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24 CHEMICAL ANALYSIS OF WATER AND WASTEWATER

24.1. GENERAL ASPECTS OF 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 or not 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.

In addition to a discussion of water analysis, this chapter covers some of the general aspects of environmental chemical analysis and the major techiques that are used to determine a wide range of analytes (species measured). Many techniques are common to water, air, soil, and biological sample analyses and reference is made to them in chapters that follow.

Error and Quality Control

A crucial aspect of any chemical analysis is the validity and quality of the data that it produces. All measurements are subject to error, which may be **systematic** (of the same magnitude and same direction) or **random** (varying in both magnitude and direction). Systematic errors cause the measured values to vary consistently from the true values, this variation is known as the **bias**. The degree to which a measured value comes close to the actual value of an analytical measurement is called the **accuracy** of the measurement, reflecting both systematic and random errors. It is essential for the analyst to determine these error components in the measurement of environmental samples, including water samples. The identification and control of systematic and random errors falls in the category of **quality control** (**QC**) procedures. It is beyond the scope of this chapter to go into any detail on these crucial procedures for which the reader is referred to a work on standard methods for the analysis of water.[1]

In order for results from a laboratory to be meaningful, the laboratory needs a quality assurance plan specifying measures taken to produce data of known quality. An important aspect of such a plan is the use of laboratory control standards consisting of samples with very accurately known analyte levels in a carefully controlled matrix. Such standard reference materials are available in the U. S. for many kinds of samples from the National Institute of Standards and Technology (NIST).

Many environmental analytes are present at very low levels which challenge the ability of the method used to detect and accurately quantify them. Therefore, the **detection limit** of a method of analysis is quite important. Defining detection limit has long been a controversial topic in chemical analysis. Every analytical method has a certain degree of noise. The detection limit is an expression of the lowest concentration of analyte that can be measured above the noise level with a specified degree of confidence in an analytical procedure. In the detection of analyte, two kinds of errors can be defined. A Type I error occurs when the measurement finds an analyte present when it actually is absent. A Type II error occurs when the measurement finds an analyte absent when it is actually present.

Detection limits can be further categorized into several different subcategories. The **instrument detection limit** (**IDL**) is the analyte concentration capable of producing a signal three times the standard deviation of the noise. The **lower level of detection** (**LLD**) is the quantity of analyte that will produce a measurable signal 99 percent of the time; it is about 2 times the IDL. The **method detection limit** (**MDL**) is measured like the LLD except that the analyte is taken through the whole analytical procedure, including steps such as extraction and sample cleanup; it is about 4 times the IDL . Finally, the **practical quantitation limit** (**PQL**), which is about 20 times the IDL, is the lowest level achievable among laboratories in routine analysis.

24.2. CLASSICAL METHODS

Before sophisticated instrumentation became available, most important water quality parameters and some air pollutant analyses were done by **classical methods**, which require only chemicals, balances to measure masses, burets, volumetric flasks

and pipets to measure volumes, and other simple laboratory glassware. The two major classical methods are **volumetric analysis**, in which volumes of reagents are measured, and **gravimetric analysis**, in which masses are measured. Some of these methods are still used today, and many have been adapted to instrumental and automated procedures.

The most common classical methods for pollutant analysis are titrations, largely used for water analysis. Some of the titration procedures used are discussed in this section.

Acidity (see Section 3.7) 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_2SO_4). 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_3^-.

Alkalinity may be determined by titration with H_2SO_4 to pH 8.3 to neutralize bases as strong as, or stronger than, carbonate ion,

$$CO_3^{2-} + H^+ \rightarrow HCO_3^- \quad (24.2.1)$$

or by titration to pH 4.5 to neutralize bases weaker than CO_3^{2-}, but as strong as, or stronger than, HCO_3^-:

$$HCO_3^- + H^+ \rightarrow H_2O + CO_2(g) \quad (24.2.2)$$

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 discussed in Sections 3.10 and 3.13. The titration reaction is

$$Ca^{2+}(\text{or } Mg^{2+}) + H_2Y^{2-} \rightarrow CaY^{2-}(\text{or } MgY^{2-}) + 2H^+ \quad (24.2.3)$$

where H_2Y^{2-} 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 MnO_2 in the presence of I^- ion to release free I_2, then titration of the liberated iodine with standard thiosulfate, using starch as an endpoint indicator:

$$Mn^{2+} + 2OH^- + {}^1/_2O_2 \rightarrow MnO_2(s) + H_2O \quad (24.2.4)$$

$$MnO_2(s) + 2I^- + 4H^+ \rightarrow Mn^{2+} + I_2 + 2H_2O \quad (24.2.5)$$

$$I_2 + 2S_2O_3^{2-} \rightarrow S_4O_6^{2-} + 2I^- \quad (24.2.6)$$

A back calculation from the amount of thiosulfate required yields the original quantity of dissolved oxygen (DO) present. Biochemical oxygen demand, BOD (see

Section 7.9), is determined by adding a microbial "seed" to the diluted sample, saturating with air, incubating for five days, and determining the oxygen remaining. The results are calculated to show BOD as mg/L of 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.

