of some of these compounds in the atmosphere may pose a significant public health risk; and (3) they contribute to a general increase in reactive hydrocarbons in the atmosphere, which can lead to the formation of photochemical oxidants. The release of these compounds in sewers and at treatment plants, especially at the headworks, is of particular concern with respect to the health of collection system and treatment plant workers. The release and control of VOCs is considered further in Chaps. 6 and 9. The physical phenomena involved in the release of VOCs are considered in detail in Ref. 24.

Pesticides and Agricultural Chemicals. Trace organic compounds, such as pesticides, herbicides, and other agricultural chemicals, are toxic to most life forms and therefore can be significant contaminants of surface waters. These chemicals are not common constituents of domestic wastewater but result primarily from surface runoff from agricultural, vacant, and park lands. Concentrations of these chemicals can result in fish kills, in contamination of the flesh of fish that decreases their value as a source of food, and in impairment of water supplies. Many of these chemicals are also classified as priority pollutants.

Measurement of Organic Content

Over the years, a number of different tests have been developed to determine the organic content of wastewaters. In general, the tests may be divided into those used to measure gross concentrations of organic matter greater than about 1 mg/L and those used to measure trace concentrations in the range of 10^{-12} to 10^{-3} mg/L. Laboratory methods commonly used today to measure gross amounts of organic matter (greater than 1 mg/L) in wastewater include: (1) biochemical oxygen demand (BOD); (2) chemical oxygen demand (COD); and (3) total organic carbon (TOC). Complementing these laboratory tests is the theoretical oxygen demand (ThOD), which is determined from the chemical formula of the organic matter.

Other methods used in the past included (1) total, albuminoid, organic, and ammonia nitrogen, and (2) oxygen consumed. These determinations, with the exception of albuminoid nitrogen and oxygen consumed, are still included in complete wastewater analyses. Their significance, however, has changed. Whereas formerly they were used almost exclusively to indicate organic matter, they are now used to determine the availability of nitrogen to sustain biological activity in industrial waste treatment processes and to foster undesirable algal growths in receiving water.

Trace organics in the range of 10^{-12} to 10^{-3} mg/L are determined using instrumental methods including gas chromotography and mass spectroscopy. Within the past 10 years, the sensitivity of the methods used for the detection of trace organic compounds has improved significantly and detection of concentrations in the range of 10^{-9} mg/L is now almost a routine matter.

The concentration of pesticides is typically measured by the carbon-chloroform extract method, which consists of separating the contaminants from the water by passing a water sample through an activated-carbon column and then extracting the contaminant from the carbon using chloroform. The chloroform can then be evaporated

and the contaminants can be weighed. Pesticides and herbicides in concentrations o 1 part per billion (ppb) and less can be determined accurately by several methods including gas chromatography and electron capture or coulometric detectors [18].

Biochemical Oxygen Demand. The most widely used parameter of organic pol lution applied to both wastewater and surface water is the 5-day BOD (BOD_5). This determination involves the measurement of the dissolved oxygen used by microor ganisms in the biochemical oxidation of organic matter. Despite the widespread use of the BOD test, it has a number of limitations (which are discussed later in this section). It is hoped that, through the continued efforts of workers in the field, one of the other measures of organic content, or perhaps a new measure, will ultimately be used in its place. Why, then, if the test suffers from serious limitations, is furthe space devoted to it in this text? The reason is that BOD test results are now used (1) to determine the approximate quantity of oxygen that will be required to biologi cally stabilize the organic matter present, (2) to determine the size of waste treatmen facilities, and (3) to measure the efficiency of some treatment processes, and (4) to determine compliance with wastewater discharge permits. Because it is likely that the BOD test will continue to be used for some time, it is important to know as much as possible about the test and its limitations.

To ensure that meaningful results are obtained, the sample must be suitably diluted with a specially prepared dilution water so that adequate nutrients and oxygen will be available during the incubation period. Normally, several dilutions are prepared to cover the complete range of possible values. The ranges of BOD that can be measured with various dilutions based on percentage mixtures and direct pipetting are reported in Table 3-10. The general procedure for preparing the BOD bottles fo incubation is illustrated in Fig. 3-11.

