Chapter 5

Measurement of Water Quality

Quantitative measurements of pollutants are obviously necessary before water pollution can be controlled. Measurement of these pollutants is, however, fraught with difficulties. Sometimes specific materials responsible for the pollution are not known. Moreover, these pollutants are generally present at low concentrations, and very accurate methods of detection are required.

Only a few of the analytical tests available to measure water pollution are discussed in this chapter. A complete volume of analytical techniques used in water and wastewater engineering is compiled as *Standard Methods for the Examination of Water and Wastewater* (Clesceri *et al.* 1998). This volume is updated every few years so that it can incorporate current information on standardized testing techniques. It is considered definitive in its field and has the weight of legal authority.

Many water pollutants are measured in terms of milligrams of the substance per liter of water (mg/L). In older publications pollutant concentrations were often expressed as parts per million (ppm), a weight/weight parameter. If the only liquid involved is water, ppm is identical with mg/L, since one liter (L) of water weighs 1000 grams (g). For many aquatic pollutants, ppm is approximately equal to mg/L; however, because of the possibility that some wastes have specific gravity different from water, mg/L is preferred to ppm.

SAMPLING

Some tests require the measurement to be conducted at the site because the process of obtaining a sample may change the measurement. For example, to measure the dissolved oxygen in a stream or lake, either the measurement should be conducted at the site or the sample must be extracted with great care to ensure that there has been no loss or addition of oxygen as the sample is exposed to the air. Similarly, it is better to measure pH at the site if you are sampling water that is poorly buffered from pH changes (see discussion on alkalinity).

Most tests may be performed on a water sample taken from the stream. The process by which the sample is obtained, however, may greatly influence the result. The three basic types of samples are grab samples, composite samples, and flow-weighted composite samples.

The grab sample, as the name implies, measures water quality at only one sampling point. Grab samples accurately represent the water quality at the moment of sampling, but say nothing about the quality before or after the sampling. A composite sample is obtained by taking a series of grab samples and mixing them together. The flow-weighted composite is obtained by taking each sample so that the volume of the sample is proportional to the flow at that time. The last method is especially useful when daily loadings to wastewater treatment plants are calculated. Whatever the technique or method, however, the analysis can only be as accurate as the sample, and often the sampling methods are far more sloppy than the analytical determination.

DISSOLVED OXYGEN

One of the most important measures of water quality is dissolved oxygen. Oxygen, although poorly soluble in water, is fundamental to aquatic life. Without free dissolved oxygen, streams and lakes become uninhabitable to aerobic organisms, including fish and most invertebrates. Dissolved oxygen is inversely proportional to temperature, and the maximum amount of oxygen that can be dissolved in water at 0°C is 14.6 mg/L. The saturation value decreases rapidly with increasing water temperature, as shown in Table 5-1. The balance between saturation and depletion is therefore tenuous.

The amount of oxygen dissolved in water is usually measured either with an oxygen probe or by iodometric titration. The latter method, known as the *Winkler* test,

Table 5-1. Solubility of Oxygen in Water

Water temperature (°C)	Saturation concentration of oxygen in water (mg/L)
0	14.6
2	13.8
4	13.1
6	12.5
8	11.9
10	11.3
12	10.8
14	10.4
16	10.0
18	9.5
20	9.2
22	8.8
24	8.5
26	8.2
28	8.0
30	7.6

was developed about 100 years ago and is the standard against which all other measurements are compared. The chemical reactions of the Winkler test are as follows:

Manganous sulfate ($MnSO_4$) and a mixture of potassium hydroxide and potassium iodide (KOH and KI) are added to a water sample. If there is no oxygen present, the $MnSO_4$ will react with the KOH to form a white precipitate, manganous hydroxide ($Mn(OH)_2$). If oxygen is present, the $Mn(OH)_2$ will react further to form a brown precipitate, manganic oxide ($MnO(OH)_2$):

$$MnSO_4 + 2KOH \rightarrow Mn(OH)_2 + K_2SO_4 \tag{5.1}$$

$$2Mn(OH)_2 + O_2 \rightarrow 2MnO(OH)_2. \tag{5.2}$$

Sulfuric acid is added, which dissolves the manganic oxide and, in conjunction with the KI added earlier, forms iodine (I_2), which imparts a yellowish orange color to the sample:

$$2MnO(OH)_2 + 4H_2SO_4 \rightarrow 2Mn(SO_4)_2 + 6H_2O \tag{5.3}$$

$$2Mn(SO_4)_2 + 4KI \rightarrow 2MnSO_4 + 2K_2SO_4 + 2I_2. \tag{5.4}$$

The quantity of iodine is measured by titrating with sodium thiosulfate ($Na_2S_2O_3$) until the orange color from I_2 is no longer apparent:

$$4Na_2S_2O_3 + 2I_2 \rightarrow 2Na_2S_4O_6 + 4NaI. \tag{5.5}$$

Starch is added near the end of the titration because it turns deep purple in the presence of I_2, and gives a more obvious color endpoint for the test.

The quantity of $MnO(OH)_2$ formed in the first step is directly proportional to the available dissolved oxygen, and the amount of iodine formed in the second step is directly proportional to the $MnO(OH)_4$. Therefore, the titration measures a quantity of iodine directly related to the original dissolved oxygen concentration. Disadvantages of the Winkler test include chemical interferences and the inconvenience of performing a wet chemical test in the field. These two disadvantages can be overcome by using a dissolved oxygen electrode, or probe.

The simplest (and historically the first) type of oxygen probe is shown in Fig. 5-1. The principle of operation is that of a galvanic cell. If lead and silver electrodes are put in an electrolyte solution with a microammeter between, the reaction at the lead electrode is

$$Pb + 2OH^- \rightarrow PbO + H_2O + 2e^-. \tag{5.6}$$

At the lead electrode, electrons are liberated and travel through the microammeter to the silver electrode where the following reaction takes place:

$$2e^- + \tfrac{1}{2}O_2 + H_2O \rightarrow 2OH^-. \tag{5.7}$$

The reaction does not occur, and the microammeter does not register any current, unless free dissolved oxygen is available. The meter must be constructed and calibrated so that

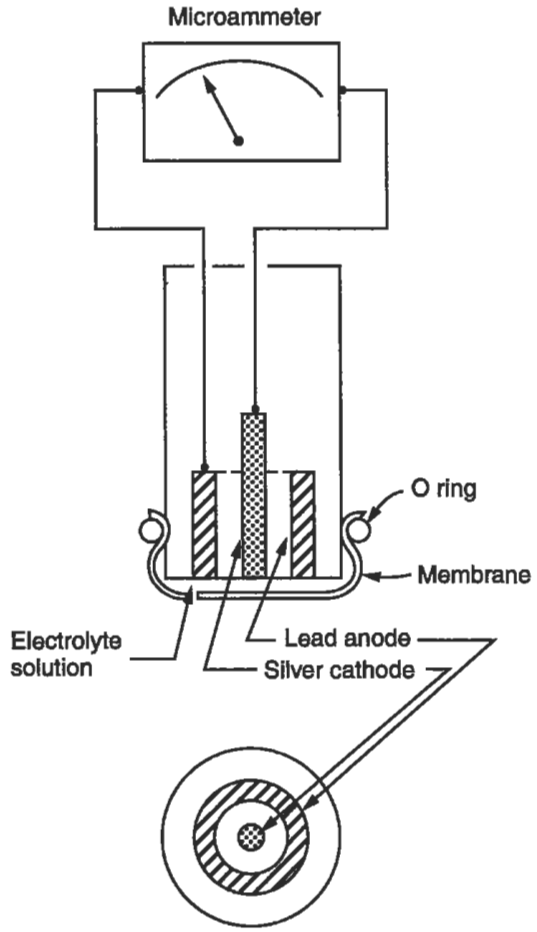

Figure 5-1. Schematic diagram of a galvanic cell oxygen probe.

the electricity recorded is proportional to the concentration of oxygen in the electrolyte solution.