24.3. SPECTROPHOTOMETRIC METHODS

Absorption Spectrophotometry

Absorption spectrophotometry of light-absorbing species in solution, historically called colorimetry when visible light is absorbed, is still used for the analysis of many water and some air pollutants. Basically, absorption spectrophotometry consists of measuring the percent transmittance (%T) of monochromatic light passing through a light-absorbing solution as compared to the amount passing through a blank solution containing everything in the medium but the sought-for constituent (100%). The absorbance (A) is defined as the following:

$$A = \log \frac{100}{\%T} \tag{24.3.1}$$

The relationship between A and the concentration (C) of the absorbing substance is given by Beer's law:

$$A = abC \tag{24.3.2}$$

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 linear relationship between A and C at constant path length indicates adherence to Beer's law. In many cases, analyses may be performed even when Beer's law is not obeyed, if a suitable calibration curve is prepared. A color-developing step usually is required in which the sought-for substance reacts to form a colored species, and in some cases a colored species is extracted into a nonaqueous solvent to provide a more intense color and a more concentrated solution.

A number of solution spectrophotometric methods have been used for the determination of water and air pollutants. Some of these are summarized in Table 24.1.

Atomic Absorption and Emission Analyses

Atomic absorption analysis is commonly used for the determination of metals in environmental samples. This technique is based upon the absorption of monochromatic light by a cloud of atoms of the analyte metal. The monochromatic light can be produced by a source composed of the same atoms as those being analyzed. The source produces intense electromagnetic radiation with a wavelength exactly the same as that absorbed by the atoms, resulting in extremely high selectivity. The basic components of an atomic absorption instrument are shown in Figure 24.1. The

Table 24.1. Solution Spectrophotometric (Colorimetric) Methods of Analysis

Analyte	Reagent and Method
Ammonia	Alkaline mercury(II) iodide reacts with ammonia, producing colloidal orange-brown $NH_2Hg_2I_3$, which absorbs light between 400 and 500 nanometers (nm)
Arsenic	Reaction of arsine, 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
Chlorine	Development of color with orthotolidine
Cyanide	Formation of a blue dye from reaction of cyanogen chloride, 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-(l-naphthyl)-ethylenediamine dihydrochloride to produce a highly colored azo dye measured at 540 nm
Nitrogen, Kjeldahl-phenate method	Digestion in sulfuric acid to NH_4^+ followed by treatment with alkaline phenol reagent and sodium hypochlorite to form blue indophenol measured at 630 nm
Phenols	Reaction with 4-aminoantipyrine at pH 10 in the presence of potassium ferricyanide, forming an antipyrine dye which 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

key element is the hollow cathode lamp in which atoms of the analyte metal are energized such that they become electronically excited and emit radiation with a very narrow wavelength band characteristic of the metal. This radiation is guided by the appropriate optics through a flame into which the sample is aspirated. In the flame, most metallic compounds are decomposed, and the metal is reduced to the elemental state, forming a cloud of atoms. These atoms absorb a fraction of radiation in the flame. The fraction of radiation absorbed increases with the concentration of the sought-for element in the sample according to the Beer's law relationship (Eq. 24.3.2). The attenuated light beam next goes to a monochromator to eliminate extraneous light resulting from the flame, and then to a detector.

