking the sample, the filter is maintained at 15–35°C at 50% relative humidity for 24 hours, then weighed. After sampling for 24 hours, the filter is removed and equilibrated for 24 hours under the same conditions used prior to its installation on the sampler. The filter is then weighed and the quantity of particulate matter per unit volume of air is calculated.

Size separation of particles can be achieved by filtration through successively smaller filters in a **stacked filter unit**. Another approach uses the **virtual impactor**, a combination of an air filter and an impactor (discussed below). In the virtual impactor, the gas stream being sampled is forced to make a sharp bend. Particles larger than about 2.5  $\mu\text{m}$  do not make the bend and are collected on a filter. The remaining gas stream is then filtered to remove smaller particles.

**Impactors** cause a relatively high velocity gas stream to undergo a sharp bend such that particles are collected on a surface impacted by the stream. The device may be called a dry or wet impactor, depending upon whether collecting surface is dry or wet; wet surfaces aid particle retention. Size segregation can be achieved with an impactor because larger particles are preferentially impacted, and smaller particles continue in the gas stream.

A number of chemical analysis techniques can be used to characterize atmospheric pollutants. These include atomic absorption, inductively coupled plasma techniques, X-ray fluorescence, neutron activation analysis, and ion-selective elec-

trodes for fluoride analysis. Chemical microscopy is an extremely useful technique for the characterization of atmospheric particles. Either visible or electron microscopy can be employed. Particle morphology and shape tell the experienced microscopist a great deal about the material being examined. Reflection, refraction, microchemical tests, and other techniques can be employed to further characterize the materials being examined. Microscopy can be used for determining levels of specific kinds of particles and for determining particle size.

## Direct Spectrophotometric Analysis of Gaseous Air Pollutants

From the foregoing discussion, it is obvious that measurement techniques that depend upon the use of chemical reagents, particularly liquids, are cumbersome and complicated. It is a tribute to the ingenuity of instrument designers that such techniques are being applied successfully to atmospheric pollutant monitoring. Direct spectrophotometric techniques are much more desirable when they are available and when they are capable of accurate analysis at the low levels required. One such technique, nondispersive infrared spectrophotometry, was described above for the analysis of carbon monoxide. Three other direct spectrophotometric methods are Fourier transform infrared spectroscopy, tunable diode laser spectroscopy, and, the most important of all, differential optical absorption spectroscopy. These techniques can be used for point air monitoring, in which a sample is monitored at a given point, generally by measurement in a long absorption cell. In-stack monitoring can be performed to measure effluents. A final possibility is the collection of long-line data (sometimes using sunlight as a radiation source), yielding concentrations in units of concentration-length (ppm-meters). If the path length is known, the concentration can be calculated. This approach is particularly useful for measuring concentrations in stack plumes.

The low levels of typical air constituents require long path lengths, sometimes up to several kilometers, for spectroscopic measurements. These can be achieved by locating the radiation source some distance from the detector, by the use of a distant retroreflector to reflect the radiation back to the vicinity of the source, or by cells in which a beam is reflected multiple times to achieve a long path length.

A typical open-path Fourier transform infrared system for remote monitoring of air pollutants uses a single unit (telescope) that functions as both a transmitter and receiver of infrared radiation (Figure 26.7). The radiation is generated by a silicon

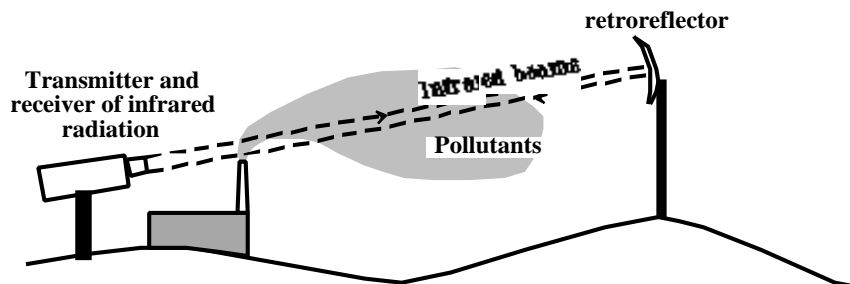


Figure 26.7 FTIR system for remote sensing of air pollutants.

carbide glower, modulated by a Michelson interferometer, and transmitted to a retroreflector, which reflects it back to the telescope, where its intensity is measured. The modulated infrared signal, called an interferogram, is processed by a mathematical algorithm, the Fourier transform, to give a spectrum of the absorbing substances. This spectrum is fitted mathematically to spectra of the absorbing species to give their concentrations.

Dispersive absorption spectrometers are basically standard spectrometers with a monochromator for selection of the wavelength to be measured. They are used to measure air pollutants by determining absorption at a specified part of the spectrum of the sought-for material. Of course, other gases or particulate matter that absorb or scatter light at the chosen wavelength interfere. These instruments are generally applied to in-stack monitoring. Sensitivity is increased by using long path lengths or by pressurizing the cell.

Second-derivative spectroscopy is a useful technique for trace gas analysis. Basically, this technique varies the wavelength by a small value around a specified nominal wavelength. The second derivative of light intensity versus wavelength is obtained. In conventional absorption spectrophotometry, a decrease in light intensity as the light passes through a sample indicates the presence of at least one substance—and possibly many—absorbing at that wavelength. Second-derivative spectroscopy, however, provides information regarding the change in intensity with wavelength, thereby indicating the presence of specific absorption lines or bands that can be superimposed on a relatively high background of absorption. Much higher specificity is obtained. The spectra obtained by second-derivative spectrometry in the ultraviolet region show a great deal of structure and are quite characteristic of the compounds being observed.

**Lidar**, which stands for *light detection and ranging* (analogous to radar, *radio detection and ranging*), is finding numerous applications in atmospheric monitoring. Lidar systems send short pulses of light or infrared radiation into the atmosphere and collect radiation scattered back from molecules or particles in the atmosphere. Computer analysis of the signal enables analysis of species in the atmosphere.