In the commercial models, the electrodes are insulated from each other with nonconducting plastic and are covered with a permeable membrane with a few drops of electrolyte between the membrane and electrodes. The amount of oxygen that travels through the membrane is proportional to the dissolved oxygen concentration. Dissolved oxygen probes are convenient for fieldwork, but need careful maintenance and calibration (usually against Winkler results). Most oxygen probes are sensitive to changes in temperature and have thermisters attached to the probe so that temperature adjustments can be made in the field.

BIOCHEMICAL OXYGEN DEMAND

The rate of oxygen use is commonly referred to as biochemical oxygen demand (BOD). Biochemical oxygen demand is not a specific pollutant, but rather a measure of the

amount of oxygen required by bacteria and other microorganisms engaged in stabilizing decomposable organic matter over a specified period of time.

The BOD test is often used to estimate the impacts of effluents that contain large amounts of biodegradable organics such as that from food processing plants and feedlots, municipal wastewater treatment facilities, and pulp mills. A high oxygen demand indicates the potential for developing a dissolved oxygen sag (see previous chapter) as the microbiota oxidize the organic matter in the effluent. A very low oxygen demand indicates either clean water or the presence of a toxic or nondegradable pollutant.

The BOD test was first used in the late 1800s by the Royal Commission on Sewage Disposal as a measure of the amount of organic pollution in British rivers. At that time, the test was standardized to run for 5 days at 18.3°C. These numbers were chosen because none of the British rivers had headwater-to-sea travel times greater than 5 days, and the average summer temperature for the rivers was 18.3°C. Accordingly, this should reveal the "worst case" oxygen demand in any British river. The BOD incubation temperature was later rounded to 20°C, but the 5-day test period remains the current, if somewhat arbitrary, standard.

In its simplest version, the 5-day BOD test (BOD_5) begins by placing water or effluent samples into two standard 60- or 300-mL BOD bottles (Fig. 5-2). One sample is analyzed immediately to measure the initial dissolved oxygen concentration in the effluent, often using a Winkler titration. The second BOD bottle is sealed and stored at 20°C in the dark. (The samples are stored in the dark to avoid photosynthetic oxygen generation.) After 5 days the amount of dissolved oxygen remaining in the sample is measured. The difference between the initial and ending oxygen concentrations is the BOD_5.

The oxidation of organic matter follows an exponential decay curve, as in Fig. 4-6. If the dissolved oxygen concentrations were measured daily, the results would produce curves like those shown in Fig. 5-3. In this example, sample A had an initial dissolved oxygen concentration of 8 mg/L, which dropped to 2 mg/L in 5 days. The BOD therefore is $8 - 2 = 6$ mg/L.

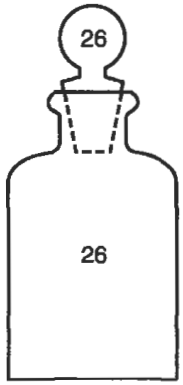

Figure 5-2. A biochemical oxygen demand (BOD) bottle.

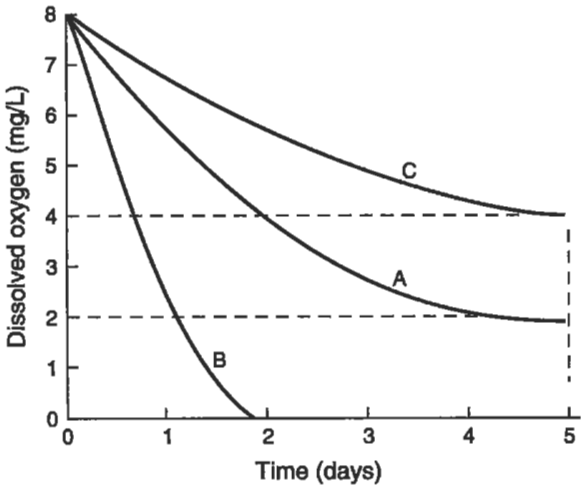

Figure 5-3. Typical oxygen uptake curves in a BOD test.

Sample B also had an initial dissolved oxygen concentration of 8 mg/L, but the oxygen was used so fast that it dropped to 0 by the second day. Since there is no measurable dissolved oxygen left after 5 days, the BOD of sample B must be more than $8 - 0 = 8$ mg/L, but we do not know how much more because the organisms in the sample might have used more dissolved oxygen if it had been available. Samples like this require diluting the sample. Typically, five $\frac{1}{10}$ dilutions are recommended for wastewaters of unknown origin. Suppose sample C in Fig. 5-3 is sample B diluted by $\frac{1}{10}$. The BOD_5 for sample B would be

$$\frac{8-4}{0.1} = 40 \text{ mg/L}.$$

It is possible to measure the BOD of any organic material (e.g., sugar) and thus estimate its influence on a stream, even though the material in its original state might not contain the microorganisms necessary to break down organic matter. *Seeding* is a process in which the microorganisms that oxidize organic matter are added to the BOD bottle. Seeding also facilitates measurement of very low BOD concentrations. The seed source can be obtained from unchlorinated domestic wastewater or surface water that receives degradable wastewater effluents.

Suppose we use the water previously described in curve A as seed water since it obviously contains microorganisms (it has a 5-day BOD of 6 mg/L). We now put 100 mL of an unknown solution into a bottle and add 200 mL of seed water, thus filling the 300-mL bottle. Assuming that the initial dissolved oxygen of this mixture is 8 mg/L and the final dissolved oxygen is 1 mg/L, the total oxygen consumed is 7 mg/L. Some of this is due to the seed water, because it also has a BOD, and only a portion is due to the decomposition of the unknown material. The oxygen consumed due to the seed water is

$$6 \times \frac{2}{3} = 4 \text{ mg/L},$$

because only two-thirds of the bottle is seed water, and only the seed water has a BOD of 6 mg/L. The remaining oxygen consumed ($7 - 4 = 3$ mg/L) must be due to the unknown material. Equation (5.8) shows how to calculate the BOD_5 for a diluted, seeded effluent sample,

$$\text{BOD (mg/L)} = \frac{(I - F) - (I' - F')(X/Y)}{D}, \tag{5.8}$$

where

I = initial dissolved oxygen in the bottle containing both effluent sample and seeded dilution water,
F = final dissolved oxygen in the bottle containing the effluent and seeded dilution water,
I' = initial dissolved oxygen of the seeded dilution water,
F' = final dissolved oxygen of the seeded dilution water,
X = mL of seeded dilution water in sample bottle,
Y = total mL in the bottle, and
D = dilution of the sample.

EXAMPLE 5.1. Calculate the BOD_5 of a water sample, given the following data:

—Temperature of sample = 20°C,
—Initial dissolved oxygen is saturation,
—Dilution is 1:30, with seeded dilution water,
—Final dissolved oxygen of seeded dilution water is 8 mg/L,
—Final dissolved oxygen bottle with sample and seeded dilution water is 2 mg/L, and
—Volume of BOD bottle is 300 mL.

From Table 5-1, dissolved oxygen saturation at 20°C is 9.2 mg/L; hence, this is the initial dissolved oxygen. Since the BOD bottle contains 300 mL, a 1:30 dilution with seeded water would contain 10 mL of sample and 290 mL of seeded dilution water, and, by Eq. (5.8)

$$\text{BOD}_5\text{ (mg/L)} = \frac{(9.2 - 2) - (9.2 - 8)(290/300)}{0.033} = 183\text{ mg/L}$$

BOD is a measure of oxygen use, or potential oxygen use. An effluent with a high BOD may be harmful to a stream if the oxygen consumption is great enough to cause anaerobic conditions. Obviously, a small trickle going into a great river will have negligible effect, regardless of the BOD concentration involved. Conversely, a large flow into a small stream may seriously affect the stream even though the

BOD concentration might be low. Engineers often talk of "pounds of BOD," a value calculated by multiplying the concentration by the flow rate, with a conversion factor, so that

$$\text{lb BOD/day} = [\text{mg/L BOD}] \times \begin{bmatrix}\text{flow in million}\\ \text{gallons per day}\end{bmatrix} \times 8.34. \tag{5.9}$$

The BOD of most domestic sewage is about 250 mg/L, while many industrial wastes run as high as 30,000 mg/L. The potential detrimental effect of untreated dairy waste that might have a BOD of 20,000 mg/L is quite obvious.