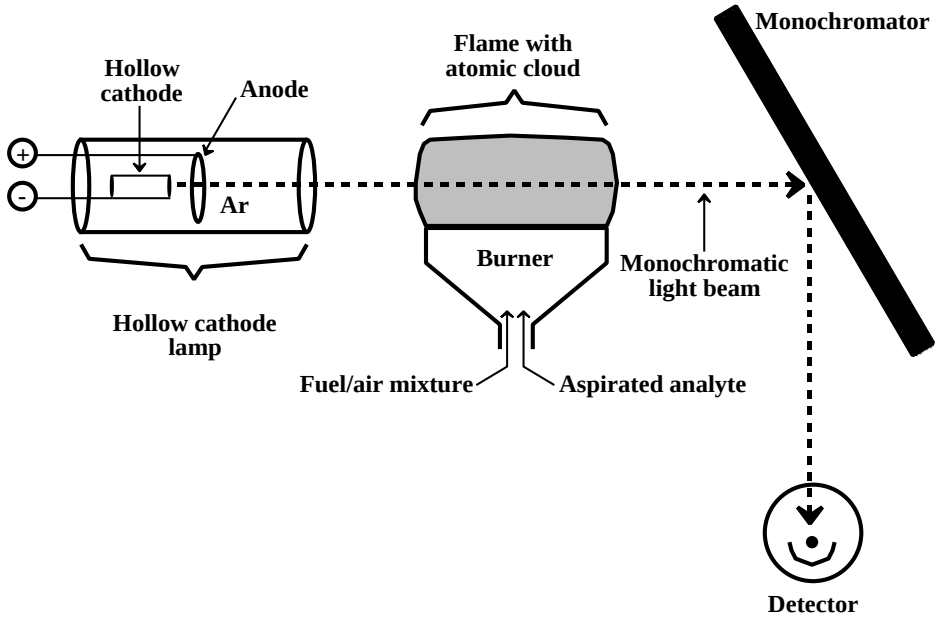

Figure 24.1. The basic components of a flame atomic absorption spectrophotometer.

Atomizers other than a flame can be used. The most common of these is the graphite furnace, an electrothermal atomization device which consists of a hollow graphite cylinder placed so that the light beam passes through it. A small sample of up to 100 µL is inserted in the tube through a hole in the top. An electric current is passed through the tube to heat it—gently at first to dry the sample, then rapidly to vaporize and excite the metal analyte. The absorption of metal atoms in the hollow portion of the tube is measured and recorded as a spike-shaped signal. A diagram of a graphite furnace with a typical output signal is shown in Figure 24.2. The major advantage of the graphite furnace is that it gives detection limits up to 1000 times lower than those of conventional flame devices.

A special technique for the flameless atomic absorption analysis of mercury involves room-temperature reduction of mercury to the elemental state by tin(II) chloride in solution, followed by sweeping the mercury into an absorption cell with air. Nanogram (10^{-9}g) quantities of mercury can be determined by measuring mercury absorption at 253.7 nm.

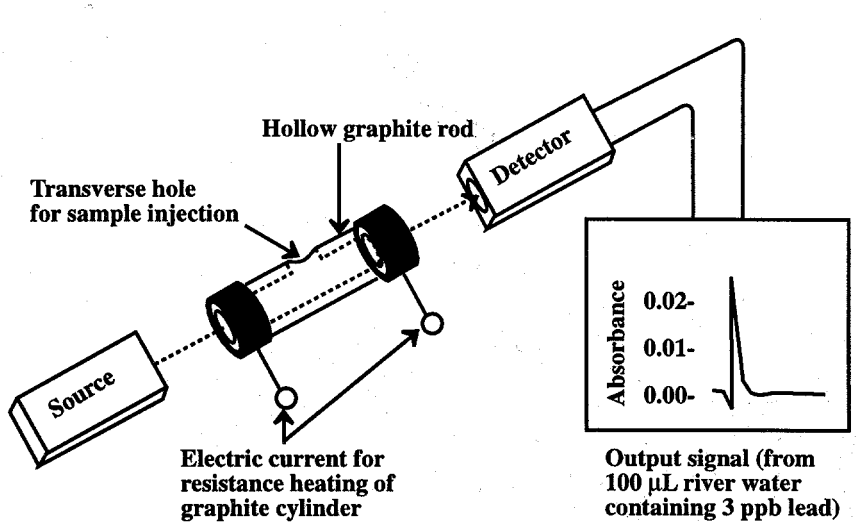

Figure 24.2. Graphite furnace for atomic absorption analysis and typical output signal.

Atomic Emission Techniques

Metals may be determined in water, atmospheric particulate matter, and biological samples very well by observing the spectral lines emitted when they are heated to a very high temperature. An especially useful atomic emission technique is inductively coupled plasma atomic emission spectroscopy (ICP/AES). The "f1ame" in which analyte atoms are excited in plasma emission consists of an incandescent plasma (ionized gas) of argon heated inductively by radiofrequency energy at 4-50 MHz and 2-5 kW (Figure 24.3). The energy is transferred to a stream of argon through an induction coil, producing temperatures up to 10,000 K. The sample atoms are subjected to temperatures around 7000 K, twice those of the hottest conventional flames (for example, nitrous oxide-acetylene operates at 3 s200 K). Since emission of light increases exponentially with temperature, lower detection limits are obtained. Furthermore, the technique enables emission analysis of some of the environmentally important metalloids such as arsenic, boron, and selenium. Interfering chemical reactions and interactions in the plasma are minimized as compared to flames. Of greatest significance, however, is the capability of analyzing as many as 30 elements simultaneously, enabling a true multielement analysis technique. Plasma atomization combined with mass spectrometric measurement of analyte elements is a relatively new technique that is an especially powerful means for multielement analysis.