When the sample contains a large population of microorganisms (untreated wastewater, for example), seeding is not necessary. If required, the dilution water i "seeded" with a bacterial culture that has been acclimated to the organic matter or othe materials that may be present in the wastewater. The seed culture that is used to prepare the dilution water for the BOD test is a mixed culture. Such cultures contain large numbers of saprophytic bacteria and other organisms that oxidize the organic matter In addition, they contain certain autotrophic bacteria that oxidize noncarbonaceous matter. A variety of commercial seed preparations are also available.

The incubation period is usually five days at 20°C, but other lengths of time and temperatures can be used. Longer time periods (typically seven days), which correspond to work schedules, are often used, especially in small plants where the laboratory staff is not available on the weekends. The temperature, however, should be constant throughout the test. The dissolved oxygen of the samples is measured (see Fig. 3-12) before and after incubation, and the BOD is calculated using Eq. 3-2 o Eq. 3-3.

When dilution water is not seeded,

$$\text{BOD, mg/L} = \frac{D_1 - D_2}{P} \qquad (3\text{-}2$$

3LE 3-10
)D measurable with various dilutions samples[a]

y using percent mixtures		By direct pipetting into 300 mL bottles	
mixture	Range of BOD	mL	Range of BOD
0.01	20,000–70,000	0.02	30,000–105,000
0.02	10,000–35,000	0.05	12,000–42,000
0.05	4,000–14,000	0.10	6,000–21,000
0.1	2,000–7,000	0.20	3,000–10,500
0.2	1,000–3,500	0.50	1,200–4,200
0.5	400–1,400	1.0	600–2,100
1.0	200–700	2.0	300–1,050
2.0	100–350	5.0	120–420
5.0	40–140	10.0	60–210
10.0	20–70	20.0	30–105
20.0	10–35	50.0	12–42
50.0	4–14	100.0	6–21
100.0	0–7	300.0	0–7

Ref. 32.

When dilution water is seeded,

$$\text{BOD, mg/L} = \frac{(D_1 - D_2) - (B_1 - B_2)f}{P} \tag{3-3}$$

where D_1 = dissolved oxygen of diluted sample immediately after preparation, mg/L
D_2 = dissolved oxygen of diluted sample after 5 d incubation at 20°C, mg/L
P = decimal volumetric fraction of sample used
B_1 = dissolved oxygen of seed control before incubation, mg/L
B_2 = dissolved oxygen of seed control after incubation, mg/L
f = ratio of seed in sample to seed in control
= (% seed in D_1)/(% seed in B_1)

Biochemical oxidation is a slow process and theoretically takes an infinite time to go to completion. Within a 20-day period, the oxidation of the carbonaceous organic matter is about 95 to 99 percent complete, and in the 5-day period used for the BOD test, oxidation is from 60 to 70 percent complete. The 20°C temperature used is an average value for slow-moving streams in temperate climates and is easily duplicated in an incubator. Different results would be obtained at different temperatures because biochemical reaction rates are temperature-dependent.

The kinetics of the BOD reaction are, for practical purposes, formulated in accordance with first-order reaction kinetics and may be expressed as