## 26.8 ANALYSIS OF BIOLOGICAL MATERIALS AND XENOBIOTICS

As defined in Chapter 23, a xenobiotic species is one that is foreign to living systems. The determination of xenobiotic substances in biological materials is very important. The greatest concern with such substances is their presence in human tissues and other samples of human origin. They may also be determined in plant or microbiological samples. The measurement of xenobiotic substances and their metabolites in blood, urine, breath, and other samples of biological origin to determine exposure to toxic substances is called **biological monitoring**. For more detailed current information regarding this area, the reader is referred to excellent reviews of the topic,<sup>6,7</sup> and several books on biological monitoring such as those by Angerer, Draper, Baselt, and Kneip and coauthors, which are listed in the back of this chapter under “Supplementary References,” are available as well.

## Indicators of Exposure to Xenobiotics

Both the type of sample and type of analyte are influenced by what happens to a xenobiotic material when it gets into the body. For some exposures, the entry site composes the sample. This is the case, for example, in exposure to asbestos fibers in the air, which is manifested by lesions to the lung. More commonly, the analyte may appear at some distance from the site of exposure, such as lead in bone that was originally taken in by the respiratory route. In other cases, the original xenobiotic is not even present in the analyte. An example of this is methemoglobin in blood, the result of exposure to aniline absorbed through the skin.

The two major kinds of samples analyzed for xenobiotics exposure are blood and urine. Both of these kinds of samples are analyzed for systemic xenobiotics, which are those that are transported in the body and metabolized in various tissues. Blood is of unique importance as a sample for biological monitoring.

Phase 1 and Phase 2 reaction products of xenobiotics (Chapter 23) tend to be converted to more polar and water soluble metabolites. These are eliminated with the urine, making it a good sample to analyze as evidence of exposure to xenobiotic substances. Urine has the advantage of being a simpler matrix than blood and one that subjects more readily give for analysis. Other kinds of samples that can be analyzed include breath (for volatile xenobiotics and volatile metabolites), air or nails (for trace elements, such as selenium), adipose tissue (fat), and milk (obviously limited to lactating females). Various kinds of organ tissue can be analyzed in cadavers to determine the toxic agent that has caused death by poisoning.

The choice of the analyte actually measured varies with the xenobiotic substance to which the subject has been exposed. Therefore, it is convenient to divide xenobiotic analysis on the basis of the type of chemical species determined. The most straightforward analyte is, of course, the xenobiotic itself. This applies to elemental xenobiotics, especially metals, which are almost always determined in the elemental form. In a few cases, organic xenobiotics can also be determined as the parent compound. However, organic xenobiotics are commonly determined as Phase 1 and Phase 2 reaction products. Often the Phase 1 reaction product is measured, frequently after it is hydrolyzed from the Phase 2 conjugate, using enzymes or acid hydrolysis procedures. Thus, for example, *trans,trans*-muconic acid can be measured as evidence of exposure to the parent compound benzene. In other cases, a Phase 2 reaction product is measured, for example, hippuric acid determined as evidence of exposure to toluene. Some xenobiotics or their metabolites form adducts with endogenous materials in the body, which are then measured as evidence of exposure. A simple example is the adduct formed between carbon monoxide and hemoglobin, carboxyhemoglobin. More-complicated examples are the adducts formed by the carcinogenic Phase 1 reaction products of polycyclic aromatic hydrocarbons with DNA or hemoglobin. Another class of analytes consists of endogenous substances produced upon exposure to a xenobiotic material. Methemoglobin formed as a result of exposure to nitrobenzene, aniline, and related compounds is an example of such a substance that does not contain any of the original xenobiotic material. Another class of substance causes measurable alterations in enzyme activity. The most common example of this is the inhibition of acetylcholinesterase enzyme by organophosphates or carbamate insecticides.

## **Analysis of Metals in Biological Samples**

Several biologically important metals can be determined directly in body fluids, especially urine, by atomic absorption. In the simplest cases, the urine is diluted with water or with acid and a portion analyzed directly by graphite furnace atomic absorption, taking advantage of the very high sensitivity of that technique for some metals. Metals that can be determined directly in urine by this approach include chromium, copper, lead, lithium, and zinc.

Many metals, including cadmium, chromium, copper, lead, manganese, and zinc, are readily determined by atomic absorption or emission in blood or urine samples wet-ashed by heating the sample with strong acid and oxidant to dryness and redissolving the residue in acid. A typical procedure is digestion of blood or urine for cadmium analysis, which consists of mixing the sample with a comparable volume of concentrated nitric acid, heating to a reduced volume, adding 30% hydrogen peroxide oxidant, heating to dryness, and dissolving in nitric acid prior to measurement by atomic absorption or emission. Mixtures of nitric, sulfuric, and perchloric acid are effective for digestion, though somewhat hazardous.

A number of procedures for the determination of metals and biological samples call for the extraction of the metal with an organic chelating agent in order to remove interferences and concentrate the metal to enable detection of low levels. The urine or blood sample can be first subjected to wet ashing to enable extraction of the metal. The availability of strongly chelating extracts for a number of metals has led to the development of procedures in which the metal is extracted from minimally treated blood or urine, then quantified by atomic absorption analysis. The metals for which such extractions can be used include cobalt, lead, and thallium extracted into organic solvent as the dithiocarbamate chelate, and nickel extracted into methyl-isobutyl ketone as a chelate formed with ammonium pyrrolidinedithiocarbamate.

Methods for several metals or metalloids involve conversion to a volatile form. Arsenic, antimony, and selenium can be reduced to their volatile hydrides,  $\text{AsH}_3$ ,  $\text{SbH}_3$ , and  $\text{H}_2\text{Se}$ , respectively, which can be determined by atomic absorption or other means. Mercury is reduced to volatile mercury metal, which is evolved from solution and measured by cold vapor atomic absorption.