24.4. ELECTROCHEMICAL METHODS OF ANALYSIS

Several useful techniques for water analysis utilize electrochemical sensors. These techniques may be potentiometric, voltammetric, or amperometric. Potentiometry is based upon the general principle that the relationship between the potential of a measuring electrode and that of a reference electrode is a function of the log of the activity of an ion in solution. For a measuring electrode responding selectively to a particular ion, this relationship is given by the Nernst equation,

$$E = E^o + \frac{2.303RT}{zF} \log(a_z) \qquad (24.4.1)$$

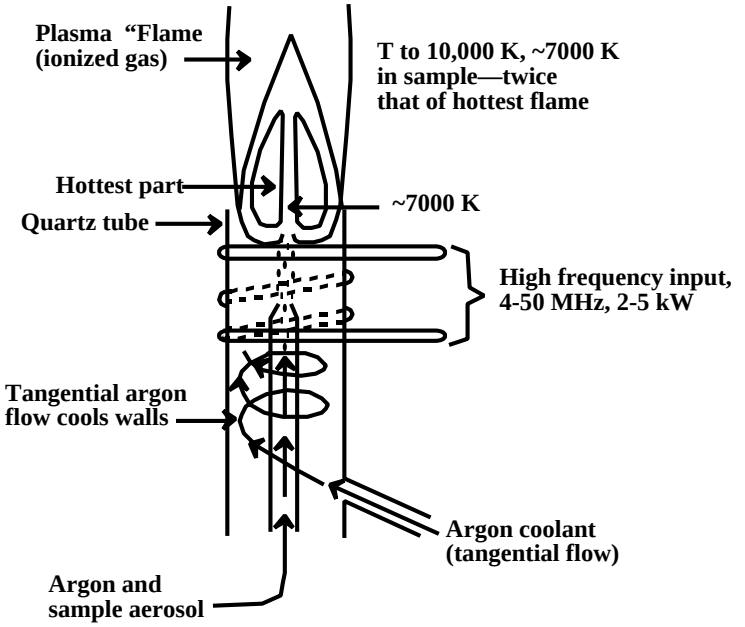

Figure 24.3. Schematic diagram showing inductively coupled plasma used for optical emission spectroscopy.

where E is the measured potential; E^o is the standard electrode potential; R is the gas constant; T is the absolute temperature; z is the signed charge (+ for cations, - for anions); *F* is the Faraday constant; and a is the activity of the ion being measured. At a given temperature, the quantity 2.303RT/*F* has a constant value; at 25°C it is 0.0592 volt (59.2 mv). At constant ionic strength, the activity, a, is directly proportional to concentration, and the Nernst equation may be written as the following for electrodes responding to Cd^{2+} and F^-, respectively:

$$E \text{ (in mv)} = E^o + \frac{59.2}{2} \log [Cd^{2+}] \qquad (24.4.2)$$

$$E = E^o - 59.2 \log [F^-] \qquad (24.4.3)$$

Electrodes that respond more or less selectively to various ions are called **ion-selective electrodes**. Generally, the potential-developing component is a membrane of some kind that allows for selective exchange of the sought-for ion. The glass electrode used for the measurement of hydrogen-ion activity and pH is the oldest and most widely used ion-selective electrode. The potential is developed at a glass membrane that selectively exchanges hydrogen ion in preference to other cations, giving a Nernstian response to hydrogen ion activity, a_{H^+}:

$$E = E^o + 59.2 \log(a_{H^+}) \qquad (24.4.4)$$

Of the ion-selective electrodes other than glass electrodes, the fluoride electrode is the most successful. It is well-behaved, relatively free of interferences, and has an adequately low detection limit and a long range of linear response. Like all ion-selective electrodes, its electrical output is in the form of a potential signal that is proportional to log of concentration. A small error in E leads to a variation in log of concentration, which leads to relatively high concentration errors.

Voltammetric techniques, the measurement of current resulting from potential applied to a microelectrode, have found some applications in water analysis. One such technique is differential-pulse polarography, in which the potential is applied to the microelectrode in the form of small pulses superimposed on a linearly increasing potential. The current is read near the end of the voltage pulse and compared to the current just before the pulse was applied. It has the advantage of minimizing the capacitive current from charging the microelectrode surface, which sometimes obscures the current due to the reduction or oxidation of the species being analyzed. Anodic-stripping voltammetry involves deposition of metals on an electrode surface over a period of several minutes followed by stripping them off very rapidly using a linear anodic sweep. The electrodeposition concentrates the metals on the electrode surface, and increased sensitivity results. An even better technique is to strip the metals off using a differential pulse signal. A differential-pulse anodic-stripping voltammogram of copper, lead, cadmium, and zinc in tap water is shown in Figure 24.4.