$$\frac{dL_t}{dt} = -kL_t \tag{3-4}$$

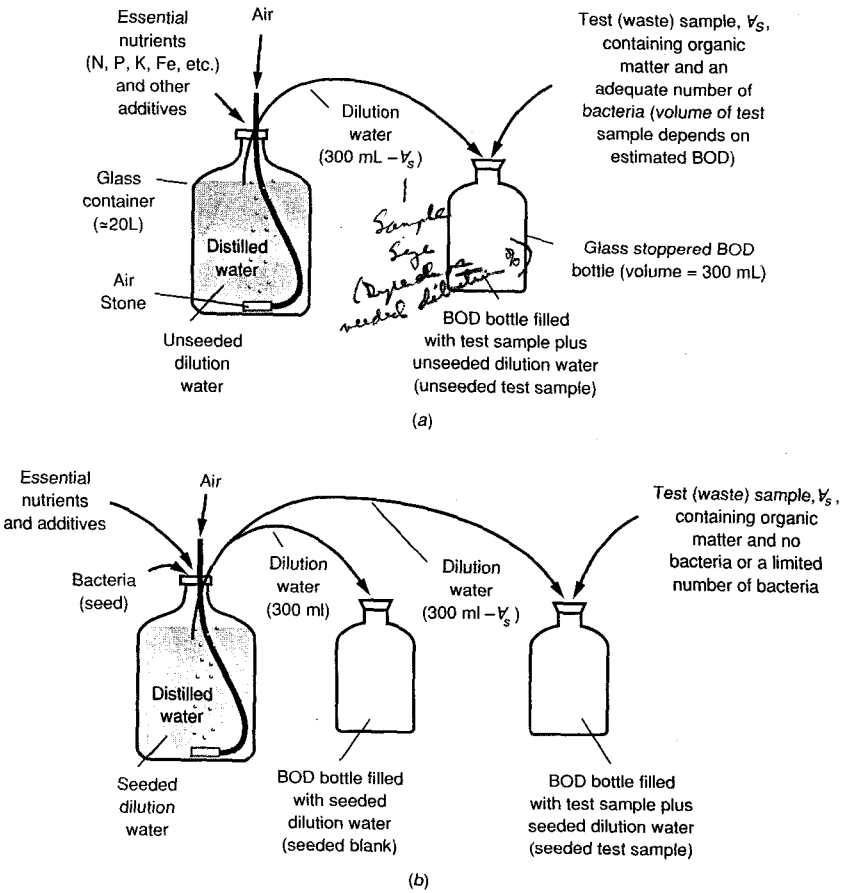


FIGURE 3-11
Procedure for setting up BOD test bottles: (*a*) with unseeded dilution water and (*b*) with seeded dilution water [23].

where L_t is the amount of the first-stage BOD remaining in the water at time t and k is the reaction rate constant. This equation can be integrated as

$$\ln L_t|_0^t = -kt \tag{3-5}$$

$$\frac{L_t}{L_0} = e^{-kt} = 10^{-Kt} \tag{3-6}$$

where L_t or BOD_L is the BOD remaining at time $t = 0$ (i.e., the total or ultimate first-stage BOD initially present). The relation between k (base e) and K (base 10) is as follows:

$$K(\text{base } 10) = \frac{k(\text{base } e)}{2.303} \tag{3-7}$$

IGURE 3-12
Measurement of oxygen in BOD bottle with a DO probe equipped with a stirring mechanism.

The amount of BOD remaining at time t equals

$$L_t = L_0(e^{-kt}) \tag{3-8}$$

and y, the amount of BOD that has been exerted at any time t, equals

$$y_t = L_0 - L_t = L_0(1 - e^{-kt}) \tag{3-9}$$

Note that the 5-day BOD equals

$$y_5 = L_0 - L_5 = L_0(1 - e^{-5k}) \tag{3-10}$$

This relationship is shown in Fig. 3-13. The use of the BOD equations is illustrated in Example 3-2.

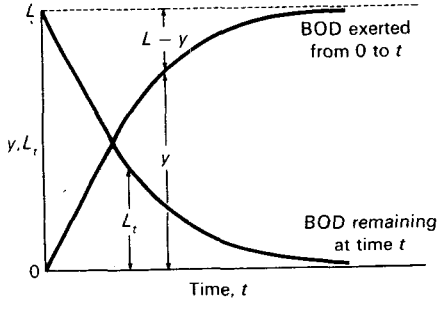


FIGURE 3-13
Formation of the first-stage BOD curve.

Example 3-2 Calculation of BOD. Determine the 1-day BOD and ultimate first-stage BOD for a wastewater whose 5-day, 20°C BOD is 200 mg/L. The reaction constant k(base e) = 0.23 d^{-1}.