## **Determination of Nonmetals and Inorganic Compounds**

Relatively few nonmetals require determination in biological samples. One important example is potentially toxic fluoride, which occurs in biological fluids as the fluoride ion,  $\text{F}^-$ . Fluoride in appropriately processed samples is readily determined potentiometrically with a fluoride ion-selective electrode.

Toxic cyanide can be isolated in a special device called a Conway microdiffusion cell by treatment with acid, followed by collection of the weakly acidic HCN gas that is evolved in a base solution. The cyanide released can be measured spectrophotometrically by formation of a colored species.

Carbon monoxide is readily determined in blood by virtue of the colored carboxyhemoglobin that it forms with hemoglobin using solution absorption spectrophotometry. The procedure consists of measuring the absorbances at wavelengths of 414, 421, and 428 nm of the blood sample, a sample through which

oxygen has been bubbled to change all the hemoglobin to the oxyhemoglobin form, and a sample through which carbon monoxide has been bubbled to change all the hemoglobin to carboxyhemoglobin. With the appropriate calculations, a percentage conversion to carboxyhemoglobin can be obtained.

## Determination of Parent Organic Compounds

A number of organic compounds can be measured as the unmetabolized compound in blood, urine, and breath. In some cases, the sample can be injected along with its water content directly into a gas chromatograph. Direct injection is used for the measurement of acetone, *n*-butanol, dimethylformamide, cyclopropane, halothane, methoxyflurane, diethyl ether, isopropanol, methanol, methyl*n*-butyl ketone, methyl chloride, methylethyl ketone, toluene, trichloroethane, and trichloroethylene.

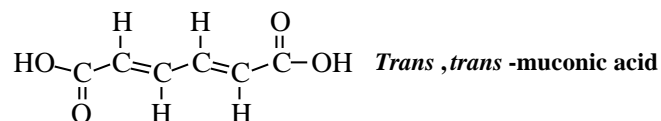
For the determination of volatile compounds in blood or urine, a straightforward approach is to liberate the analyte at an elevated temperature allowing the volatile compound to accumulate in headspace above the sample followed by direct injection of headspace gas into a gas chromatograph. A reagent such as perchloric acid, may be added to deproteinize the blood or urine sample and facilitate release of the volatile xenobiotic compound. Among the compounds determined by this approach are acetaldehyde, dichloromethane, chloroform, carbon tetrachloride, benzene, trichloroethylene, toluene, cyclohexane, and ethylene oxide. Purge-and-trap techniques that evolve volatile analytes from blood or urine in a gas stream and onto a trap for subsequent chromatographic analysis have been developed. Such a technique employing gas chromatographic separation and Fourier transform infrared detection has been described for a number of volatile organic compounds in blood.<sup>8</sup>

## Measurement of Phase 1 and Phase 2 Reaction Products

### Phase 1 Reaction Products

For a number of organic compounds, the most accurate indication of exposure is to be obtained by determining their Phase 1 reaction products. In cases where a significant fraction of the xenobiotic compound has undergone a Phase 2 reaction, the Phase 1 product can be regenerated by acid hydrolysis.

One of the compounds commonly determined as its Phase 1 metabolite is benzene, which is metabolized to phenol in the body (see Chapter 23, Section 23.13 and Figure 23.16). The phenol metabolic product of benzene is measured in urine, usually by gas chromatography. The urine sample is treated with perchloric acid to hydrolyze phenol conjugates and the phenol is extracted into diisopropyl ether for chromatographic analysis. Two other metabolic products of benzene, *trans,trans*-muconic acid and S-phenyl mercapturic acid, are now commonly measured as more-specific biomarkers of benzene exposure.







**Table 26.8 Phase 1 Reaction Products of Xenobiotics Determined**

Parent compound	Metabolite	Method of analysis
Cyclohexane	Cyclohexanol	Extraction of acidified, hydrolyzed urine with dichloromethane followed by gas chromatography
Diazinone	Organic phosphates	Colorimetric determination of phosphates
<i>p</i> -Dichlorobenzene	2,5-Dichlorophenol	Extraction into benzene, gas chromatographic analysis
Dimethylformamide	Methylformamide	Gas chromatography with direct sample introduction
Dioxane	-hydroxyethoxyacetic acid	Formation of volatile methyl ester, gas chromatography
Ethylbenzene	Mandelic acid and related aryl acids	Extraction of acids, formation of volatile derivatives, gas chromatography
Ethylene glycol monomethyl ether	Methoxyacetic acid	Extracted with dichloromethane, converted to volatile methyl derivative, gas chromatography
Formaldehyde	Formic acid	Gas chromatography of volatile formic acid derivative
Hexane	2,5-Hexanedione	Gas chromatography after extraction with dichloromethane
<i>n</i> -Heptane	2-Heptanone, valerolactone, 2,5-heptanedione	Measurement in urine by GC/MS
Isopropanol	Acetone	Gas chromatography following extraction with methylethyl ketone
Malathion	Organic phosphates	Colorimetric determination of phosphates
Methanol	Formic acid	Gas chromatography of volatile formic acid derivative
Methyl bromide	Bromide ion	Formation of volatile organobromine compounds, gas chromatography
Nitrobenzene	<i>p</i> -Nitrophenol	Gas chromatography of volatile derivative
Parathion	<i>p</i> -Nitrophenol	Gas chromatography of volatile derivative
Polycyclic aryl hydrocarbons	1-Hydroxypyrene	HPLC of urine

**Table 26.8. (Cont.)**

Styrene	Mandelic acid	Extraction of acids, formation of volatile derivatives, gas chromatography
Tetrachloroethylene, trichloroethane, trichloroethylene	Trichloroacetic acid	Extracted into pyridine and measured colorimetrically

## Mercapturates

Mercapturates are proving to be very useful Phase 2 reaction products for measuring exposure to xenobiotics, especially because of the sensitive determination of these substances by HPLC separation, and fluorescence detection of their *o*-phthalaldehyde derivatives. In addition to toluene mentioned above, the xenobiotics for which mercapturates can be monitored include styrene, structurally similar to toluene; acrylonitrile; allyl chloride; atrazine; butadiene; and epichlorohydrin.

