Kirk-Othmer Encyclopedia of Chemical Technology.

WATER, ANALYSIS

Since 1970, new analytical techniques, eg, ion chromatography, have been developed, and others, eg, atomic absorption and emission, have been improved (1–5). Detection limits for many chemicals have been dramatically lowered. Many wet chemical methods have been automated and are controlled by microprocessors which allow greater data output in a shorter time. Perhaps the best known continuous-flow analyzer for water analysis is the Autoanalyzer system manufactured by Technicon Instruments Corp. (Tarrytown, N.Y.) (6). Isolation of samples is maintained by pumping air bubbles into the flow line. Recently, flow-injection analysis has also become popular, and a theoretical comparison of it with the segmented flow analyzer has been made (7–9). Several books are available regarding automated chemical analysis (10, 11) (see Analytical methods; also Biotechnology).

Although simple analytical tests often provide the needed information regarding a water sample, such as the formation and presence of chloroform and other organohalides in drinking water, require some very specialized methods of analysis. The separation of trace metals into total and uncomplexed species also requires special sample handling and analysis (12).

A list of all water analyses would be extremely long since, under some conditions and with enough time, water can solubilize everything to some extent. Fortunately, a great deal can be learned about a water supply by carrying out a few physical and chemical tests. These simple tests might be all that are needed to characterize a water supply for many purposes, and it is usually the purpose for which the water is to be used that determines the type and extent of testing. The methods described in this review are intended primarily for freshwater analysis and may not be suitable for the analysis of saline water. In addition, there are several books, manuals, and annual review articles available that detail water analysis for different substances and uses (13–21).

1. Physical Properties

1.1. Temperature

Water temperature is an important parameter in calculations of oxygen solubility, calcium carbonate saturation and stability, and various forms of alkalinity, as well as in determining basic hydrobiological characteristics. The temperature should be taken *in situ* for accuracy, and a standard mercury thermometer with readings to the nearest 0.1°C should be used. It should be calibrated against a precision thermometer certified by the National Bureau of Standards. A thermistor is preferable when attempting to measure temperature at different depths and for automated monitoring and surveillance, and should be similarly calibrated (see Temperature measurement).

1.2. Specific Conductance

The specific conductance depends on the total concentration of the dissolved ionized substances, ie, the ionic strength of a water sample. It is an expression of the ability of the water to conduct an electric current.

Freshly distilled water has a conductance of 0.5–2 μS/cm, whereas that of potable water generally is 50–1500 μS/cm. The conductivity of a water sample is measured by means of an a-c Wheatstone-bridge circuit with a null indicator and a conductance cell. Each cell has an associated constant which, when multiplied by the conductance, yields the specific conductance.

The concentration of dissolved ionic substances can be roughly estimated by multiplying the specific conductance by an empirical factor of 0.55–0.9, depending on temperature and soluble components. Since specific conductance is temperature dependent, all samples should be measured at the same temperature. Alternatively, an appropriate temperature-correction factor obtained by comparisons with known concentrations of potassium chloride may be used. Instruments are available that automatically correct conductance measurements for different temperatures.

1.3. Color

Many water samples have a yellow to brownish-yellow color which is caused by natural substances, eg, leaves, bark, humus, and peat material. Turbidity in a sample can make the measurement of color uncertain and is usually removed by centrifugation prior to analysis. The color is usually measured by comparison of the sample with known concentrations of colored solutions. A platinum–cobalt solution is used as the standard, and the unit of color is that produced by 1 mg/L platinum as chloroplatinate ion. The standard is prepared from potassium chloroplatinate (K_2PtCl_6) and cobalt chloride ($CoCl_2{\cdot}6H_2O$). The sample may also be compared to suitably calibrated special glass color disks.

Three special tristimulus light filters are available which, when combined with a specific light source and a filter photometer, can be used to obtain color data (20). Although this method provides added precision and accuracy, it is seldom worth the extra effort required (see Color).

1.4. Turbidity

Turbidity in natural water is caused by the presence of suspended matter which scatters light. The suspended material is usually clay or silt, finely divided organic and inorganic material, or microorganisms. It is measured either visually or by a nephelometric method. The former is based on the light path through a sample that just causes the image of the flame of a standard candle to disappear. Longer light paths are indicative of lower turbidities. Suspensions of clay are used as standards and results are reported in Jackson turbidity units (JTU). The lowest turbidity value that can be measured using this method is 25 JTU.