As discussed in Chapter 4, the BOD curve can be modeled using Eq. (4.8):

$$\text{BOD}(t) = L_0\left(1 - e^{-k_1' t}\right),$$

where

$\text{BOD}(t)$ = amount of oxygen required by the microorganisms at any time t (mg/L),
L_0 = ultimate carbonaceous oxygen demand (mg/L),
k_1' = deoxygenation rate constant (days^{-1}), and
t = time (days).

When it is necessary to know both k_1' and L_0, as when modeling the dissolved oxygen profile in a stream, both are measured using laboratory BOD tests.

There are a number of techniques for calculating k_1' and L_0. One of the simplest is a method devised by Thomas (1950). Rewriting Eq. (4.8) using common logarithms results in

$$\text{BOD}(t) = L_0\left(1 - 10^{-k_1' t}\right),$$

which can be rearranged to read

$$\left(\frac{t}{\text{BOD}(t)}\right)^{1/3} = \left(2.3\,k_1' L_0\right)^{-1/3} + \left(\frac{{k_1'}^{2/3}}{3.43 L_0^{1/3}}\right) t. \tag{5.10}$$

This equation is in the form of a straight line

$$x = a + bt,$$

where x is $(t/\text{BOD}(t))^{1/3}$, the intercept (a) is $(2.3k_1'L_0)^{-1/3}$, and the slope (b) is ${k_1'}^{2/3}/(3.43L_0^{1/3})$.

By plotting BOD versus t, the slope (b) and intercept (a) can be used to solve for k_1' and L_0:

$$k_1' = 2.61\,(b/a)$$
$$L_0 = 1/(2.3k_1'a^3).$$

EXAMPLE 5.2. The BOD versus time data for the first 5 days of a BOD test are obtained as follows:

Time (days)	BOD (mg/L)
2	10
4	16
6	20

Calculate k_1' and L_0.

The $(t/\text{BOD}(t))^{1/3}$ values 0.585, 0.630, and 0.669 are plotted as shown in Fig. 5-4. The intercept $(a) = 0.545$ and the slope $(b) = 0.021$. Thus:

$$k_1' = 2.61\left(\frac{0.021}{0.545}\right) = 0.10 \text{ day}^{-1}$$

$$L_0 = \frac{1}{2.3(0.10)(1.545)^3} = 26.8 \text{ mg/L}.$$

If, instead of stopping the BOD test after 5 days, we allowed the test to continue and measured the dissolved oxygen each day, we might get a curve like that shown in Fig. 5-5. Note that after about 5 days the curve turns sharply upward. This discontinuity is due to the demand for oxygen by the microorganisms that decompose nitrogenous organic compounds to inorganic nitrogen. In the following example, microorganisms decompose a simple organic nitrogen compound, urea ($NH_2 \cdot CO \cdot NH_2$), releasing

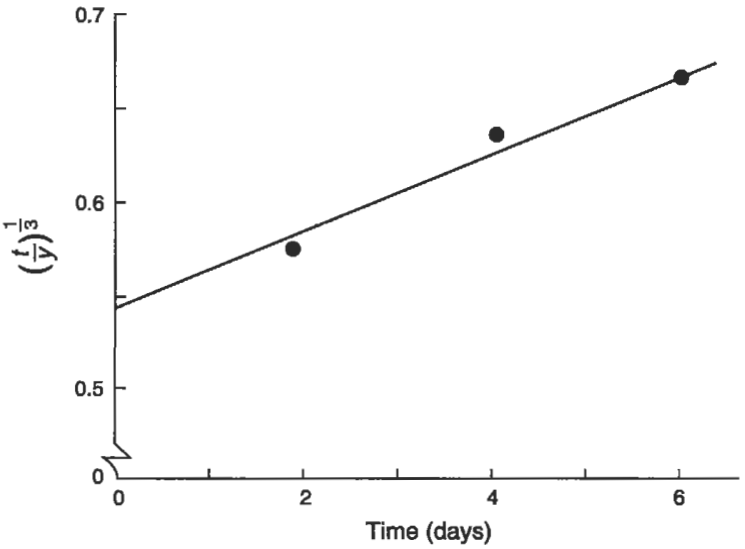

Figure 5-4. Plot of k_1' and L_0, for Example 5.2.

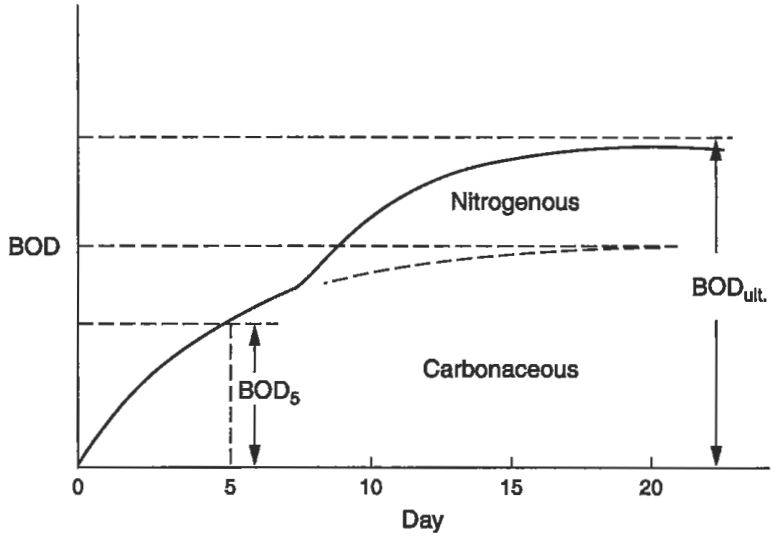

Figure 5-5. Long-term BOD. Note that BOD_{ult} here includes both ultimate carbonaceous BOD (L_0) and ultimate nitrogenous BOD.

ammonia (NH_3; NH_4^+ in ionized form), which is further decomposed into nitrite (NO_2^-) and nitrate (NO_3^-):

$$NH_2 \cdot CO \cdot NH_2 + H_2O \rightarrow 2NH_3 + CO_2 \qquad \text{ammonification} \qquad (5.11)$$

$$NH_4^+ + 1\tfrac{1}{2}O_2 \rightarrow NO_2^- + 2H^+ + H_2O \qquad \text{nitrification, step 1} \qquad (5.12)$$

$$NO_2^- + \tfrac{1}{2}O_2 \rightarrow NO_3^-. \qquad \text{nitrification, step 2} \qquad (5.13)$$

Note that the first step, ammonification, does not require oxygen; it can be done by a wide variety of aerobic and anaerobic plants, animals, and microbes.

The BOD curve is thus divided into nitrogenous and carbonaceous BOD areas. The ultimate BOD, as shown in Fig. 5-5, includes both nitrogenous and carbonaceous BOD. For streams and rivers with travel times greater than about 5 days, the ultimate demand for oxygen must include the nitrogenous demand.

Although the use of BOD_{ult} (carbonaceous plus nitrogenous) in dissolved oxygen sag calculations is not strictly accurate, the ultimate BOD may be estimated as

$$BOD_{ult} = a(BOD_5) + b(TKN), \qquad (5.14)$$

where TKN is the total Kjeldahl nitrogen (organic nitrogen plus ammonia, in mg/L), and a and b are constants.

The state of North Carolina, for example, has used $a = 1.2$ and $b = 4.0$ for calculating the ultimate BOD, which was then substituted for the ultimate carbonaceous BOD (L_0) in the dissolved oxygen sag equation.