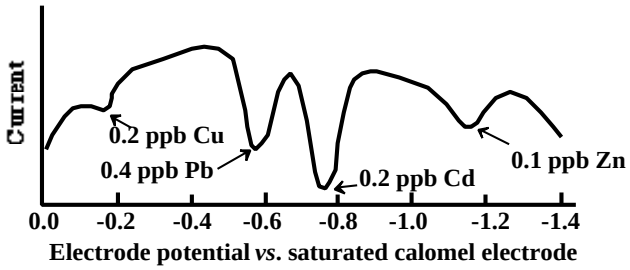

Figure 24.4. Differential-pulse anodic-stripping voltammogram of tap water at a mercury-plated, wax-impregnated graphite electrode.

24.5. CHROMATOGRAPHY

First described in the literature in the early 1950s, gas chromatography has played an essential role in the analysis of organic materials. Gas chromatography is both a qualitative and quantitative technique; for some analytical applications of environmental importance, it is remarkably sensitive and selective. Gas chromatography is based upon the principle that when a mixture of volatile materials transported by a carrier gas is passed through a column containing an adsorbent solid phase or, more commonly, an absorbing liquid phase coated on a solid material, each volatile component will be partitioned between the carrier gas and the solid or liquid. The length of time required for the volatile component to traverse the column is proportional to the degree to which it is retained by the nongaseous phase. Since different components may be retained to different degrees, they will emerge from the

end of the column at different times. If a suitable detector is available, the time at which the component emerges from the column and the quantity of the component are both measured. A recorder trace of the detector response appears as peaks of different sizes, depending upon the quantity of material producing the detector response. Both quantitative and (within limits) qualitative analyses of the sought-for substances are obtained.

The essential features of a gas chromatograph are shown schematically in Figure 24.5. The carrier gas generally is argon, helium, hydrogen, or nitrogen. The sample is injected as a single compact plug into the carrier gas stream immediately ahead of the column entrance. If the sample is liquid, the injection chamber is heated to vaporize the liquid rapidly. The separation column may consist of a metal or glass tube packed with an inert solid of high surface area covered with a liquid phase, or it may consist of an active solid, which enables the separation to occur. More commonly, capillary columns are now employed which consist of very small diameter, very long tubes in which the liquid phase is coated on the inside of the column.

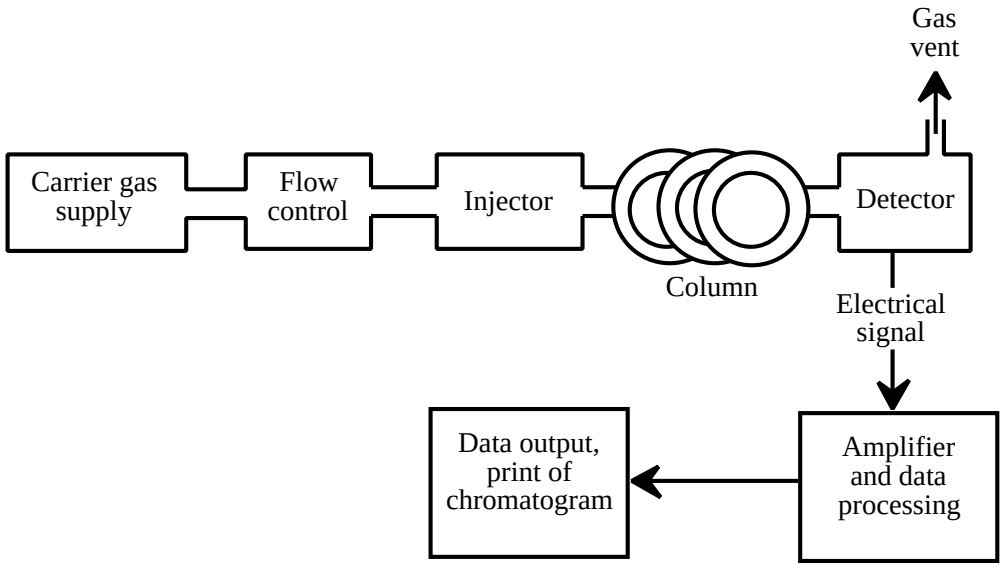

Figure 24.5. Schematic diagram of the essential features of a gas chromatograph.

The component that primarily determines the sensitivity of gas chromatographic analysis and, for some classes of compounds, the selectivity as well, is the detector. One such device is the thermal conductivity detector, which responds to changes in the thermal conductivity of gases passing over it. The electron-capture detector, which is especially useful for halogenated hydrocarbons and phosphorus compounds, operates through the capture of electrons emitted by a beta-particle source. The flame-ionization gas chromatographic detector is very sensitive for the detection of organic compounds. It is based upon the phenomenon by which organic compounds form highly conducting fragments, such as C^+, in a flame. Application of a potential gradient across the flame results in a small current that may be readily

measured. The mass spectrometer, described in Section 24.6, may be used as a detector for a gas chromatograph. A combined gas chromatograph/mass spectrometer (GC/MS) instrument is an especially powerful analytical tool for organic compounds.