The nephelometric method involves illuminating the sample in a turbidimeter and measuring the amount of light scattered at 90° to the incident beam. The higher the intensity of scattered light, the greater the sample turbidity. A formazan polymer suspension is used as the standard and results are reported in nephelometric turbidity units (NTU). The greater precision, sensitivity, and wider applicability of this method make it preferable to the visual method.

1.5. Taste and Odor

The measurement of taste and odor is somewhat subjective and depends on the personal judgements of individuals. Panels of not less than five observers, and preferably more than ten, are used. The sample is diluted with odor-free water until a ratio at which the odor is just perceptible is determined; this ratio is called the threshold odor number (TON). A similar method is used to detect a distinct taste in water (see Flavor characterization).

1.6. Dissolved Solids

Dissolved solids are materials that pass through a glass-fiber filter and remain after evaporation and drying at 180°C.

1.7. Suspended Solids

Suspended solids are determined by filtering a known volume of water through a glass-fiber filter and weighing the filter before and after filtration. The filter is dried at 105–110°C, and the weight difference is equal to the suspended solids.

1.8. pH

The pH of most natural waters is 4–9 and should be measured *in situ* since it is subject to change once a sample has been isolated. It can be measured either colorimetrically or potentiometrically. The former method relies on color-indicator papers which are impregnated with pH-sensitive dyes. The potentiometric method requires the use of a pH-sensitive glass electrode, which is generally interference-free at pH 4–9. The electrode should be calibrated frequently against standard buffer solutions of known pH (see Hydrogen-ion activity).

2. Principal Mineral Constituents and Gases

2.1. Alkalinity

The alkalinity of a water sample is its acid-neutralizing capacity. Bicarbonate and carbonate ions are the predominant contributors to alkalinity in most waters, and their chemical equilibria generally maintain the pH of 5–9. The presence of enough hydroxide ion to affect the alkalinity determination in natural waters is rare. Silica, borate, or phosphate do contribute to the overall alkalinity if present in large enough quantities.

The alkalinity is determined by titration of the sample with a standard acid (sulfuric or hydrochloric) to a definite pH. If the initial sample pH is >8.3, the titration curve has two inflection points reflecting the conversion of carbonate ion to bicarbonate ion and finally to carbonic acid (H_2CO_3). A sample with an initial pH <8.3 only exhibits one inflection point corresponding to conversion of bicarbonate to carbonic acid. Since most natural-water alkalinity is governed by the carbonate–bicarbonate ion equilibria, the alkalinity titration is often used to estimate their concentrations.

2.2. Acidity

Acidity is the base-neutralizing capacity of a sample of water. It is determined by titration of the sample with standard base to pH 8.3 (phenolphthalein end point). Generally, a sample is not reported as acidic unless its initial pH is <4.5. The acidity may be the result of free acids, eg, HCl or H_2SO_4, or the hydrolysis of certain metal cations.

The free-acid content is determined by titration of a cold solution to pH 4.5. The total acidity is determined by titration to pH 8.3 in a boiling solution. Some natural-water samples might be complex, and the best determination of acidity results from visual inspection of the plotted titration curve.

2.3. Hardness (Calcium and Magnesium)

The term *hardness* has its origins in the household laundry use of water. Some waters were considered harder to use for laundering because they required more soap to produce suds. The hardness of water was then taken

to be a measure of the capacity of the water to cause the precipitation of soap. This is actually a result of the reaction of soap with calcium or magnesium ions. Thus, water hardness is generally a measure of the total concentration of calcium and magnesium. The portion of hardness that disappears with boiling is temporary or carbonate hardness and is primarily caused by calcium and magnesium bicarbonates. They precipitate as their carbonates by the loss of carbon dioxide during boiling. The hardness remaining after boiling is the permanent or noncarbonate hardness. Other cations, eg, strontium or barium, also contribute to hardness, but their concentration is usually insignificant (see Dispersants; Detergency).