The formation of mercapturates or mercapturic acid derivatives by metabolism of xenobiotics is the result of a Phase 2 conjugation by glutathione. **Glutathione** (commonly abbreviated GSH) is a crucial conjugating agent in the body. This compound is a tripeptide, meaning that it is composed of three amino acids linked together. These amino acids and their abbreviations are glutamic acid (Glu), cysteine (Cys), and glycine (Gly). The formula of glutathione can be represented as illustrated in [Figure 26.8](#), where the SH is shown specifically because of its crucial role

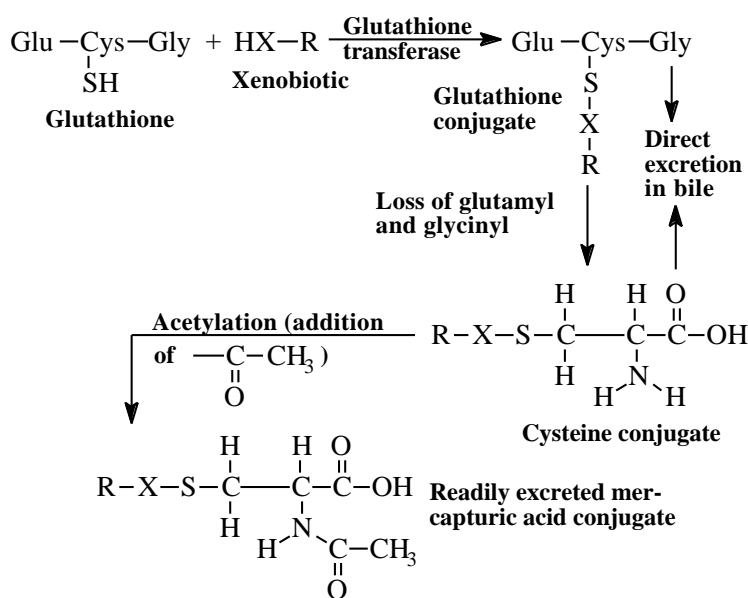


Figure 26.8 Glutathione conjugate of a xenobiotic species (HX-R) followed by formation of glutathione and cysteine conjugate intermediates (which may be excreted in bile) and acetylation to form readily excreted mercapturic acid conjugate.

in forming the covalent link to a xenobiotic compound. Rarely, glutathione conjugate may be excreted directly, but it usually undergoes further biochemical reactions that produce mercapturic acids (compounds with N-acetylcysteine attached) or other species. The specific mercapturic acids can be monitored as biological markers of exposure to the xenobiotic species that result in their formation. The overall process for the production of mercapturic acids as applied to a generic xenobiotic species, HX-R (see previous discussion), is illustrated in [Figure 26.8](#).

## Determination of Adducts

Determination of adducts is often a useful and elegant means of measuring exposure to xenobiotics. Adducts, as the name implies, are substances produced when xenobiotic substances add to endogenous chemical species. The measurement of carbon monoxide from its hemoglobin adduct was discussed in above. In general, adducts are produced when a relatively simple xenobiotic molecule adds to a large macromolecular biomolecule that is naturally present in the body. The fact that adduct formation is a mode of toxic action, such as occurs in the methylation of DNA during carcinogenesis (Chapter 22, Section 23.8), makes adduct measurement as a means of biological monitoring even more pertinent.

Adducts to hemoglobin are perhaps the most useful means of biological monitoring by adduct formation. Hemoglobin is, of course, present in blood, which is the most accurate type of sample for biological monitoring. The measurement of hemoglobin adducts is emerging as a method of choice for a number of xenobiotics including acrylamide, acrylonitrile, 1,3-butadiene, 3,3'-dichlorobenzidine, ethylene oxide, and hexahydrophthalic anhydride.

## Immunological Methods of Xenobiotics Analysis

As discussed in Chapter 25, Section 25.12, immunoassay methods offer distinct advantages in specificity, selectivity, simplicity, and costs. Although used in simple test kits for blood-glucose and pregnancy testing, immunoassay methods have been limited in biological monitoring of xenobiotics, in part because of interferences in complex biological systems. Because of their inherent advantages, however, it can be anticipated that immunoassays will grow in importance for biological monitoring of xenobiotics.

## CHAPTER SUMMARY

*The chapter summary below is presented in a programmed format to review the main points covered in this chapter. It is used most effectively by filling in the blanks, referring back to the chapter as necessary. The correct answers are given at the end of the summary.*

The commonly determined physical properties of water are <sup>1</sup>\_\_\_\_\_.

Usually, <sup>2</sup>\_\_\_\_\_ samples must be collected for chemical and biological analysis because <sup>3</sup>\_\_\_\_\_.