Solution

1. Determine ultimate BOD.

$$L_t = L_0 e^{-kt}$$
$$y_5 = L_0 - L_5 = L(1 - e^{-kt})$$
$$200 = L_0(1 - e^{-5(0.23)}) = L_0(1 - 0.316)$$
$$L_0 = 293 \text{ mg/L}$$

2. Determine 1-day BOD.

$$L_t = L_0 e^{-kt}$$
$$L_1 = 293(e^{-0.23(1)}) = 293(0.795) = 233 \text{ mg/L}$$
$$y_1 = L_0 - L_1 = 293 - 233 = 60 \text{ mg/L}$$

For polluted water and wastewater, a typical value of k (base e, 20°C) is 0.23 d^{-1} (= 0.10 d^{-1} k base 10). The value of reaction-rate constant varies significantly, however, with the type of waste. The range may be from 0.05 to 0.3 d^{-1} (base e) or more. For the same ultimate BOD, the oxygen uptake will vary with time and with different reaction-rate constant values (see Fig. 3-14).

As mentioned, the temperature at which the BOD of a wastewater sample is determined is usually 20°C. It is possible, however, to determine the reaction constant k at a temperature other than 20°C. The following approximate equation, which is derived from the van't Hoff-Arrhenius relationship, may be used:

$$k_T = k_{20}\theta^{(T-20)} \tag{3-11}$$

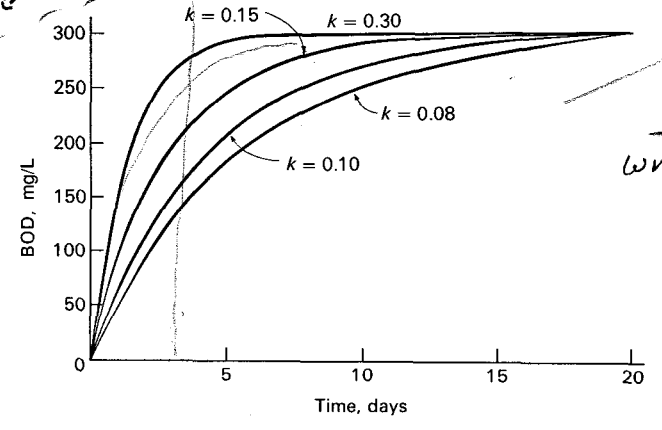


FIGURE 3-14
Effect of the rate constant k on BOD (for a given L value).

ie value of θ has been found to vary from 1.056 in the temperature range between and 30°C to 1.135 in the temperature range between 4 and 20°C [15]. A value of often quoted in the literature is 1.047 [14], but it has been observed that this value es not apply at cold temperatures (e.g., below 20°C) [15].

Nitrification in the BOD test. Noncarbonaceous matter, such as ammonia, produced during the hydrolysis of proteins. Two groups of autotrophic bacteria are pable of oxidizing ammonia to nitrite and subsequently to nitrate. The generalized actions are as follows:

$$NH_3 + \tfrac{3}{2}O_2 \xrightarrow{\text{nitrite-forming bacteria}} HNO_2 + H_2O \qquad (3\text{-}12)$$

$$HNO_2 + \tfrac{1}{2}O_2 \xrightarrow{\text{nitrate-forming bacteria}} HNO_3 \qquad (3\text{-}13)$$

$$NH_3 + 2O_2 \longrightarrow HNO_3 + H_2O \qquad (3\text{-}14)$$

he oxygen demand associated with the oxidation of ammonia to nitrate is called ie nitrogenous biochemical oxygen demand (NBOD). The normal exertion of the xygen demand in a BOD test for a domestic wastewater is shown in Fig. 3-15. ecause the reproductive rate of the nitrifying bacteria is slow, it normally takes from to 10 days for them to reach significant numbers and to exert a measurable oxygen emand. However, if a sufficient number of nitrifying bacteria are present initially, ie interference caused by nitrification can be significant.