Calcium and magnesium can be titrated readily with disodium ethylenediaminetetraacetate, with Eriochrome Black T as the indicator. The solution is buffered at pH 10.0. Certain metal ions interfere with this procedure by causing fading or indistinct end points. Cyanide, sulfide, or hydroxylamine can be used to eliminate or minimize the interferences.

Hardness can also be calculated by summation of the individually determined alkaline earths by means of atomic absorption analysis. Basic samples must be acidified, and lanthanum chloride must be added to minimize interferences from phosphate, sulfate, and aluminum. An ion-selective electrode that utilizes a liquid ion exchanger is also available for hardness measurement; however, this electrode is susceptible to interferences from other dissolved metal ions.

Magnesium, calcium, barium, and strontium can also be determined by ion chromatography with *m*-phenylenediamine in perchloric acid as the eluent. Ion chromatography by conductimetric detection has been described, and applications to environmental waters have been discussed (1, 22, 23).

2.4. Sodium and Potassium

Sodium and potassium can be determined by either atomic emission or absorption. Large concentrations of sodium can interfere with the potassium determination in either of these methods. Excess sodium can be added to both the potassium standards and samples to minimize any variations in the samples. Proper positioning of the flame helps reduce sodium interference in atomic absorption.

2.5. Chloride

Chloride is common in freshwater because almost all chloride salts are very soluble in water. Its concentration is generally 10^{-4} to 10^{-3} M. Chloride can be titrated with mercuric nitrate. Diphenylcarbazone, which forms a purple complex with the excess mercuric ions at pH 2.3–2.8, is used as the indicator. The pH should be controlled to ± 0.1 pH unit. Bromide and iodide are the principal interferences, whereas chromate, ferric, and sulfite ions interfere at levels greater than 10 mg/L. Chloride can also be determined by a colorimetric method based on the displacement of thiocyanate ion from mercuric thiocyanate by chloride ion. The liberated SCN^- reacts with ferric ion to form the colored complex of ferric thiocyanate. The method is suitable for chloride concentrations from 10^{-6} to 10^{-3} M.

Ion chromatography can be used to determine chloride concentrations of 2–1000 ppb with a carbonate–bicarbonate eluent (23). Fluoride, nitrite, phosphate, bromide, nitrate, and sulfate do not interfere and can be measured simultaneously with a total analysis time of <30 min.

An ion-selective electrode is available for chloride analysis; chloride can be measured potentiometrically at $10^{-6} - 1$ M. Iodide and sulfide are the principal interferences.

2.6. Sulfate

Mine drainage may contribute to high sulfate concentrations resulting from pyrite oxidation. High concentrations may exhibit a cathartic action. Sulfate concentrations of 10^{-5} to 10^{-3} M can be titrated in an alcoholic solution with standard barium chloride and using Thorin as an indicator. Barium reacts with Thorin to form

a deep red complex. The sample should be kept at pH 2–5, and the sample must be passed through a strong cation-exchange column prior to the titration. This is done to remove any multivalent cations which would also form intensely colored complexes with Thorin. High concentrations of sulfate can be determined by gravimetric analysis. The sulfate precipitates as barium sulfate. The ion-chromatographic response to sulfate is linear from 2 to 10^4 ppb (23).

2.7. Nitrate and Nitrite

Nitrate is usually present in trace quantities in surface waters but occasionally occurs in high concentrations in some groundwaters. If present in excessive amounts, it can contribute to the illness infant methemoglobinemia. Nitrate is an essential nutrient for many photosynthetic autotrophs. Nitrite is an intermediate in the reduction of nitrate as well as in the oxidation of ammonia; it is also used as a corrosion inhibitor in some industrial processes.

Nitrite can be determined by reaction with sulfanilamide to form the diazo compound, which couples with *N*-(1-naphthyl)ethylenediamine dihydrochloride to form an intensely colored red azo dye. Nitrate can be determined in a similar manner after reduction to nitrite. Suitable reducing agents are cadmium filings or hydrazine. This method is useful at a nitrogen concentration of $10^{-7} - 10^{-4}\ M$.

Nitrate can also be measured potentiometrically with an ion-selective electrode at $10^{-5} - 10^{-1}\ M$ (24, 25). This method is suggested as a screening method for determining the approximate nitrate concentration (20). Ion chromatography can be used for nitrate concentrations of 2 to 10^4 ppb (23).