CHEMICAL OXYGEN DEMAND

One problem with the BOD test is that it takes 5 days to run. If the organic compounds were oxidized chemically instead of biologically, the test could be shortened considerably. Such oxidation can be accomplished with the chemical oxygen demand (COD) test. Because nearly all organic compounds are oxidized in the COD test, while only some are decomposed during the BOD test, COD results are always higher than BOD results. One example of this is wood pulping waste, in which compounds such as cellulose are easily oxidized chemically (high COD) but are very slow to decompose biologically (low BOD).

The standard COD test uses a mixture of potassium dichromate and sulfuric acid to oxidize the organic matter (HCOH), with silver (Ag^+) added as a catalyst. A simplified example of this reaction is illustrated below, using dichromate ($Cr_2O_7^{2-}$) and hydrogen ions (H^+):

$$2Cr_2O_7^{2-} + 3HCOH + 16H^+ \xrightarrow{\text{heat} + Ag^+} 3CO_2 + 11H_2O + 4Cr^{3+}. \qquad (5.15)$$

A known amount of a solution of $K_2Cr_2O_7$ in moderately concentrated sulfuric acid is added to a measured amount of sample, and the mixture is boiled in air. In this reaction, the oxidizing agent, hexavalent chromium (Cr^{VI}), is reduced to trivalent chromium (Cr^{III}). After boiling, the remaining Cr^{VI} is titrated against a reducing agent, usually ferrous ammonium sulfate. The difference between the initial amount of Cr^{VI} added to the sample and the Cr^{VI} remaining after the organic matter has been oxidized is proportional to the chemical oxygen demand.

TOTAL ORGANIC CARBON

Since the ultimate oxidation of organic carbon is to CO_2, the total combustion of a sample yields some information about the potential oxygen demand in an effluent sample. A far more common application of total organic carbon testing is to assess the potential for creating *disinfection by-products*. Disinfection by-products are the result of halogens (e.g., bromine, chlorine) or ozone interacting with naturally occurring organic carbon compounds during the drinking water disinfection process. For example, trihalomethane, a carcinogen, is created when halogens displace three hydrogen ions on methane. Water that is high in total organic carbon has a greater potential to develop disinfection by-products. Some of the organics can be removed by adding levels of treatment specific for organic carbon absorption; however, it is usually not economically feasible to remove all naturally occurring organics from finished drinking water.

Total organic carbon is measured by oxidizing the organic carbon to CO_2 and H_2O and measuring the CO_2 gas using an infrared carbon analyzer. The oxidation is done by direct injection of the sample into a high-temperature (680–950°C) combustion chamber or by placing a sample into a vial containing an oxidizing agent such as potassium persulfate, sealing and heating the sample to complete the oxidation, then measuring the CO_2 using the carbon analyzer.

TURBIDITY

Water that is not clear but is "dirty," in the sense that light transmission is inhibited, is known as turbid water. Many materials can cause turbidity, including clays and other tiny inorganic particles, algae, and organic matter. In the drinking water treatment process, turbidity is of great importance, partly because turbid water is aesthetically displeasing, and also because the presence of tiny colloidal particles makes it more difficult to remove or inactivate pathogenic organisms.

Turbidity is measured using a turbidimeter. Turbidimeters are photometers that measure the intensity of scattered light. Opaque particles scatter light, so scattered light measured at right angles to a beam of incident light is proportional to the turbidity. Formazin polymer is currently used as the primary standard for calibrating turbidimeters, and the results are reported as nephelometric turbidity units (NTU).

COLOR, TASTE, AND ODOR

Color, taste, and odor are important measurements for determining drinking water quality. Along with turbidity, color, taste, and odor are important from the standpoint of aesthetics. If water looks colored, smells bad, or tastes swampy, people will instinctively avoid using it, even though it might be perfectly safe from the public health aspect. Color, taste, and odor problems in drinking water are often caused by organic substances such as algae or humic compounds, or by dissolved compounds such as iron.

Color can be measured visually by comparison with potassium chloroplatinate standards or by scanning at different spectrophotometric wavelengths. Turbidity interferes with color determinations, so the samples are filtered or centrifuged to remove suspended material. Odor is measured by successive dilutions of the sample with odor-free water until the odor is no longer detectable. (Odor-free water is prepared by passing distilled, deionized water through an activated charcoal filter.) This test is obviously subjective and depends entirely on the olfactory senses of the tester. Panels of testers are used to compensate for variations in individual perceptions of odor.

Taste is evaluated using three methods: the flavor threshold test (FTT), the flavor rating assessment (FRA), and the flavor profile analysis (FPA). For the FTT, water samples are diluted with increasing amounts of reference water until a panel of taste testers concludes that there is no perceptible flavor. In the FRA, a panel of testers is asked to rate the flavor from very favorable to very unfavorable. The oldest, and most useful, of the taste tests is the FPA, which measures both taste and odor of a water sample in comparison to taste and odor reference standards. The intensity of specific tastes and odors are described on a 12-point, ranging from no taste or odor (0) to taste or odor (12).

pH

The pH of a solution is a measure of hydrogen (H^+) ion concentration, which is, in turn, a measure of acidity. Pure water dissociates slightly into equal concentrations of

hydrogen and hydroxyl (OH^-) ions:

$$H_2O \leftrightarrow H^+ + OH^-. \tag{5.16}$$

An excess of hydrogen ions makes a solution acidic, whereas a dearth of H^+ ions, or excess of hydroxyl ions, makes it basic. The equilibrium constant for this reaction, K_w, is the product of H^+ and OH^- concentrations and is equal to 10^{-14}. This relationship may be expressed as

$$[H^+][OH^-] = K_w = 10^{-14}, \tag{5.17}$$

where $[H^+]$ and $[OH^-]$ are the concentrations of hydrogen and hydroxyl ions, respectively, in moles per liter. Considering Eq. (5.16) and solving Eq. (5.17), in pure water, $[H^+]$ and $[OH^-]$ are in equal concentrations:

$$[H^+] = [OH^-] = 10^{-7} \text{ moles/L}.$$

The hydrogen ion concentration is so important in aqueous solutions that an easier method of expressing it has been devised. Instead of speaking in terms of moles per liter, we define a quantity pH as the negative logarithm of $[H^+]$ so that

$$pH = -\log_{10}[H^+] = \log_{10}\frac{1}{[H^+]} \tag{5.18}$$

or

$$[H^+] = 10^{-pH}. \tag{5.19}$$

In a neutral solution the H^+ concentration is 10^{-7}, so the pH is 7. As the H^+ concentration increases the pH decreases. For example, if the H^+ concentration is 10^{-4}, the pH is 4, and the solution is acidic. In this solution, we see that the OH^- concentration is $10^{-14}/10^{-4}$, or 10^{-10}. Since 10^{-4} is much greater than 10^{-10}, the solution contains a large excess of H^+ ions, confirming that it is indeed acidic. Any solution where the H^+ concentration is less than 10^{-7}, or the pH is greater than 7, would be basic. The pH range in dilute samples is from 0 (very acidic) to 14 (very alkaline), and in water samples is rarely below 4 or above 10.

The measurement of pH is now almost universally done using electronic pH meters. A typical pH meter consists of a potentiometer, a glass electrode and a reference electrode (or a single, "combination" electrode), and a temperature-compensating device. The glass electrode is sensitive to H^+ activity and converts the signal to electric current, which can be read as electrode potential (mV) or pH.

The pH of an effluent or water sample is important in almost all phases of drinking water and wastewater treatment. In water treatment as well as in disinfection and corrosion control, pH is important in ensuring proper chemical treatment. Aquatic organisms are sensitive to pH changes, as well as to the actual pH of the water. Few aquatic organisms tolerate waters with a pH less than 4 or greater than 10. Acid mine drainage, unregulated acids or bases in industrial effluents, or atmospheric acid deposition may alter the pH of a water body substantially and have detrimental effects on aquatic life.

ALKALINITY

Alkalinity measures the buffering capacity of the water against changes in pH. Water that has a high alkalinity can accept large doses of acids or bases without altering the pH significantly. Waters with low alkalinity, such as rainwater or distilled water, can experience a drop in the pH with only a minor addition of an acid or base.