When nitrification occurs in the BOD test, erroneous interpretations of treatnent operating data are possible. For example, assume that the effluent BOD from biological treatment process is 20 mg/L without nitrification and 40 mg/L with itrification. If the influent BOD to the treatment process is 200 mg/L, then the cor-

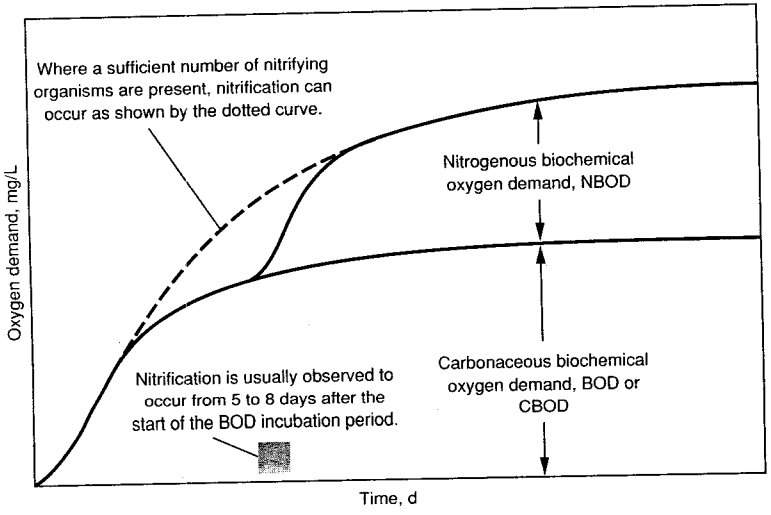


FIGURE 3-15
Definition sketch for the exertion of the carbonaceous and nitrogenous biochemical oxygen demand in a waste sample.

responding BOD removal efficiency would be reported as 90 and 80 percent without and with nitrification, respectively. Thus, if nitrification is occurring but is not suspected, it might be concluded that the treatment process is not performing well when in actuality it is performing quite well.

Carbonaceous biochemical oxygen demand (CBOD). The interference caused by the presence of nitrifying bacteria can be eliminated by pretreatment of the sample or by the use of inhibitory agents. Pretreatment procedures include pasteurization, chlorination, and acid treatment. Inhibitory agents are usually chemical in nature and include compounds such as methylene blue, thiourea and allylthiourea, 2-chlor-6 (trichloromethyl) pyridine, and other proprietary products [37]. Suppression of the nitrification reaction in the BOD test is listed as a standard procedure in the latest edition of *Standard Methods* [18]. The results of the suppressed BOD test should be reported as CBOD (carbonaceous biochemical oxygen demand). The CBOD test is now being used as substitue for the BOD test in discharge permits, especially where nitrification is known to occur.

Analysis of BOD data. The value of k is needed if the BOD_5 is to be used to obtain L, the ultimate or 20-day BOD. The usual procedure followed when these values are unknown is to determine k and L from a series of BOD measurements. There are several ways to do this, including the method of least-squares, the method of moments [11], the daily-difference method [27], the rapid-ratio method [16], the Thomas method [26], and the Fujimoto method [5]. The least-squares method and the Fujimoto method are illustrated in the following discussion.

The least-squares method involves fitting a curve through a set of data points, so that the sum of the squares of the residuals (the difference between the observed value and the value of the fitted curve) must be a minimum. Using this method, a variety of different types of curves can be fitted through a set of data points. For example, for a time series of BOD measurements on the same sample, the following equation may be written for each of the various n data points:

$$\left.\frac{dy}{dt}\right|_{t=n} = k(L - y_n) \qquad (3\text{-}15)$$

In this equation both k and L are unknown. If it is assumed that dy/dt represents the value of the slope of the curve to be fitted through all the data points for a given k and L value, then because of experimental error, the two sides of Eq. 3-15 will not be equal but will differ by an amount R. Rewriting Eq. 3-15 in terms of R for the general case yields