Chromatographic analysis requires that a compound exhibit at least a few mm of vapor pressure at the highest temperature at which it is stable. In many cases, organic compounds that cannot be chromatographed directly may be converted to derivatives that are amenable to gas chromatographic analysis. It is seldom possible to analyze organic compounds in water by direct injection of the water into the gas chromatograph; higher concentration is usually required. Two techniques commonly employed to remove volatile compounds from water and concentrate them are extraction with solvents and purging volatile compounds with a gas, such as helium; concentrating the purged gases on a short column; and driving them off by heat into the chromatograph.

High-Performance Liquid Chromatography

A liquid mobile phase used with very small column-packing particles enables high-resolution chromatographic separation of materials in the liquid phase. Very high pressures up to several thousand psi are required to get a reasonable flow rate in such systems. Analysis using such devices is called **high-performance liquid chromatography** (HPLC) and offers an enormous advantage in that the materials analyzed need not be changed to the vapor phase, a step that often requires preparation of a volatile derivative or results in decomposition of the sample. The basic features of a high-performance liquid chromatograph are the same as those of a gas chromatograph, shown in Figure 24.5, except that a solvent reservoir and high-pressure pump are substituted for the carrier gas source and regulator. A hypothetical HPLC chromatogram is shown in Figure 24.6. Refractive index and ultraviolet detectors are both used for the detection of peaks coming from the liquid chromatograph column. Fluorescence detection can be especially sensitive for some classes of compounds. Mass spectrometric detection of HPLC effluents has lead to the development of LC/MS analysis. Somewhat difficult in practice, this technique can be a powerful tool for the determination of analytes that cannot be subjected to gas chromatography. High-performance liquid chromatography has emerged as a very useful technique for the analysis of a number of water pollutants.

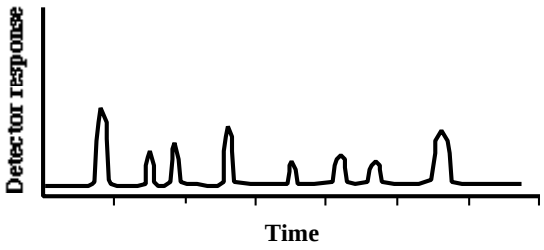

Figure 24.6. Hypothetical HPLC chromatogram.

Chromatographic Analysis of Water Pollutants

The U. S. Environmental Protection Agency has developed a number of chromatography-based standard methods for determining water pollutants.[2] Some of these methods use the purge-and-trap technique, bubbling gas through a column of water to purge volatile organics from the water followed by trapping the organics on solid sorbents, whereas others use solvent extraction to isolate and concentrate the organics. These methods are summarized in Table 24.2.

Ion Chromatography

The liquid chromatographic determination of ions, particularly anions, has enabled the measurement of species that used to be very troublesome for water chemists. This technique is called **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.

24.6. MASS SPECTROMETRY

Mass spectrometry is particularly useful for the identification of specific organic pollutants. It depends upon the production of ions by an electrical discharge or chemical process, followed by separation based on the charge-to-mass ratio and measurement of the ions produced. The output of a mass spectrometer is a mass spectrum, such as the one shown in Figure 24.8. A mass spectrum is characteristic of a compound and serves to identify it. Computerized data banks for mass spectra have been established and are stored in computers interfaced with mass spectrometers. Identification of a mass spectrum depends upon the purity of the compound from which the spectrum is taken. Prior separation by gas chromatography with continual sampling of the column effluent by a mass spectrometer, commonly called gas chromatography-mass spectrometry (GC/MS), is particularly effective in the analysis of organic pollutants.

24.7. ANALYSIS OF WATER SAMPLES

The preceding sections of this chapter have covered the major kinds of analysis techniques that are used on water. In this section several specific aspects of water analysis are addressed.

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

Table 24.2. Chromatography-based EPA Methods for Organic Compounds in Water

Class of compounds	Method Number GC	GC/MS	HPLC	Example analytes
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 PCB's	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

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).

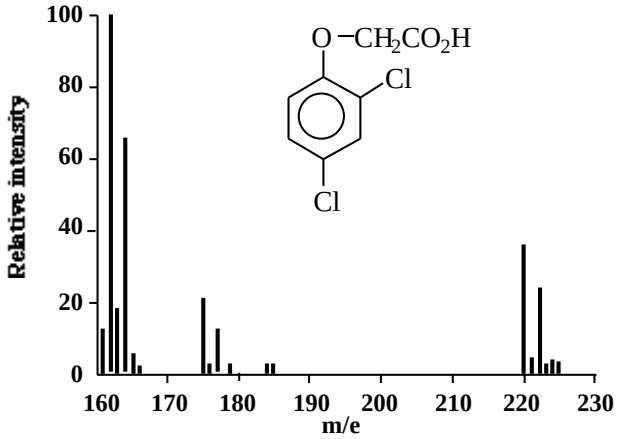

Figure 24.7. Partial mass spectrum of the herbicide 2,4-dichlorophenoxyacetic acid (2,4-D), a common water pollutant.