In natural waters much of the alkalinity is provided by the carbonate/bicarbonate buffering system. Carbon dioxide (CO_2) dissolves in water to form carbonic acid (H_2CO_3), which dissociates and is in equilibrium with bicarbonate (HCO_3^-) and carbonate (CO_3^{2-}) ions:

$$CO_2 \text{ (gas)} \leftrightarrow CO_2 \text{ (dissolved)} \tag{5.20}$$

$$CO_2 \text{ (dissolved)} + H_2O \leftrightarrow H_2CO_3 \leftrightarrow H^+ + HCO_3^- \leftrightarrow 2H^+ + CO_3^{2-}. \tag{5.21}$$

If an acid is added to the water, the hydrogen ion concentration is increased, and this combines with both the carbonate and bicarbonate ions, driving the equilibrium to the left, releasing carbon dioxide into the atmosphere. As long as there is bicarbonate and carbonate, the added hydrogen ions will be absorbed by readjustment of the equilibrium equation. Only when all of the carbonate and bicarbonate ions are depleted will the addition of acid cause a drop in pH.

The amount of bicarbonate in water is supplemented by naturally occurring carbonates such as $CaCO_3$ (limestone) that dissolve as acidic rain water comes into contact with watershed soils or the stream bed. The $CaCO_3$ dissolves to form calcium bicarbonate ($Ca(HCO_3)_2$), which dissociates and increases the bicarbonate concentration in the water:

$$CaCO_3 + H_2CO_3 \rightarrow Ca(HCO_3)_2 \leftrightarrow Ca^{2+} + 2HCO_3^-. \tag{5.22}$$

The effect of alkalinity on the pH of a water sample is shown in Fig. 5-6.

Alkalinity is determined by measuring the amount of acid needed to lower the pH in a water sample to a specific endpoint; the results are usually reported in standardized units as milligrams $CaCO_3$ per liter. Poorly buffered water may have alkalinities lower than 40 mg $CaCO_3$/L while water sampled from a stream flowing through a limestone or "karst" region may have alkalinities greater than 200 mg $CaCO_3$/L.

SOLIDS

Wastewater treatment is complicated by the dissolved and suspended inorganic material it contains. In discussion of water treatment, both dissolved and suspended materials are called solids. The separation of these solids from the water is one of the primary objectives of treatment.

Total solids include any material left in a container after the water is removed by evaporation, usually at 103–105°C. Total solids can be separated into *total suspended solids* (solids that are retained on a 2.0-μm filter) and *total dissolved solids*

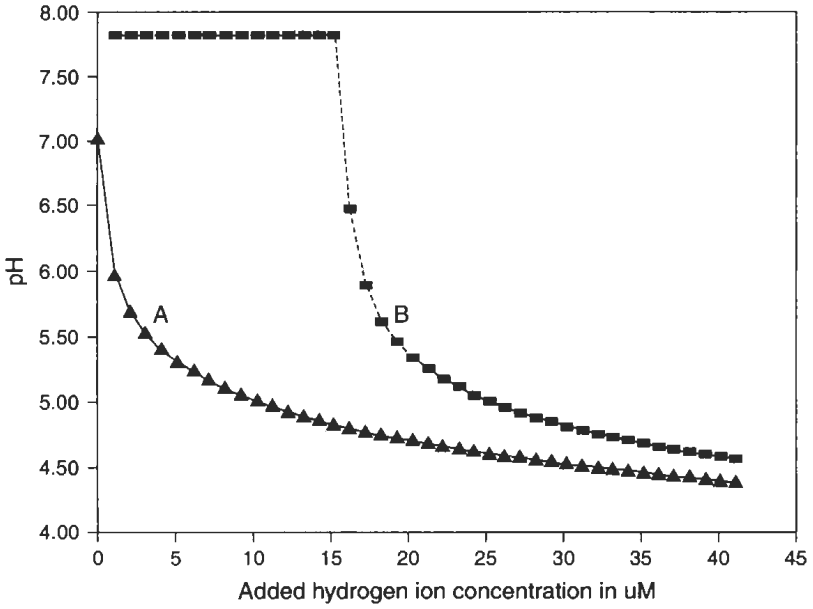

Figure 5-6. Effect of alkalinity in buffering against pH changes. (A) acid is added to deionized water (very low alkalinity); (B) acid is added to monobasic phosphate buffer solution (high alkalinity).

(dissolved and colloidal material that passes through the filter). The difference between total suspended solids and total dissolved solids is illustrated in the following example:

A teaspoonful of table salt dissolves in a glass of water, forming a water-clear solution. However, the salt will remain behind if the water evaporates. Sand, however, will not dissolve and will remain as sand grains in the water and form a turbid mixture. The sand will also remain behind if the water evaporates. The salt is an example of a dissolved solid, whereas the sand is a suspended solid.

Suspended solids are separated from dissolved solids using a special crucible, called a *Gooch crucible*. The Gooch crucible has holes on the bottom on which a glass fiber filter is placed (Fig. 5-7). The water sample is drawn through the crucible with the aid of a vacuum. The suspended material is retained on the filter, while the dissolved fraction passes through. If the initial dry weight of the crucible and filter is known, the subtraction of this from the total weight of the crucible, filter, and the dried solids caught in the filter yields the weight of suspended solids, expressed in milligrams per liter.

Solids may be classified in another way: those that are volatilized at a high temperature (550°C) and those that are not. The former are known as *volatile solids*, the later as *fixed solids*. Volatile solids are usually organic compounds. At 550°C some inorganics are also decomposed and volatilized, but this is not considered as a serious drawback. Example 5.3 illustrates the relationship between total solids and total volatile solids.

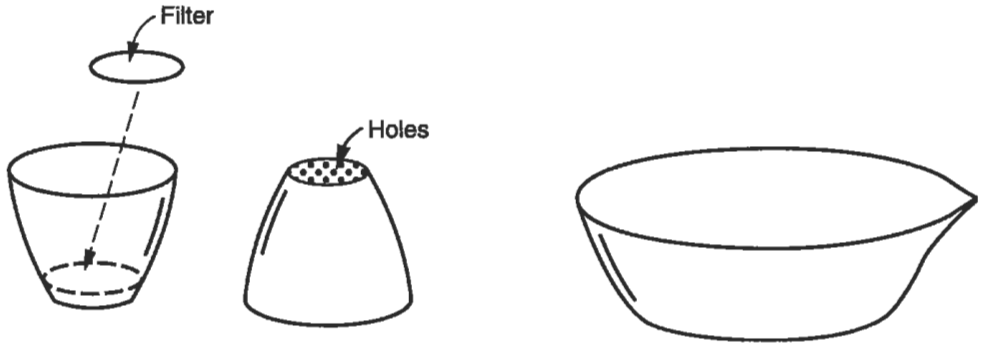

Figure 5-7. The Gooch crucible, with filter, for determining suspended solids, and the evaporating dish used for determining total solids.

EXAMPLE 5.3. Given the following data:

—Weight of a dish (such as shown in Fig. 5-7) = 48.6212 g,
—100 mL of sample is placed in the dish and evaporated. New weight of dish and dry solids = 48.6432 g.
—The dish is placed in a 550°C furnace, then cooled. New weight = 48.6300 g.

Find the total, volatile, and fixed solids.

$$\text{Total solids} = \frac{(\text{dish} + \text{dry solids}) - (\text{dish})}{\text{sample volume}}$$

$$= \frac{48.6432 - 48.6212}{100}$$

$$= (220)10^{-6}\ \text{g/mL}$$

$$= (220)10^{-3}\ \text{mg/mL}$$

$$= 220\ \text{mg/L}.$$

$$\text{Fixed solids} = \frac{(\text{dish} + \text{unburned solids}) - (\text{dish})}{\text{sample volume}}$$

$$= \frac{48.6300 - 48.6212}{100}$$

$$= 88\ \text{mg/L}$$

$$\text{Total volatile solids} = \text{Total solids} - \text{Total fixed solids}$$

$$= 220 - 88$$

$$= 132\ \text{mg/L}$$

NITROGEN AND PHOSPHORUS

Recall from Chap. 4 that nitrogen and phosphorus are important nutrients for biological growth. Nitrogen occurs in five major forms in aquatic environments: organic nitrogen, ammonia, nitrite, nitrate, and dissolved nitrogen gas; phosphorus occurs almost entirely as organic phosphate and inorganic orthophosphate or polyphosphates.