2.8. Fluoride

A fluoride concentration of ca 1 mg/L is helpful in preventing dental caries. Fluoride is determined potentiometrically with an ion-selective electrode. A buffer solution of high total ionic strength is added to the solution to eliminate variations in sample ionic strength and to maintain the sample at pH 5–8, the optimum range for measurement. (Cyclohexylenedinitrilo)tetraacetic acid (CDTA) is usually added to the buffer solution to complex aluminum and thereby prevent its interference. If fluoroborate ion is present, the sample should be distilled from a concentrated sulfuric acid solution to hydrolyze the fluoroborate to free fluoride prior to the electrode measurement (26, 27).

Several colorimetric procedures for fluoride are available, but it is usually desirable to distill the sample from concentrated sulfuric acid prior to analysis to eliminate interferences. One method is based upon bleaching a dye formed by the reaction of zirconium and sodium 2-(*p*-sulfophenylazo)-1,8-dihydroxy-3,6-naphthalenedisulfonate (SPADNS reagent) (28).

2.9. Phosphate

Phosphorus occurs in water primarily as a result of natural weathering, municipal sewage, and agricultural runoff. The most common form in water is the phosphate ion. A sample containing phosphate can react with ammonium molybdate to form molybdophosphoric acid ($H_3P(Mo_3O_{10})_4$). This compound is reduced with stannous chloride in sulfuric acid to form a colored molybdenum-blue complex, which can be measured colorimetrically. Silica and arsenic are the chief interferences.

Some water samples contain phosphorus forms other than phosphate, eg, polyphosphate, hexametaphosphate, and organic phosphates. These forms can be hydrolyzed to phosphate in hot sulfuric acid solution and determined by the preceding method. The more refractory organic phosphates require digestion in a sulfuric acid–ammonium persulfate solution. Ion chromatography can also be used to measure PO^{3-}_4 at 2 to 10^4 ppb (21).

2.10. Boron and Borates

Boron is an essential element for plant growth; however, concentrations >2 mg/L are harmful to some plants. Natural-water concentrations of boron are usually well below this value, although higher concentrations can occur as a result of industrial waste effluents or cleaning agents.

Two colorimetric methods are recommended for boron analysis. One is the curcumin method, where the sample is acidified and evaporated after addition of curcumin reagent. A red product called rosocyanine remains; it is dissolved in 95 wt % ethanol and measured photometrically. Nitrate concentrations >20 mg/L interfere with this method. Another colorimetric method is based upon the reaction between boron and carminic acid in concentrated sulfuric acid to form a bluish-red or blue product. Boron concentrations can also be determined by atomic absorption spectroscopy with a nitrous oxide–acetylene flame or graphite furnace. Atomic emission with an argon plasma source can also be used for boron measurement.

2.11. Silica

The silica content of natural waters is usually 10^{-5} to $(5 \times 10^{-4})\,M$. Its presence is considered undesirable for some industrial purposes because of the formation of silica and silicate scales. The heteropoly-blue method is used for the measurement of silica. The sample reacts with ammonium molybdate at pH 1.2, and oxalic acid is added to reduce any molybdophosphoric acid produced. The yellow molybdosilicic acid is then reduced with 1-amino-2-naphthol-4-sulfonic acid and sodium sulfite to heteropoly blue. Color, turbidity, sulfide, and large amounts of iron are possible interferences. A digestion step involving $NaHCO_3$ can be used to convert any molybdate-unreactive silica to the reactive form. Silica can also be determined by atomic absorption with a nitrous oxide–acetylene flame or by atomic emission involving either a d-c or inductively coupled argon plasma source.

2.12. Oxygen

The solubility of atmospheric oxygen in water depends primarily on pressure, temperature, and salt content. The most reliable results for oxygen measurement are obtained from fresh samples. The longer the time lag between sampling and measurement, the greater the chance that the dissolved oxygen concentration diminishes because of chemical or biological activity in the sample. The Winkler titration has been the preferred method for dissolved oxygen determination for many years. Several modifications of the basic method have been made to minimize interferences (20). The basis of this analysis is the quantitative oxidation of alkaline manganous hydroxide by the oxygen in the sample. Upon acidification in the presence of excess iodide, an amount of iodine equivalent to the dissolved oxygen is released. The iodine can then be titrated with standard sodium thiosulfate.