\_\_\_\_\_ . A composite sample has the advantage of providing <sup>4</sup> \_\_\_\_\_. A conventional solid phase extractor collects analyte on <sup>5</sup> \_\_\_\_\_. The most general method of sample preservation is <sup>6</sup> \_\_\_\_\_. Water samples that can be kept longest before analysis are those to be analyzed for <sup>7</sup> \_\_\_\_\_. Acidity, alkalinity, and hardness in water can all be determined by <sup>8</sup> \_\_\_\_\_. Arsenic, boron, nitrate, and surfactants in water can all be analyzed by <sup>9</sup> \_\_\_\_\_. EPA methods 601, 608, 613, and 1624 are all methods that use <sup>10</sup> \_\_\_\_\_ to determine <sup>11</sup> \_\_\_\_\_ in water. A technique that uses a dissolved oxidizing agent promoted by ultraviolet light is used to measure <sup>12</sup> \_\_\_\_\_ in water. Metals in water are normally determined by some form of <sup>13</sup> \_\_\_\_\_ analysis. The methods included in the "SW-846" compilation are for the analysis of <sup>14</sup> \_\_\_\_\_. To analyze a solid-waste sample by atomic spectrophotometric techniques for metals, it must first be <sup>15</sup> \_\_\_\_\_. In analyzing solid-waste samples, microwave heating can be used to <sup>16</sup> \_\_\_\_\_. Means of isolating nonvolatile and semivolatile analytes from solid waste samples include <sup>17</sup> \_\_\_\_\_ . Two major approaches used to isolate and concentrate volatile analytes from waste samples for subsequent measurement are <sup>18</sup> \_\_\_\_\_. Sample cleanup refers to processes used to <sup>19</sup> \_\_\_\_\_. Materials used for this purpose include <sup>20</sup> \_\_\_\_\_. The <sup>21</sup> \_\_\_\_\_ is designed to estimate the availability to organisms of both inorganic and organic species in hazardous materials. The extractants used in this procedure are <sup>22</sup> \_\_\_\_\_. The atmosphere is a particularly difficult analytical system because of <sup>23</sup> \_\_\_\_\_ . The ideal atmospheric analysis techniques are those that <sup>24</sup> \_\_\_\_\_. The most common technique for sampling atmospheric particulate matter is <sup>25</sup> \_\_\_\_\_. The reference method for the analysis of sulfur dioxide is the <sup>26</sup> \_\_\_\_\_ method. A method for the determination of gaseous inorganic air pollutants that involves their conversion to ions is <sup>27</sup> \_\_\_\_\_. The favored method of NO<sub>x</sub> analysis is <sup>28</sup> \_\_\_\_\_, for which the reaction producing a measurable signal is <sup>29</sup> \_\_\_\_\_. The atmospheric oxidants that are commonly determined include <sup>30</sup> \_\_\_\_\_, the classic manual method for which involves <sup>31</sup> \_\_\_\_\_. The currently favored method for oxidant (ozone) analysis uses <sup>32</sup> \_\_\_\_\_. Carbon monoxide is commonly analyzed in the atmosphere by <sup>33</sup> \_\_\_\_\_.

Monitoring hydrocarbons in atmospheric samples uses <sup>34</sup> \_\_\_\_\_  
 \_\_\_\_\_. The device commonly used to sample atmospheric  
 particles is the <sup>35</sup> \_\_\_\_\_, which can sample 2000 m<sup>3</sup> over a  
 24-hour period. Impactors used to sample atmospheric particles cause a relatively  
 high velocity gas stream to <sup>36</sup> \_\_\_\_\_, such that  
 particles are collected on a surface. Direct spectrophotometric techniques for the  
 measurement of air pollutants include, in addition to nondispersive infrared spectro-  
 photometry, <sup>37</sup> \_\_\_\_\_  
 \_\_\_\_\_.

Lidar systems for atmospheric pollutant measurement operate by <sup>38</sup> \_\_\_\_\_  
 \_\_\_\_\_  
 \_\_\_\_\_.

Biological monitoring is <sup>39</sup> \_\_\_\_\_  
 \_\_\_\_\_  
 \_\_\_\_\_. The two major kinds  
 of samples analyzed for xenobiotics exposure are <sup>40</sup> \_\_\_\_\_.  
 The most straightforward analyte to measure in xenobiotics analysis is <sup>41</sup> \_\_\_\_\_  
 \_\_\_\_\_, and other analytes that actually include the xenobiotic  
 material or its metabolites are <sup>42</sup> \_\_\_\_\_  
 \_\_\_\_\_.

Metals in biological samples are most commonly determined by <sup>43</sup> \_\_\_\_\_  
 \_\_\_\_\_. Nonmetals commonly determined in  
 biological samples include <sup>44</sup> \_\_\_\_\_.  
 Two metabolic products other than phenol that can be measured as evidence of  
 exposure to benzene are <sup>45</sup> \_\_\_\_\_.  
 Exposure to toluene, the xylenes, benzoic acid, and ethylbenzene can be determined  
 by measuring <sup>46</sup> \_\_\_\_\_. A class of metabolites useful for  
 measuring exposure to xenobiotic materials and that are formed by a process  
 beginning with conjugation by glutathion are <sup>47</sup> \_\_\_\_\_. A limitation  
 to using immunoassay methods for xenobiotics analysis is <sup>48</sup> \_\_\_\_\_  
 \_\_\_\_\_.

### *Answers to Chapter Summary*

1. color, residue (solids), odor, temperature, specific conductance, and turbidity
2. separate
3. the sampling and preservation techniques differ significantly
4. an overall picture from only one analysis
5. an extracting solid in a column
6. refrigeration to 4°C
7. metals
8. titration
9. solution spectrophotometry
10. gas chromatography
11. organics
12. total organic carbon
13. atomic spectrophotometric

14. solid wastes
15. digested to get the analyte metals in solution
16. assist digesting the samples
17. Soxhlet extraction, pressurized fluid extraction, sonication with ultrasound and supercritical fluid extraction
18. headspace analysis and purge-and-trap
19. remove extraneous interfering matter from samples
20. alumina, silica gel, and Florisil
21. Toxicity Characteristic Leaching Procedure
22. acetic acid/sodium acetate buffer
23. the very low levels of substances to be analyzed; sharp variations in pollutant level with time and location; differences in temperature and humidity; and difficulties encountered in reaching desired sampling points
24. work successfully without sampling
25. filtration
26. spectrophotometric West-Gaeke pararosaniline
27. ion chromatography
28. gas-phase chemiluminescence
29.  $\text{NO} + \text{O}_3 \rightarrow \text{NO}_2^* + \text{O}_2$
30. ozone, hydrogen peroxide, organic peroxides, and chlorine
31. oxidation of  $\text{I}^-$  to  $\text{I}_3^-$
32. the chemiluminescent reaction between ozone and ethylene
33. nondispersive infrared spectrometry
34. the hydrogen flame ionization detector
35. Hi-Vol sampler
36. undergo a sharp bend
37. Fourier transform infrared spectroscopy, tunable diode laser spectroscopy, and differential optical absorption spectroscopy
38. sending short pulses of light or infrared radiation into the atmosphere and collecting radiation scattered back from molecules or particles in the atmosphere
39. the measurement of xenobiotic substances and their metabolites in blood, urine, breath, and other samples of biological origin
40. blood and urine
41. the xenobiotic itself
42. Phase 1 and Phase 2 reaction products and adducts with endogenous substances
43. atomic spectrometric
44. fluoride, carbon monoxide, and cyanide
45. *trans,trans*-muconic acid and S-phenyl mercapturic acid
46. hippuric acid compounds
47. mercapturates
48. interferences in complex biological systems

## LITERATURE CITED

1. Rivasseau, Corinne, Pascale Racaud, Alain Deguin, and Marie Claire Hennion, "Evaluation of an ELISA Kit for Monitoring Microcystins (Cyanobacterial toxins) in Water and Algae Environmental Samples," *Environmental Science and Technology*, **33**, 1520-1527 (1999).