$$R = k(L - y) - \frac{dy}{dt} \qquad (3\text{-}16)$$

Simplifying and using the notation y' for dy/dt gives

$$R = kL - ky - y' \qquad (3\text{-}17)$$

Substituting a for kL and $-b$ for k gives

$$R = a + by - y' \qquad (3\text{-}18)$$

low, if the sum of the squares of the residuals R is to be a minimum, the following quations must hold:

$$\frac{\partial}{\partial a}\sum R^2 = \sum 2R\frac{\partial R}{\partial a} = 0 \tag{3-19}$$

$$\frac{\partial}{\partial b}\sum R^2 = \sum 2R\frac{\partial R}{\partial b} = 0 \tag{3-20}$$

f the indicated operations in Eqs. 3-19 and 3-20 are carried out using the value of he residual R defined by Eq. 3-18, the following set of equations result:

$$na + b\sum y - \sum y' = 0 \tag{3-21}$$

$$a\sum y + b\sum y^2 - \sum yy' = 0 \tag{3-22}$$

where n = number of data points
$a = -bL$
$b = -k$(base e)
$L = -a/b$
$y = y_t$, mg/L
$y' = \dfrac{y_{n+1} - y_{n-1}}{2\Delta t}$

Application of the least-squares method in the analysis of BOD data is illustrated in Example 3-3, which follows the discussion of the Fujimoto method.

In the Fujimoto method [5], an arithmetic plot is prepared of BOD_{t+1} versus BOD_t. The value at the intersection of the plot with a line of slope 1 corresponds to the the ultimate BOD. After the BOD_L has been determined, the rate constant is determined using Eq. 3-9 and one of the BOD values. The application of the Fujimoto method is illustrated in Example 3-3.

Example 3-3 Calculation of BOD constants using the least squares and the Fujimoto methods. Compute L and k using the least-squares and Fujimoto methods for the following BOD data reported for a stream receiving some treated effluent:

t, d	2	4	6	8	10
y, mg/L	11	18	22	24	26

Solution

1. Set up a computation table and perform the indicated steps.

Time	y	y^2	y'	yy'
2	11	121	4.50	49.5
4	18	324	2.75	49.5
6	22	484	1.50	33.0
8	24	576	1.00	24.0
	75	1,505	9.75	156.0

The slope y' is computed as follows:

$$\frac{dy}{dt} = y' = \frac{y_{n+1} - y_{n-1}}{2\Delta t}$$

2. Substitute the values computed in step 1 in Eqs. 3-21 and 3-22, and solve for a and b.

$$4a + 75b - 9.75 = 0$$

$$75a + 1505b - 156.0 = 0$$

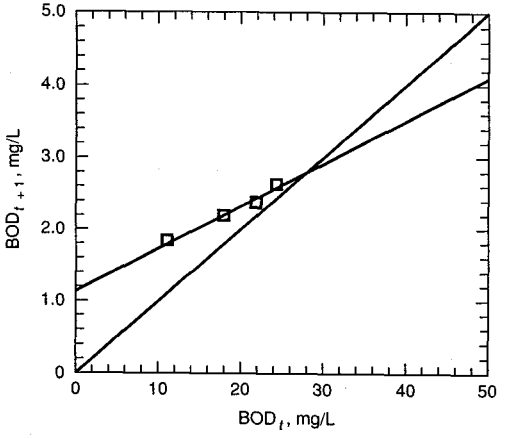
$$a = 7.5 \text{ and } b = -0.271$$

3. Determine the values of k and L.

$$k = -b = 0.271 \text{ (base } e\text{)}$$

$$L = -\frac{a}{b} = -\frac{7.5}{-0.271} = 27.7 \text{ mg/L}$$

4. Prepare an arithmetic plot of BOD_{t+1} versus BOD_t, and on the same plot draw a line with a slope of 1. The value at the intersection of the two lines (BOD = 27.8 mg/L) corresponds to the ultimate BOD.