Considerable care is required in the collection of samples for dissolved-oxygen analysis. The errors associated with sampling can be minimized by an *in situ* method. Membrane-covered dissolved-oxygen electrodes are ideally suited to this purpose. These electrodes can be either polarographic or galvanic. The electrodes are protected by an oxygen-permeable polymeric membrane, which provides a rigorously defined diffusion barrier against solution impurities. For the polarographic type, an external voltage must be applied to the working or sensing electrode and must be sufficient to reduce molecular oxygen. With the galvanic type, two solid metal electrodes are used, such that the reduction of oxygen occurs spontaneously and no external voltage source is necessary. In both cases and under steady-state conditions, the resulting current is proportional to the dissolved-oxygen concentration in solution. The use and operation of dissolved-oxygen electrodes are thoroughly described in several publications (29, 30).

3. Minor Mineral Constituents and Gases

3.1. Metals

The method of choice for metal analysis generally depends upon the concentration as well as the number of metals to be analyzed per sample and, to a lesser degree, the number of samples. When there is a large number of metals per sample, an emission spectroscopy method is preferred because of its simultaneous multielement capabilities. This technique has become much more popular for water analysis because of the development of a new emission source, the argon plasma. This source combines the advantages of the flame with the high temperature of an electric arc or spark. The plasma can be generated either through an induction process or by a direct current. When coupled with a polychromator in a direct-reading fashion, this method can be used to measure up to 60 elements in approximately 1 min (31–33). Limits of detection for many elements are comparable to or better than flame atomic absorption and, in some cases, to graphite-furnace atomic absorption.

Atomic absorption spectroscopy is more suited to samples where the number of metals is small, because it is essentially a single-element technique. The conventional air–acetylene flame is used for most metals; however, elements that form refractory compounds, eg, Al, Si, V, etc, require the hotter nitrous oxide–acetylene flame. The use of a graphite furnace provides detection limits much lower than either of the flames. A cold-vapor-generation technique combined with atomic absorption is considered the most suitable method for mercury analysis (34).

3.2. Nonmetals

3.2.1. Arsenic

Total arsenic concentration can be determined by reduction of all forms to arsine (AsH_3) and collection of the arsine in a pyridine solution of silver diethyldithiocarbamate. Organoarsenides must be digested in acidic potassium persulfate prior to reduction. The complex that forms is deep red, and this color can be measured spectrophotometrically. Reduction is carried out in an acidic solution of KI–$SnCl_2$, and AsH_3 is generated by addition of zinc.

Atomic absorption spectroscopy is an alternative to the colorimetric method. Arsine is still generated but is purged into a heated open-end tube furnace or an argon–hydrogen flame for atomization of the arsenic and measurement. Arsenic can also be measured by direct sample injection into the graphite furnace. The detection limit with the air–acetylene flame is too high to be useful for most water analysis.

3.2.2. Selenium

Selenium is determined by atomic absorption after the organoselenides are broken down with acidic persulfate and all forms of selenium have been converted to H_2Se. The reduction is brought about in acidic solution of KI–$SnCl_2$ or borohydride, and H_2Se is generated by addition of zinc. The dihydrogen selenide is purged into an open-end tube furnace or argon–hydrogen flame for atomization and measurement. Selenium can also be determined by direct sample injection into the graphite furnace.

3.2.3. Cyanide

Industrial processes frequently discharge significant concentrations of cyanide, which can be extremely toxic at very low levels. Cyanide compounds are classified as either simple or complex. It is usually necessary to decompose complex cyanides by an acid reflux. The cyanide is then distilled into sodium hydroxide to remove compounds that would interfere in analysis. Extreme care should be taken during the distillation as toxic hydrogen cyanide is generated. The cyanide in the alkaline distillate can then be measured potentiometrically with an ion-selective electrode. Alternatively, the cyanide can be determined colorimetrically. It is converted to

cyanogen chloride by reaction with chloramine-T at pH <8. The CNCl then reacts with a pyridine barbituric acid reagent to form a red-blue dye.