2. *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods*, EPA Publication SW-846, 3rd ed., (1986), as amended by Updates I (1992), II (1993, 1994, 1995) and III (1996), U.S. Government Printing Office, Washington, D.C.
3. *Understanding Analytical Methods*, CD-ROM Version 2.0, Genium Publishing Corporation, Schenectady, NY, 1998.
4. "Toxicity Characteristic Leaching Procedure," Test Method 1311 in *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods*, EPA Publication SW-846, 3rd ed., (November, 1986), as amended by Updates I, II, IIA, U.S. Government Printing Office, Washington, D.C.
5. 40 *Code of Federal Regulations*, Part 50, Office of the Federal Register, National Archives and Records Administration, Washington, D.C., July 1, annually.
6. Draper, William M., Kevin Ashley, Clifford R. Glowacki, and Paul R. Michael, "Industrial Hygiene Chemistry: Keeping Pace with Rapid Change in the Workplace," *Analytical Chemistry*, **71**, 33R-60R (1999). A comprehensive review of this topic is published every 2 years in *Analytical Chemistry*.
7. Atio, A., "Special Issue: Biological Monitoring in Occupational and Environmental Health," *Science of the Total Environment*, **199**, 1-226 (1997).
8. Ojanpera, Ilkka, Katja Pihlainen, and Erkki Vuori, "Identification Limits for Volatile Organic Compounds in the Blood by Purge-and-Trap GC-FTIR," *Journal of Analytical Toxicology*, **22**, 290-295 (1998).
9. Angerer, J., M. Schildbach, and A. Kramer, "S-Toluylmercapturic Acid in the Urine of Workers Exposed to Toluene: A New Biomarker for Toluene Exposure," *Archives of Toxicology*, **72**, 119-123 (1998).
10. De Ruij, Ben M., Pieter J. Boogard, Jan N. M. Commandeur, Nico J. van Sittert, and Nico P. E. Verneulen, "Allylmercapturic Acid as Urinary Biomarker of Human Exposure to Allyl Chloride," *Occupational and Environmental Medicine*, **54**, 653-661 (1997).

## SUPPLEMENTARY REFERENCES

- Angerer, J. K., and K. H. Schaller, *Analyses of Hazardous Substances in Biological Materials*, Vol. 1, VCH, Weinheim, Germany, 1985.
- Angerer, J. K., and K. H. Schaller, *Analyses of Hazardous Substances in Biological Materials*, Vol. 2, VCH, Weinheim, Germany, 1988.
- Angerer, J. K., and K. H. Schaller, *Analyses of Hazardous Substances in Biological Materials*, Vol. 3, VCH, Weinheim, Germany, 1991.
- Angerer, J. K., and K. H. Schaller, *Analyses of Hazardous Substances in Biological Materials*, Vol. 4, VCH, Weinheim, Germany, 1994.
- Angerer, J. K., and K. H. Schaller, *Analyses of Hazardous Substances in Biological Materials*, Vol. 5, John Wiley & Sons, New York, 1996.

- Angerer, J. K., and K. H. Schaller, *Analyses of Hazardous Substances in Biological Materials*, Vol. 6, John Wiley & Sons, New York, 1999.
- Baselt, Randall C., *Biological Monitoring Methods for Industrial Chemicals*, 2nd ed., PSG Publishing Company, Inc., Littleton, MA, 1988.
- Bucholtz, Frank, Ed., *Environmental Monitoring and Instrumentation*, Optical Society of America, Washington, D.C., 1997.
- Committee on National Monitoring of Human Tissues, Board on Environmental Studies and Toxicology, Commission on Life Sciences, *Monitoring Human Tissues for Toxic Substances*, National Academy Press, Washington, D.C., 1991.
- Dieken, Fred P., *Methods Manual for Chemical Analysis of Water and Wastes*, Alberta Environmental Centre, Vergeville, Alberta, Canada (1996).
- Draper, William M., Kevin Ashley, Clifford R. Glowacki, and Paul R. Michael, "Industrial Hygiene Chemistry: Keeping Pace with Rapid Change in the Workplace," *Analytical Chemistry*, **71**, 33R-60R (1999). A comprehensive review of this topic is published every two years in *Analytical Chemistry*.
- Ellenberg, Hermann, *Biological Monitoring: Signals from the Environment*, Braunschweig, Vieweg, Germany, 1991.
- Garbarino, John R. and Tedmund M. Struzeski, *Methods Of Analysis by the U.S. Geological Survey National Water Quality Laboratory—Determination of Elements in Whole-Water Digests Using Inductively Coupled Plasma-Optical Emission Spectrometry and Inductively Coupled Plasma-Mass Spectrometry*, U.S. Department of the Interior U. S. Geological Survey, Denver, 1998.
- Gavasci, R., F. Lombardi, A. Polettini, and P. Sirini, "Leaching Tests on Solidified Products," *Journal of Solid Waste Technology Management*, **25**, 14-20 (1998).
- Hee, Shane Que, *Biological Monitoring: An Introduction*, Van Nostrand Reinhold, New York, 1993.
- Ioannides, Costas, Ed., *Cytochromes P450: Metabolic and Toxicological Aspects*, CRC Press, Boca Raton, FL, 1996..
- Jacob, Daniel J., *Introduction to Atmospheric Chemistry*, Princeton University Press, Princeton, NJ, 1999.
- Keith, Lawrence H., *Environmental Sampling and Analysis: A Practical Guide*, Lewis Publishers, Boca Raton, FL, 1991.
- Keith Lawrence H. and Mary M. Walker, Eds., *Handbook of Air Toxics: Sampling, Analysis, and Properties*, CRC Press/Lewis Publishers, Boca Raton, FL, 1995.
- Kneip, Theodore J. and John V. Crable, *Methods for Biological Monitoring*, American Public Health Association, Washington, DC, 1988.
- Lauwerys, Robert R. and Perrine Hoet, *Industrial Chemical Exposure: Guidelines for Biological Monitoring*, 2nd ed., CRC Press/Lewis Publishers, Boca Raton, FL, 1993.