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 may 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 may 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 may 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 composite 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.[3] The pesticide analytes are eluted from the SPE with ethyl acetate and measured by gas chromatography. A mean recovery of 85% has been reported.

A clever approach to sulfide analysis using SPE has been described.[4] The water sample is sucked into an airtight syringe to prevent exposure to sulfide-oxidizing atmospheric oxygen and is immediately reacted with N,N-dimethyl-*p*-phenylenediamine sulfate and $FeCl_3$, which produces methylene blue, a colored compound used as an indicator. The resulting solution is forced through a Sep-Pak C18 solid phase extractor to remove the methylene blue, which is stable for at least 30 days on the solid phase. After elution with a mixture of methanol and 0.01 M HCl, the absorbance of the methylene blue is measured at 659 nm to quantitate the sulfide.

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.[5]

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}Tc, ^{137}Cs, ^{90}Sr, ^{238}Pu.[6] Organic materials sampled from water with such disks include haloacetic acids[7] and acidic and neutral herbicides.[8]

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 24.3.

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—which may 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.[9] Instructions should be followed for each kind of sample in order to ensure meaningful results.

Table 24.3. 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	Formation of 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

Total Organic Carbon in Water

The importance and possible detrimental effects of dissolved organic compounds in water were discussed in Chapter 7. 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 doxide. The amount of carbon dioxide evolved is taken as a measure of TOC.

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 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, HO•, discussed extensively as a photochemical reaction intermediate in Chapters 9, 12, and 13. These active species bring about the rapid oxidation of dissolved organic compounds as shown in the following general reaction:

$$\text{Organics} + HO\bullet \rightarrow CO_2 + H_2O \qquad (24.7.1)$$

After oxidation is complete, the 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 24.8 is a schematic of a TOC analyzer.

Measurement of Radioactivity in Water

There are several potential sources of radioactive materials that may contaminate water (see Section 7.13). 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

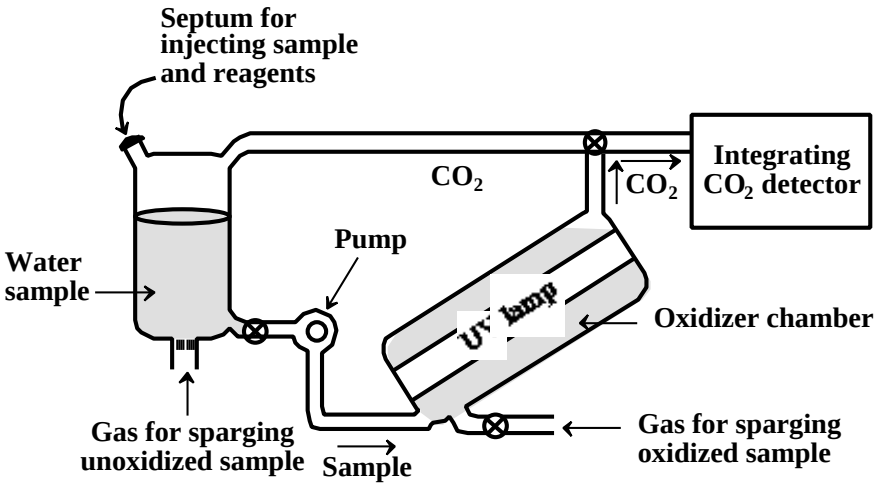

Figure 24.8. TOC analyzer employing UV-promoted sample oxidation.

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 25.5) for such toxins has been described.[10]

Summary of Water Analysis Procedures

The main chemical parameters commonly determined in water are summarized in Table 24.4. 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.

24.8. AUTOMATED WATER ANALYSES

Huge numbers of water analyses must often be performed in order to get meaningful results and for reasons of economics. This has resulted in the development of a number of automated procedures in which the samples are introduced through a sampler and the analyses performed and results posted without manual manipulation of reagents and apparatus. Such procedures have been developed and instruments marketed for the determination of a number of analytes, including alkalinity, sulfate,