3.2.4. Bromide and Iodide

The spectrophotometric determination of trace bromide concentration is based on the bromide catalysis of iodine oxidation to iodate by permanganate in acidic solution. Iodide can also be measured spectrophotometrically by selective oxidation to iodine by potassium peroxymonosulfate ($KHSO_5$). The iodine reacts with colorless leucocrystal violet to produce the highly colored leucocrystal violet dye. Greater than 200 mg/L of chloride interferes with the color development. Trace concentrations of iodide are determined by its ability to catalyze ceric ion reduction by arsenous acid. The reduction reaction is stopped at a specific time by the addition of ferrous ammonium sulfate. The ferrous ion is oxidized to ferric ion, which then reacts with thiocyanate to produce a deep red complex.

Both of these halides can also be determined potentiometrically with an appropriate ion-selective electrode. Sulfide and cyanide both interfere with the electrode response.

3.3. Gases

3.3.1. Hydrogen Sulfide

Sulfide ion from 10^{-7} to 1 M can be measured potentiometrically with an ion-selective electrode. Mercuric ion interferes at concentrations $>10^{-7}$ M . The concentration of hydrogen sulfide can be calculated knowing the sample pH and the pK_a for H_2S.

3.3.2. Ammonia

The most reliable results for ammonia are obtained from fresh samples. Storage of acidified samples at 4°C is the best way to minimize losses if prompt analysis is impossible. The sample acidity is neutralized prior to analysis. Ammonia concentrations of $10^{-6} - 0.5$ M can be determined potentiometrically with the gas-sensing, ion-selective electrode. Volatile amines are the only known interferents.

The most common colorimetric technique involves a reaction between ammonia and a reagent containing mercuric iodide in potassium iodide (Nessler reagent) to form a reddish-brown complex. Turbidity, color, and hardness are possible interferences that can be removed by preliminary distillation at pH 9.5.

4. Organic Materials

4.1. Nonspecific Organics

4.1.1. Biochemical Oxygen Demand

The biochemical oxygen demand (BOD) test is an empirical determination of the oxygen requirement of a sample. It is most often applied to wastewaters, industrial effluents, and polluted waters. The decrease in the dissolved oxygen concentration resulting primarily from biological action is measured after storage for 5 d at 20°C.

If the sample has very low initial dissolved oxygen, it must be aerated; if it has a very high BOD, it may be necessary to dilute the sample. The dilution water is a phosphate buffer containing magnesium sulfate, calcium chloride, and ferric chloride. The percentage dilution must usually be determined by trial and error, although rough estimates may be made depending on sample type (20).

The dissolved oxygen concentrations are determined immediately and after five days. The method for dissolved measurement involves either a modified Winkler titration or a membrane-covered oxygen electrode. The difference between initial and final dissolved oxygen multiplied by the dilution factor is the BOD value.

4.1.2. Chemical Oxygen Demand

The chemical oxygen demand (COD) test measures the oxygen equivalent of the organic matter in a sample that is susceptible to oxidation by a strong oxidant (20). The sample is refluxed with a known amount of potassium dichromate in sulfuric acid for 2 hs. Silver sulfate is added to catalyze the oxidation of straight-chain compounds, and mercuric sulfate is added to the sample prior to refluxing to react with chloride ion and prevent its oxidation. The amount of unreacted dichromate is then titrated with standard ferrous ammonium sulfate.

4.1.3. Organic Carbon

The total organic carbon (TOC) in a water sample is determined by injecting a microliter sample into a heated, packed tube in a stream of oxygen. The water is vaporized and carbon is converted to carbon dioxide, which is detected with a nondispersive infrared analyzer. Nitrogen is bubbled through the acidified sample prior to injection to remove inorganic carbon and other volatiles.

4.1.4. Detergents

The most widely used surfactant in synthetic detergents is the readily biodegradable linear alkyl sulfonate (LAS). Since the detergent industry began using this ingredient, the occurrence of foaming incidents has all but disappeared (see Surfactants). The methylene-blue method is used to measure LAS in addition to alkyl sulfates and alkyl poly(ethoxyl sulfate)s. The blue salt that forms is extracted with chloroform and measured colorimetrically. There are many organic and inorganic interferences associated with this method and, since a large number of surfactants react with methylene blue, the test is designated as one for methylene-blue-active substances. If this test shows a significant amount of surfactant, confirmation of the LAS should be made by other methods, eg, thin-layer chromatography followed by infrared spectroscopy (35).