Matson, P. A. and R. C. Harriss, Eds., *Biogenic Trace Gases: Measuring Emissions from Soil and Water*, Blackwell Science, Cambridge, MA, 1995.

Meier, Arndt, *Determination of Atmospheric Trace Gas Amounts and Corresponding Natural Isotopic Ratios by Means of Ground-Based FTIR Spectroscopy in the High Arctic*, Alfred-Wegener-Institut für Polar und Meeresforschung ; Bremen, Germany, 1997.

Mendelsohn, Mortimer L., John P. Peeters, and Mary Janet Normandy, Eds., *Biomarkers and Occupational Health: Progress and Perspectives*, Joseph Henry Press, Washington, D.C., 1995.

Meyers, R. A., Ed., *The Encyclopedia of Environmental Analysis and Remediation*, John Wiley and Sons, New York, 1998.

Minear, Roger A., Allan M. Ford, Lawrence L. Needham, and Nathan J. Karch, Eds., *Applications of Molecular Biology in Environmental Chemistry*, CRC Press/Lewis Publishers, Boca Raton, FL, 1995.

Optical Society of America, *Laser Applications to Chemical and Environmental Analysis*, Optical Society of America, Washington, D.C., 1998.

Patnaik, Pradyot, *Handbook of Environmental Analysis: Chemical Pollutants in Air, Water, Soil, and Solid Wastes*, CRC Press/Lewis Publishers, Boca Raton, FL, 1997.

Pradyot, Patnaik, Ed., *Handbook of Environmental Analysis: Chemical Pollutants in Air, Water, Soil, and Solid Wastes*, CRC Press, Boca Raton, FL (1997).

Richardson, Mervyn, Ed., *Environmental Xenobiotics*, Taylor & Francis, London, 1996.

Richardson, Susan D., "Water Analysis," *Analytical Chemistry*, **71**, 281R-215R (1999).

Saleh, Mahmoud A., Jerry N. Blancato, and Charles H. Nauman, *Biomarkers of Human Exposure to Pesticides*, American Chemical Society, Washington, D.C., 1994.

Seinfeld, John H., *Atmospheric Chemistry and Physics*, John Wiley & Sons, Inc., New York, NY, 1998.

Singh, Ved Pal, Ed., *Biotransformations: Microbial Degradation of Health-Risk Compounds*, Elsevier, Amsterdam, 1995.

Travis, Curtis C., Ed., *Use of Biomarkers in Assessing Health and Environmental Impacts of Chemical Pollutants*, Plenum Press, New York, 1993.

Wight, Gregory D., *Fundamentals of Air Sampling*, CRC Press/Lewis Publishers, Boca Raton, FL, 1994.

Willeke, Klaus, and Paul A. Baron, Eds., *Aerosol Measurement: Principles, Techniques, and Applications*, Van Nostrand Reinhold, New York, 1993.

Williams, W. P., *Human Exposure to Pollutants: Report on the Pilot Phase of the Human Exposure Assessment Locations Programme*, United Nations Environment Programme, New York, 1992.

Williford, Clint W., Jr. and R. Mark Bricka, "Extraction of TNT from Aggregate Soil Fractions, *Journal of Hazardous Materials*, **66**, 1-13 (1999).

Winegar, Eric D. and Lawrence H. Keith, Eds., *Sampling and Analysis of Airborne Pollutants*, CRC Press/Lewis Publishers, Boca Raton, FL, 1993.

World Health Organization, *Biological Monitoring of Chemical Exposure in the Workplace*, World Health Organization, Geneva, Switzerland, 1996.

## QUESTIONS AND PROBLEMS

1. A soluble water pollutant forms ions in solution and absorbs light at 535 nm. What are two physical properties of water influenced by the presence of this pollutant?
2. A sample was taken from the bottom of a deep, stagnant lake. Upon standing, bubbles were evolved from the sample; the pH went up; and a white precipitate formed. From these observations, what can be said about the dissolved  $\text{CO}_2$  and hardness in the water?
3. For which of the following analytes can nitric acid be used as a water sample preservative:  $\text{H}_2\text{S}$ ;  $\text{CO}_2$ ; metals; coliform bacteria; cyanide?
4. In the form of what compound is oxygen fixed in the Winkler analysis of  $\text{O}_2$ ?
5. Manganese from a standard solution was oxidized to  $\text{MnO}_4^-$  and diluted such that the final solution contained 1.00 mg/L of Mn. This solution had an absorbance of 0.316. A 10.00 mL wastewater sample was treated to develop the  $\text{MnO}_4^-$  color and diluted to 250.0 mL. The diluted sample had an absorbance of 0.296. What was the concentration of Mn in the original wastewater sample?
6. A water sample was run through the colorimetric procedure for the analysis of nitrate, giving 55.0% transmittance. A sample containing 1.00 ppm nitrate run through the exactly identical procedure gave 24.6% transmittance. What was the concentration of nitrate in the first sample?
7. What is the molar concentration of HCl in a water sample containing HCl as the only contaminant and having a pH of 3.80?
8. A 200-mL sample of water required 25.12 mL of 0.0200N standard  $\text{H}_2\text{SO}_4$  for titration to the methyl orange endpoint, pH 4.5. What was the total alkalinity of the original sample?
9. Analysis of a lead-containing sample by graphite-furnace atomic absorption analysis gave a peak of 0.075 absorbance units when 50 microliters of pure sample was injected. Lead was added to the sample such that the added concen-

tration of lead was 6.0 micrograms per liter. Injection of 50 microliters of “spiked” sample gave an absorbance of 0.115 absorbance units. What was the concentration of lead in the original sample?