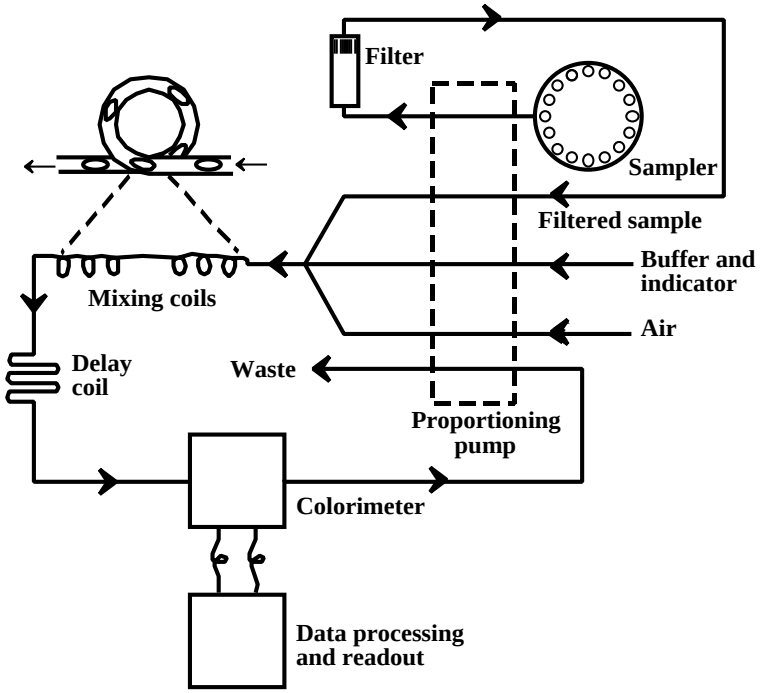

Figure 24.9. Automated analyzer system for the determination of total alkalinity in water. Addition of a water sample to a methyl orange solution buffered to pH 3.1 causes a loss of color in proportion to the alkalinity in the sample.

Table 24.4. 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,[1] ICP[2]
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 24.4 (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)	Proteinaceous material	Spectrophotometry
(organic)	Organic pollution indicator	Spectrophotometry
Oil and grease	Industrial pollution	Gravimetry
Organic carbon	Organic pollution indicator	Oxidation-CO_2 measurement
Organic contaminants	Organic pollution indicator	Activated carbon adsorption
Oxygen	Water quality	Titration, electrochemical
Oxygen demand (biochemical)	Water quality and pollution	Microbiological-titration
(chemical)	Water quality and pollution	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 24.4 (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

[1] AA denotes atomic absorption
[2] ICP stands for inductively coupled plasma techniques, including atomic emission and detection of plasma-atomized atoms by mass spectrometry.

ammonia, nitrate/nitrite, and metals. Colorimetric procedures are popular for such automated analytical instruments, using simple, rugged colorimeters for absorbance measurements. Figure 24.9 shows an automated analytical system for the determination of alkalinity. The reagents and sample liquids are transported through the analyzer by a peristaltic pump consisting basically of rollers moving over flexible tubing. By using different sizes of tubing, the flow rates of the reagents are proportioned. Air bubbles are introduced into the liquid stream to aid mixing and to separate one sample from another. Mixing of the sample and various reagents is accomplished in mixing coils. Since many color-developing reactions are not rapid, a delay coil is provided that allows the color to develop before reaching the colorimeter. Bubbles are removed from the liquid stream by a debubbler pror to introduction into the flowcell for colorimetric analysis.

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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 may be said about the dissolved CO_2 and hardness in the water?

3. For which of the following analytes may nitric acid be used as a water sample preservative: H_2S; CO_2; metals; coliform bacteria; cyanide?

4. In the form of what compound is oxygen fixed in the Winkler analysis of O_2?

5. Of the following analytical techniques, the water analysis technique that would best distinguish between the hydrated $Ag(H_2O)_6^+$ ion and the complex $Ag(NH_3)_2^+$ ion by direct measurement of the uncomplexed ion is: (a) neutron-activation analysis, (b) atomic absorption, (c) inductively coupled plasma atomic emission spectroscopy, (d) potentiometry, (e) flame emission.

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 H_2SO_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 concentration 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 2.63×10^{-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. What was the concentration of fluoride in the sample?

11. The activity of iodine-131 ($t_{1/2}$ = 8 days) in a water sample 24 days after collection was 520 pCi/liter. What was the activity on the day of collection?

12. Neutron irradiation of exactly 2.00 mL of a standard solution containing 1.00 mg/L of unknown heavy metal "X" for exactly 30 seconds gave an activity of 1,257 counts per minute, when counted exactly 33.5 minutes after the irradiation, measured for a radionuclide product of "X" having a half-life of 33.5

minutes. Irradiation of an unknown water sample under identical conditions (2.00 mL, 30.0 seconds, same neutron flux) gave 1,813 counts per minute when counted 67.0 minutes after irradiation. What was the concentration of "X" in the unknown sample?

13. Why is magnesium-EDTA chelate added to a magnesium-free water sample before it is to be titrated with EDTA for Ca^{2+} ?

14. For what type of sample is the flame-ionization detector most useful?

15. Manganese from a standard solution was oxidized to 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 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?