4.1.5. Oil and Grease

Industrial processes contribute most of the grease and oil found in water. Oil and grease can cause problems in wastewater-treatment processes as well as prevent the use of the sludge as fertilizer. The amount of oil and grease can be determined by extraction of an acidified sample with an organic solvent followed by evaporation of the solvent and weighing the residue. During the last part of the solvent evaporation, the sample must not be overheated to prevent the loss of low boiling oils.

4.2. Specific Organics

Large quantities of specific organic materials are used annually in industrial and agricultural applications, and these compounds or their degradation products are present in surface and groundwaters. The volume of publications dealing with analytical methodology for specific organics is enormous. The development of glass capillary columns has improved the application of gas–liquid chromatographic (glc) separations. In addition, the application of the mass spectrometer (ms) as a detector for gas–liquid chromatography has made the positive identification of peaks possible. High performance liquid chromatography (hplc), which involves various detectors, can be used to measure hydrophilic and hydrophobic organic compounds in water.

Various methods for the glc monitoring of EPA Consent Decree Priority Pollutants in water have been described (36) (see Regulatory agencies). The determination of organic pollutants in water by glc and ms methods has also been detailed (37, 38). Nonvolatile organic compounds in drinking water have been determined by hplc (39) (see Water, pollution).

4.2.1. Pesticides

Chlorinated hydrocarbon insecticides are determined with an electron-capture detector following extraction with an organic solvent (20). If polychlorinated biphenyls (PCBs) are known to be present or if the extract contains so many pesticides that separation by glc is difficult, the extract should be passed through a Florisil column. Elution of the column with different solvents allows certain group separations of the pesticides. The following organochlorinated pesticides and PCBs have been determined by the method: lindane, heptachlor, heptachlor epoxide, aldrin, dieldrin, *p,p′*-1,1-dichloro-2,2-bis(*p*-chlorophenyl)ethane (*p,p′*-TDE), *p,p′*1,1,1-trichloro-2,2-bis(*p*-chlorophenyl)ethane (*o,p′*-DDT), *o,p′*-DDT, *p,p′*-1,1-dichloro-2,2-bis(*p*-chlorophenyl)ethylene (*p,p′*-DDE), endrin, *p,p′*-methoxychlor, α-endosulfan, β-endosulfan, *cis*-chlordane, *trans*-chlordane, Aroclor 1248, Aroclor 1254, and Aroclor 1260. Quantitation is by comparison of chromatograms with standard concentrations of pure compounds treated in an identical manner. The phenoxy acid herbicides (2,4-dichlorophenoxy)acetic acid (2,4-D), silvex, and (2,4,5-trichlorophenoxy)acetic acid (2,4,5-T) can be determined by electron-capture detection after extraction and conversion to the methyl esters with BF_3-methanol. The water sample must be acidified to pH $\leq$2 prior to extraction with chloroform.

Identification of the pesticides is based on retention time on at least two dissimilar glc columns. A nonpolar and a relatively polar packing are generally used, for example, OV-17 and a mixture of QF-1 and DC-200.

Organophosphorus pesticides are determined with a flame photometric detector, which is sensitive only to compounds containing phosphorus or sulfur (20). The water sample is extracted with benzene, and the solvent is concentrated to a small volume prior to glc analysis. The following organophosphates are determined by this method: ethyl guthion, guthion, trithion, ruelene, diazinon, di-syston, ethion, imidan, malathion, methyl parathion, methyl trithion, parathion, thimet, and trolene (see Insect control technology).

High performance liquid chromatography with electrochemical detection has been used to determine 2–7 ppb of carbamate pesticides in water (40). The investigated pesticides were aminocarb, asulam, *sec*-butyl phenylmethylcarbamate (BPMC), carbaryl, carbendazim, chlorpropham, desmedipham, and phenmedipham.