10. In a  $2.63 \times 10^{-4}$  M standard fluoride solution, a fluoride electrode read -0.100 volts versus a reference electrode, and it read -0.118 volts in an appropriately processed fluoride sample. Considering Equation 25.8.3 in Chapter 25, what was the concentration of fluoride in the sample?
11. Why is magnesium-EDTA chelate added to a magnesium-free water sample before it is to be titrated with EDTA for  $\text{Ca}^{2+}$  ?
12. For what type of sample is the flame-ionization detector most useful?
13. Explain the uses of microwave in hazardous waste analysis. How is ultrasound employed in hazardous waste analysis?
14. Does sample digestion necessarily give an analysis leading to total metals? Why might it not be advantageous to measure total metals in a sample?
15. What is the distinction between a Kuderna-Danish apparatus and a Soxhlet apparatus?
16. How is anhydrous  $\text{Na}_2\text{SO}_4$  used in organics analysis?
17. What is the purpose of sample cleanup? Why is cleanup more commonly applied to samples to be analyzed for organic contaminants than for metals?
18. What is the principle of immunoassay? What makes it specific for compounds or narrow classes of compounds? Why might it be especially suitable as a survey technique for hazardous waste sites? What is ELISA?
19. In what sense is the TCLP a measure of available toxicants?
20. What device is employed to make a nondispersive infrared analyzer selective for the compound being determined?
21. Suggest how mass spectrometry would be most useful in air pollutant analysis.
22. If 0.250 g of particulate matter is the minimum quantity required for accurate weighing on a Hi-Vol sampler filter, how long must such a sampler be operated at a flow rate of  $2.00 \text{ m}^3/\text{min}$  to collect a sufficiently large sample in an atmosphere containing  $5 \text{ }\mu\text{g}/\text{m}^3$  of particulate matter?
23. Assume that the signal from a chemiluminescence analyzer for NO is proportional to NO concentration. For the same rate of air flow, an instrument gave a signal of 135 microamp for an air sample that had been passed over a thermal converter and  $49 \text{ }\mu\text{amp}$  with the converter out of the stream. A standard sample containing 0.233 ppm NO gave a signal of  $80 \text{ }\mu\text{amp}$ . What was the level of  $\text{NO}_2$  in the atmospheric sample?
24. An atmosphere contains 0.10 ppm by volume of  $\text{SO}_2$  at  $25^\circ\text{C}$  and 1.00 atm pressure. Considering the gas laws presented in Chapter 2, what volume of air would have to be sampled to collect 1.00 mg of  $\text{SO}_2$  in tetrachloromercurate solution?

25. Assume that 20% of the surface of a membrane filter used to collect particulate matter consists of circular openings with a uniform diameter of 0.45  $\mu\text{m}$ . How many openings are on the surface of a filter with a diameter of 5.0 cm?
26. Some atmospheric pollutant analysis methods have been used in the past that later have been shown to not give the “true” value. In what respects can such methods still be useful?
27. Suggest how ion chromatography can be used for the analysis of nonionic gases.
28. Personnel monitoring in the workplace is commonly practiced with vapor samplers that workers carry around. How does this differ from biological monitoring? In what respects is biological monitoring superior?
29. Why is blood arguably the best kind of sample for biological monitoring? What are some of the disadvantages of blood in terms of sampling and sample processing? What are some disadvantages of blood as a matrix for analysis? What are the advantages of urine? Discuss why urine might be the kind of sample most likely to show metabolites and least likely to show parent species.
30. Distinguish among the following kinds of analytes measured for biological monitoring: parent compound, Phase 1 reaction product, Phase 2 reaction product, adducts.
31. What is wet ashing? For what kinds of analytes is wet ashing of blood commonly performed? What kinds of reagents are used for wet ashing, and what are some of the special safety precautions that should be taken with the use of these kinds of reagents for wet ashing?
32. What species is commonly measured potentiometrically in biological monitoring?
33. Compare the analysis of Phase 1 and Phase 2 metabolic products for biological monitoring. How are Phase 2 products converted back to Phase 1 metabolites for analysis?
34. Name a biomolecule that is commonly involved in the formation of adducts for biological monitoring. What is a simple inorganic species that can be determined as an adduct?
35. What is a use of immunology in biological monitoring? What is a disadvantage of immunological techniques? Discuss the likelihood that immunological techniques will find increasing use in the future as a means of biological monitoring.
36. The determination of DNA adducts is a favored means of measuring exposure to carcinogens. Based upon what is known about the mechanism of carcinogenicity, why would this method be favored? What might be some limitations of measuring DNA adducts as evidence of exposure to carcinogens?
37. How are mercapturic acid conjugates formed? What special role do they play in biological monitoring? What advantage do they afford in terms of measurement?

38. For what kinds of xenobiotics is trichloroacetic acid measured? Suggest the pathways by which these compounds might form trichloroacetic acid metabolically.
39. Match each xenobiotic species from the column on the left below with the analyte that is measured in its biological monitoring from the column on the right.
- |                      |                          |
|----------------------|--------------------------|
| A. Methanol          | 1. Mandelic acid         |
| B. Malathion         | 2. A diketone            |
| C. Styrene           | 3. Organic phosphates    |
| D. Nitrobenzene      | 4. Formic acid           |
| E. <i>n</i> -Heptane | 5. <i>p</i> -Nitrophenol |