Ammonia is one of the intermediate compounds formed during biological metabolism and, together with organic nitrogen, is considered an indicator of recent pollution. Aerobic decomposition of organic nitrogen and ammonia eventually produces nitrite (NO_2^-) and finally nitrate (NO_3^-). High nitrate concentrations, therefore, may indicate that organic nitrogen pollution occurred far enough upstream that the organics have had time to oxidize completely. Similarly, nitrate may be high in groundwater after land application of organic fertilizers if there is sufficient residence time (and available oxygen) in the soils to allow oxidation of the organic nitrogen in the fertilizer.

Because ammonia and organic nitrogen are pollution indicators, these two forms of nitrogen are often combined in one measure, called *Kjeldahl nitrogen*, after the scientist who first suggested the analytical procedure. A popular alternative to the technically difficult Kjeldahl test is to measure total nitrogen and nitrate + nitrite separately. The difference between the two concentrations equals organic nitrogen plus ammonia.

Phosphorus is usually measured as total phosphorus (all forms combined) or dissolved phosphorus (portion that passes through a 0.45-μm membrane filter). Dissolved orthophosphate (PO_4^-) is an important indicator of water pollution because it is easily and rapidly taken up by biota, and therefore is almost never found in high concentrations in unpolluted waters.

The various forms of nitrogen and phosphorus can all be measured analytically by colorimetric techniques. In colorimetry, the ion in question combines with a reagent to form a colored compound; the color intensity is proportional to the original concentration of the ion. For example, in the "Phenate Method" for ammonia analysis, an intensely blue compound (indophenol) is created from the reaction between ammonia, hypochlorite, and phenol, with sodium nitroprusside as a catalyst (Clesceri *et al.* 1999). The color is measured photometrically, or occasionally by visual comparison to color standards.

A photometer, illustrated in Fig. 5-8, consists of a light source, a filter, the sample, and a photocell. The filter allows only those wavelengths of light to pass through that the compounds being measured will absorb. Light passes through the sample to the photocell, which converts light energy into electric current. An intensely colored sample will absorb a considerable amount of light and allow only a limited amount of light to pass through and thus create little current. On the other hand, a sample containing very little of the chemical in question will be lighter in color and allow almost all of the light to pass through, and set up a substantial current.

The intensity of light transmitted by the colored solution obeys the *Beer–Lambert Law*

$$\log_{10} \frac{P_0}{P} = ebc = A, \tag{5.23}$$

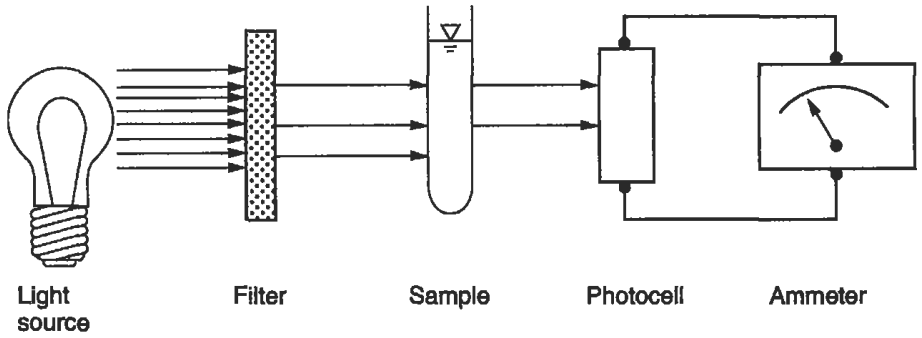

Figure 5-8. Elements of a filter photometer.

where

P_0 = radiant power of incident light,
P = radiant power of light after it passes through the sample,
e = absorbtivity ($L\,mol^{-1}\,cm^{-1}$),
b = path length (cm),
c = concentration of absorbing substance (moles L^{-1}), and
A = absorbance (no units).

A photometer, as shown in Fig. 5-8, measures the difference between the intensity of light passing through the sample (P in Eq. (5.23)) and the intensity of light passing through clear distilled water or a reference sample (P_0) and reports *absorbance* (A) as well as *percent transmission* ($\%T$):

$$A = \log_{10} \frac{1}{T} = \log_{10} \frac{100}{\%T}. \tag{5.24}$$

Typically, in colorimetric analyses, a standard dilution series is used to estimate the concentration of an unknown sample, as illustrated in Example 5.4.

EXAMPLE 5.4. Several known concentrations of ammonia and an unknown sample were analyzed using the phenate method, and the color was measured with a photometer. Find the ammonia concentration of the unknown sample.

Standards	Absorbance
0 μg/L of ammonia	0.050
5 μg/L of ammonia	0.085
10 μg/L of ammonia	0.121
50 μg/L of ammonia	0.402
100 μg/L of ammonia	0.747
350 μg/L of ammonia	2.450
Unknown sample	1.082

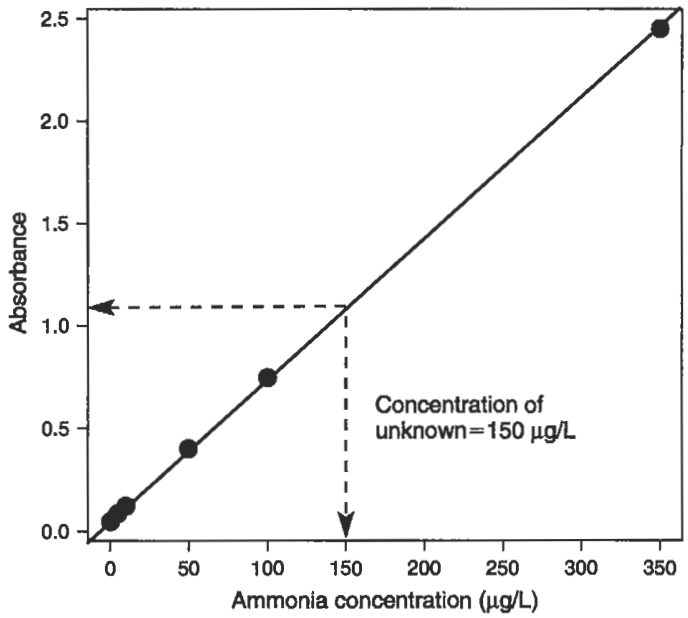

Figure 5-9. Calculation using colorimetric standards.

From Fig. 5-9 where ammonia concentration of the standards vs absorbance results in a straight line, we see that an absorbance of 1.082 (the unknown) corresponds to an ammonia concentration of 150 µg/L.

Although most nitrogen and phosphorus analyses are done using a spectrophotometer, other techniques are growing in acceptance. Selective ion electrodes are available for measuring ammonia, nitrite, and nitrate (the pH meters described earlier are selective ion electrodes that measure H^+). Ion chromatography (ICP) can be used to measure nitrite, nitrate, and phosphate, as well as total nitrogen and total phosphorus if the samples are first digested (oxidized) to convert all forms of nitrogen or phosphorus to nitrate and phosphate. Ion chromatography involves passing a water sample through a series of ion exchange columns that separate the anions so that they are released to a detector at different times. For simple (i.e., not particularly accurate) measurements, field kits that provide premeasured packets of chemicals for testing nitrogen and phosphorus in water and soil samples are now available. These kits usually use colorimetric techniques similar to the more sophisticated versions used in analytical labs, but rely on color reference cards rather than a spectrophotometer for determining chemical concentrations.