4.2.2. Trihalomethanes

Wherever chlorine is used as a disinfectant in drinking-water treatment, trihalomethanes (THMs) generally are present in the finished water. The THMs usually formed are trichloromethane (chloroform), bromodichloromethane, dibromochloromethane, and tribromomethane (bromoform). There are four main techniques for the analysis of THMs: headspace, liquid– liquid extraction (lle), adsorption–elution (purge–trap), and direct aqueous injection. The final step in each technique involves separation by gas–liquid chromatography with a 2 mm ID coiled glass column containing 10 wt % squalene on chromosorb-W-AW (149–177 μm (80–100 mesh)) with detection generally by electron capture.

The purge–trap method is the most widely accepted method for THMs as well as for other purgeable organohalides (41). The purgeable organics are stripped from the water sample with a stream of inert gas and are adsorbed in a porous polymer trap. The compounds are thermally desorbed from the trap into a gas chromatograph. All of the lle methods involve extraction of a small volume of water with a much smaller volume organic solvent (42). An aliquot of the extract is then gas-chromatographed. Different lle techniques have been evaluated to be as sensitive and accurate as the purge–trap methods (42, 43).

5. Radioactive Materials

Radioactivity in environmental waters can originate from both natural and artificial sources. The natural or background radioactivity usually amounts to $\leq$100 mBq/L. The development of the nuclear power industry as well as other industrial and medical uses of radioisotopes (qv) necessitates the determination of gross alpha and beta activity of some water samples. These measurements are relatively inexpensive and are useful for

screening samples. The gross alpha or beta activity of an acidified sample is determined after an appropriate volume is evaporated to near dryness, transferred to a flat sample-mounting dish, and evaporated to dryness in an oven at 103–105°C. The amount of original sample taken depends on the amount of residue needed to provide measurable alpha or beta activity.

Alpha counting is done with an internal proportional counter or a scintillation counter. Beta counting is carried out with an internal or external proportional gas-flow chamber or an end-window Geiger-Mueller tube. The operating principles and descriptions of various counting instruments are available, as are techniques for determining various radioelements in aqueous solution (20, 44). A laboratory manual of radiochemical procedures has been compiled for analysis of specific radionuclides in drinking water (45). Detector efficiency should be determined with commercially available sources of known activity.

6. Bacteria

A bacteriological examination of water is primarily carried out to determine the possible presence of harmful microorganisms. Testing is actually done to detect relatively harmless bacteria called *colon bacilli*, commonly called the coliform group, which are present in the intestinal tract of humans and animals. If these organisms are present in a water in sufficient number, then this is taken to be evidence that other harmful pathogenic bacteria may also be present.

One standard test used to determine the presence of the coliform group is called the multiple-tube fermentation technique (sometimes called the presumptive test). If this test indicates the presence of these bacteria, then a confirmed test must be done. If only negative colonies or no colonies develop during this test, it is considered negative; otherwise, a completed test must be undertaken. Positive results obtained in the completed test are evidence for the presence of coliform bacteria. Testing methods have been given by the APHA, and the detailed procedures contained therein should be consulted (20).

Another standard test, which is much simpler and more convenient, is the membrane filter technique. A suitable volume of sample is filtered through a sterile, 0.45-μm membrane filter. The filter is placed in a petri dish containing a specific growth medium (M-Endo nutrient broth, M-Endo medium) and incubated for 24 h at 35°C. If after this time the colonies show the characteristic green sheen, this is taken as positive evidence for the presence of the coliform group (see Water, sewage).

6.1. Fecal Coliforms

Fecal coliforms are those originating from the intestines of warm-blooded animals. Fecal coliforms can be determined by a multiple-tube procedure, which must be applied to a positive presumptive test for optimum recovery of fecal coliforms (20). Incubation must be at 44.5 ± 0.2°C for 24 ± 2 h. Gas production during incubation is positive evidence of fecal coliform pollution.

A membrane filter technique can also be used to determine the presence of fecal coliforms, and this procedure is said to be 93% accurate (20). A sample is passed through a membrane filter, and this filter is placed in a petri dish containing an enriched lactose medium. The dishes are incubated at 44.5 ± 0.2°C for 24 h. Following the incubation period, the fecal coliform colonies appear blue.

Both multiple-tube and membrane-filter methods are also available for testing for the fecal streptococcal group (20). These assays can be used to provide supplementary data regarding the bacteriological quality of water. Other fecal indicators should also be used concurrently because of the survival characteristics of the fecal streptococci.

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