PATHOGENS

From the public health standpoint, the bacteriological quality of water is as important as the chemical quality. A large number of infectious diseases may be transmitted by water,

Table 5-2. Examples of Common Waterborne Pathogens

Microorganism	Effects on humans
Bacteria	
Campylobacter	Gastroenteritis
Clostridium botulinum	Gastroenteritis (botulism)
Clostridium perfringens	Gastroenteritus
E. coli O157:H7	Gastroenteritis
Legionella	Pneumonia-like pulmonary disease
Salmonella paratyphi	Paratyphoid
Salmonella typhi	Typhoid fever
Shigella (several species)	Shigellosis (dysentery)
Staphylococcus aureus	Gastroenteritis
Vibrio comma (*V. cholerae*)	Cholera
Yersinia enterocolitica	Gastroenteritis
Protozoans	
Cryptosporidium	Cryptosporidiasis
Entamoeba histolytica	Amoebic dysentery
Giardia lamblia	Giardiasis
Viruses	
Hepatitis A virus	Hepatitis
Poliovirus	Poliomyelitis

among them typhoid and cholera. Although we clearly desire drinking water that is not contaminated by *pathogens* (disease-causing organisms), determining whether the organisms are present in water, and whether they represent a health threat, is relatively complicated. First, there are many pathogens. Table 5-2 lists just a few of the most common waterborne microbial pathogens. Each has a specific detection procedure and must be screened individually. Second, the concentration of these organisms, although large enough to spread disease, may be so small as to make their detection impossible, like the proverbial needle in a haystack.

How can we measure for bacteriological quality? The answer lies in the concept of *indicator organisms* that, while not necessarily directly harmful, indicate the possible presence of other pathogens.

The indicator most often used is *Escherichia coli* (*E. coli*), a member of the *coliform* bacteria group (coliform bacteria are nonspore forming, rod-shaped bacteria capable of fermenting lactose within 48 h at 35°C). Although many coliforms occur naturally in aquatic environments, *E. coli*, often called fecal coliforms, are associated with the digestive tracts of warm-blooded animals. Fecal coliforms are particularly good indicator organisms because they are easily detected with a simple test, generally harmless (some strains are very pathogenic, but most are not), and do not survive long outside their host. The presence of fecal coliforms in a water sample does not prove the presence of pathogens, nor does the absence of fecal coliforms ensure the absence of

pathogens. However, if a large number of fecal coliforms are present, there is a good chance of recent pollution by wastes from warm-blooded animals.

This last point should be emphasized. The presence of coliforms does not prove that there are pathogenic organisms in the water, but indicates that such organisms *might* be present. A high coliform count is thus suspicious, and the water should not be consumed, even though it may be safe.

There are several ways to measure fecal coliforms. One of the most widely used methods is the membrane filter (MF) technique. A water sample is filtered through a sterile micropore filter by suction, thereby capturing any coliforms. The filter is placed in a Petri dish containing a sterile culture medium that promotes the growth of the fecal coliforms while inhibiting other organisms. After 24 h of incubation at 35°C, the number of shiny metallic red dots (fecal coliform colonies) is counted. The concentration of coliforms is typically expressed as coliforms/100 mL of sample. The equipment used for such tests is shown in Fig. 5-10.

The second method of measuring for coliforms is called the most probable number (MPN) test. This test is based on the observation that in lactose broth, coliforms will produce gas and make the broth cloudy. The production of gas is detected by placing a small tube upside down inside a larger tube (Fig. 5-11) so as not to have air bubbles in the smaller tube. After incubation, if gas is produced, some of the gas will become trapped in the smaller tube and this, along with a cloudy broth, will indicate that tube has been inoculated with at least one coliform. The MPN test is often used when the sample is very turbid, brackish, or from a mud or sediment sample, all of which are conditions that interfere with the MF technique.

A third way of measuring the coliforms is by a proprietary device called a Coli-Count. A sterile pad with all the necessary nutrients is dipped into the water sample and incubated, and the colonies are counted. The pad is designed to absorb exactly 1 mL of sample water so that the colonies counted give a coliform concentration per milliliter. Although fast and simple, Coli-Count results are not accepted for testing drinking water.

A growing concern in pathogen testing is detecting the presence of virulent strains of *E. coli* (e.g., *E. coli* O157:H7) in food and drinking water supplies. The standard MF and MPN tests do not distinguish between pathogenic and harmless strains of *E. coli*; genetic testing is normally used to determine which strains of the bacteria are present.

Over the past two decades we have seen an increasing emphasis on using other indicator microorganisms to supplement or replace the *E. coli* test. For example, the enterococcus subgroup of fecal streptococcus bacteria (*Streptococcus faecalis*, *S. faecium*, *S. gallinarum*, and *S. avium*) has been found to be excellent indicators of the quality of recreational waters (e.g., swimming beaches). As with *E. coli*, enterococcus bacteria are normal inhabitants in the gastrointestinal tract of warm-blooded animals and are easily enumerated using membrane filtration followed by incubation on selective growth medium.

Pathogenic viruses constitute a particularly difficult group of organisms to identify and enumerate. Because of this, routine testing for viruses is rarely done unless there is an outbreak of disease or you are testing the safety of reclaimed wastewater. (Low coliform counts are not a reliable measure of pathogen inactivation in reclaimed

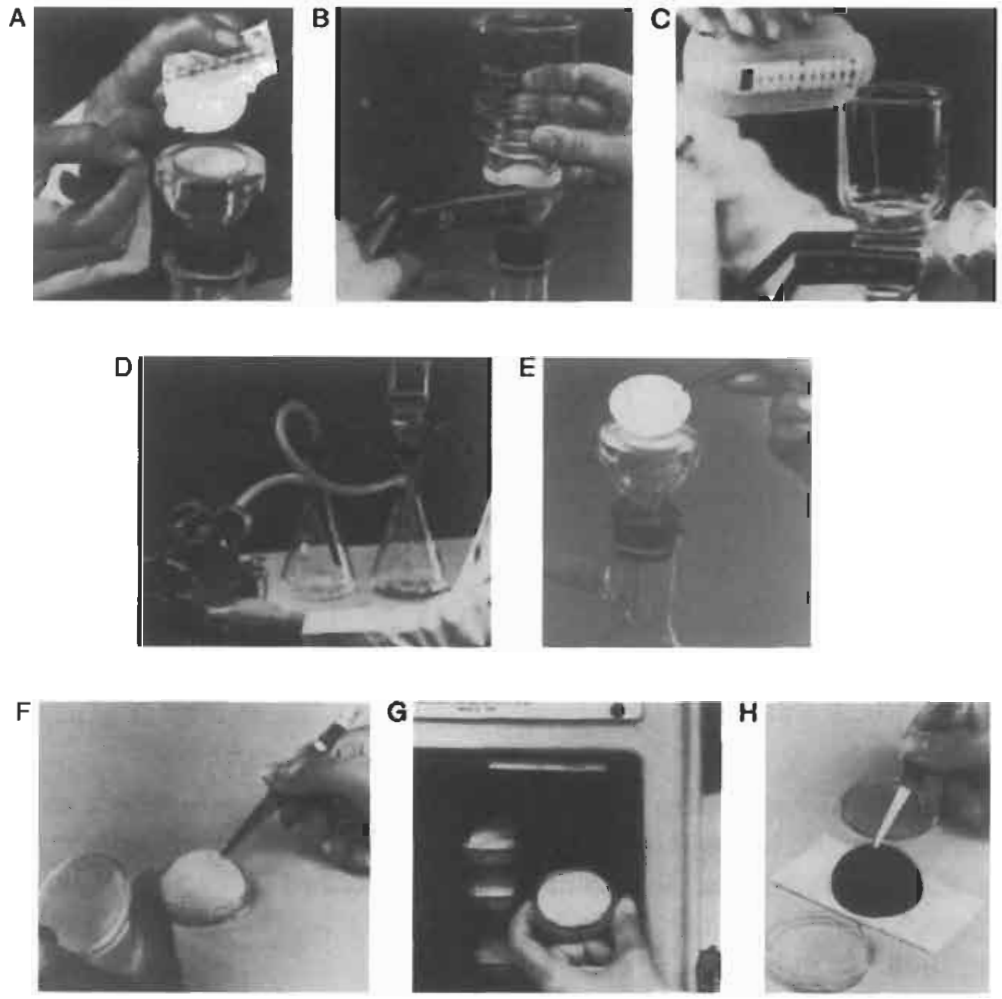

Figure 5-10. Millipore filter apparatus for coliform measurement. The procedure is illustrated in the sequence of photos starting at top left: (A) Millipore filter is put on filter support; (B) funnel is replaced; (C) measured sample is poured into funnel; (D) suction is applied using laboratory vacuum; (E) suction is released and filter removed; (F) filter is centered on growth medium in Petri dish; (G) Petri dish is incubated at 35°C for 24 h; (H) coliform colonies are counted using a microscope.

wastewater because some pathogens are more resistant to disinfection methods than coliforms.)

HEAVY METALS

Heavy metals such as arsenic, copper, and mercury can harm aquatic organisms, or bioaccumulate in the food chain, even if the metal concentration in water is relatively low. Consequently, the method of measuring metals in water must be very sensitive. There are a large variety of methods available to measure metals in water samples, and the choice of method often depends on the desired sensitivity as well as cost. Heavy metals are usually measured using flame, electrothermal (graphite furnace), or

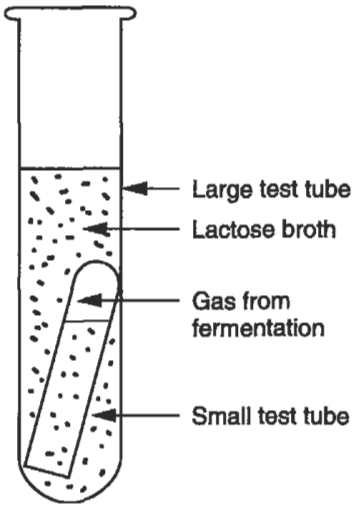

Figure 5-11. Test tubes used for most probable number (MPN) coliform test.

cold-vapor atomic absorption (AA), inductively coupled plasma (ICP) and inductively coupled plasma/mass spectrometry (ICP/MS), and colorimetric techniques. Samples can be filtered and analyzed for dissolved metals or digested using strong acids to measure total metals.

In flame AA a solution of lanthanum chloride is added to the sample, and the treated sample is sprayed into a flame using an atomizer. Each metallic element in the sample imparts a characteristic color to the flame, whose intensity is then measured spectrophotometrically. Graphite furnace AA methods use an electrically heated device to atomize metal elements, and can measure much lower concentrations of metals than flame AA, but often have "matrix" interference problems caused by salts and other compounds in the sample. Cold vapor AA is used primarily to measure arsenic and mercury. Inductively coupled plasma and ICP/MS are less sensitive to matrix problems and cover a wide range of concentrations.

OTHER ORGANIC COMPOUNDS

One of the most diverse (and difficult) areas of pollution assessment is the measurement of toxic, carcinogenic, or other potentially harmful organic compounds in water. These organics encompass the disinfection by-products introduced earlier, as well as pesticides, detergents, industrial chemicals, petroleum hydrocarbons, and degradation products that these chemicals become as they are altered chemically or biologically in the environment (e.g., DDT biodegrades to hazardous DDD and DDE).

Some of the methods described earlier in this chapter can be used to assess the overall content of organics in water (e.g., total organic carbon analysis). *Gas chromatography* (GC) and *high-performance liquid chromatography* (HPLC) are effective methods for measuring minute quantities of specific organics. Gas chromatography uses a mobile phase (carrier gas) and a stationary phase (column packed with an inert

granular solid) to separate organic chemicals. The organics are vaporized, and then allowed to move through the column at different rates that are unique to each organic chemical. After separation in the column, the amount of each organic is determined using a detector that is sensitive to the type of organic being measured. Peak height and travel time are used to identify and quantify each organic. High-performance liquid chromatography is similar to gas chromatography except that the mobile phase is a high-pressure liquid solvent.

CONCLUSION

Only a few of the most important tests used in water pollution control have been discussed in this chapter. Hundreds of analytical procedures have been documented, many of which can be performed only with special equipment and skilled technicians. Understanding this, and realizing the complexity, variations, and objectives of some of the measurements of water pollution, how would you answer someone who brings a jug of water to your office, sets it on your desk, and asks, "Can you tell me if this water is polluted?"

PROBLEMS

5.1 Given the following BOD test results:

—Initial dissolved oxygen = 8 mg/L
—Final dissolved oxygen = 0 mg/L
—Dilution = 1/10

what can you say about

a. BOD_5?
b. BOD ultimate?
c. COD?

5.2 If you had two bottles full of lake water and kept one dark and the other in daylight, which would have a higher dissolved oxygen after a few days? Why?

5.3 Name three types of samples you would need to seed if you wanted to measure their BOD.

5.4 The following data were obtained for a sample:

—total solids = 4000 mg/L
—suspended solids = 5000 mg/L
—volatile suspended solids = 2000 mg/L
—fixed suspended solids = 1000 mg/L

Which of these numbers is questionable and why?

5.5 A sample of water has a BOD_5 of 10 mg/L. The initial dissolved oxygen in the BOD bottle was 8 mg/L, and the dilution was 1/10. What was the final dissolved oxygen in the BOD bottle?

5.6 If the BOD_5 of a waste is 100 mg/L, draw a curve showing the effect of adding progressively higher doses of chromium (a toxic chemical) on the BOD_5.

5.7 An industry discharges 10 million gallons a day of waste that has a BOD_5 of 2000 mg/L. How many pounds of BOD_5 are discharged?

5.8 If you dumped half a gallon of milk every day into a stream, what would be your discharge in pounds of BOD_5 per day?

5.9 Consider the following data from a BOD test:

Day	DO (mg/L)	Day	DO (mg/L)
0	9	5	6
1	9	10	6
2	9	15	4
3	8	20	3
4	7	25	3

What is the: (a) BOD_5, (b) ultimate carbonaceous BOD (L_0), and (c) ultimate BOD (BOD_{ult})? Why was there no oxygen used until the third day? If the sample had been seeded, would the final dissolved oxygen have been higher or lower? Why?

5.10 Given the same standard ammonia samples as in Example 5.4, what would the ammonia concentration be if your unknown measured an absorbance of 0.050?

5.11 Suppose you ran a multiple-tube coliform test and got the following results: 10-mL samples, all 5 positive; 1-mL samples, all 5 positive; 0.1-mL samples, all 5 negative. Use the table in *Standard Methods* to estimate the concentration of coliforms.

5.12 If fecal coliform bacteria were to be used as an indicator of viral pollution as well as an indicator of bacterial pollution, what attributes must *E. coli* have relative to viruses?

5.13 Draw a typical BOD curve. Label the (a) ultimate carbonaceous BOD (L_0), (b) ultimate nitrogenous BOD, (c) ultimate BOD (BOD_{ult}), and (d) 5-day BOD. On the same graph, plot the BOD curve if the test had been run at 30°C instead of at the usual temperature. Also plot the BOD curve if a substantial amount of toxic materials were added to the sample.

5.14 Consider the BOD data below (no dilution, no seed).

a. What is the ultimate carbonaceous BOD?
b. What might have caused the lag at the beginning of the test?
c. Calculate k_1' (the reaction rate constant).

Day	DO (mg/L)
0	8
1	8
3	7
5	6.5
7	6
15	4
20	4

5.15 A sample of wastewater is estimated to have a BOD of 200 mg/L.

a. What dilution is necessary for this BOD to be measured by the usual technique?
b. If the initial and final dissolved oxygen of the test thus conducted is 9.0 and 4.0 mg/L, and the dilution water has a BOD of 1.0 mg/L, what is the dilution?