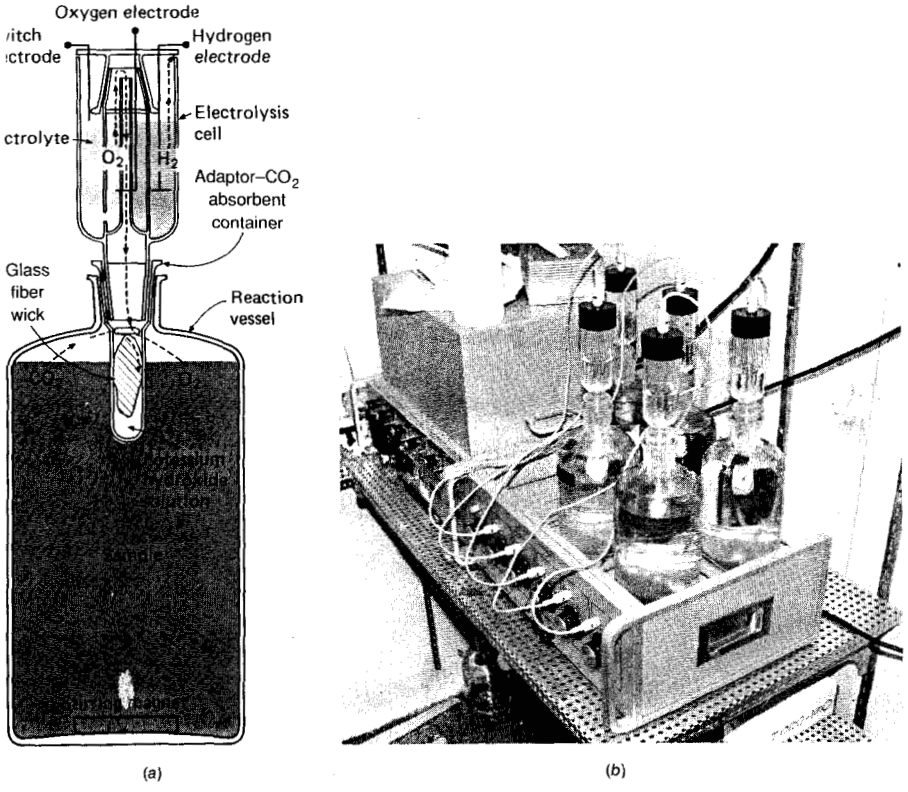
5. Determine the k value using Eq. 3-9.

$$y_6 = L - L_6 = L(1 - e^{-6K'})$$

$$22 = L - L_6 = 27.8(1 - e^{-6K'})$$

$$k = 0.293 \text{ d}^{-1}$$

Respirometric determination of BOD. Determination of the BOD value and the corresponding rate constant k can be accomplished more efficiently in the laboratory using an instrumented large-volume (1.0 L) electrolysis cell or a laboratory respirometer. An electrolysis cell (see Fig. 3-16*a*) may also be used to obtain a continuous BOD [38,39]. Within the cell, oxygen pressure over the sample is maintained constant by continually replacing the oxygen used by the micoorganisms. Oxygen



IGURE 3-16
lectrolytic respirometer for BOD determination: (*a*) schematic [37,38] and (*b*) commercial respirom-ter with multiple electrolysis cells.

eplacement is accomplished by means of an electrolysis reaction in which oxygen is ›roduced in response to changes in the pressure. The BOD readings are determined ›y noting the length of time that the oxygen was generated and by correlating it to he amount of oxygen produced by the electrolysis reaction. Advantages of the electrolysis cell over a conventional laboratory respirometer are that (1) the use of a arge (1 L) sample minimizes the errors of grab sampling and pipetting in dilutions, and (2) the value of the BOD is available directly. A typical example of a commercially available electrolytic respirometer with multiple electrolysis cells is also shown in Fig. 3-16*b*.

Limitations in the BOD test. The limitations of the BOD test are as follows: (1) a high concentration of active, acclimated seed bacteria is required; (2) pretreatment is needed when dealing with toxic wastes, and the effects of nitrifying organisms must be reduced; (3) only the biodegradable organics are measured; (4) the test does not have stoichiometric validity after the soluble organic matter present in solution has been used (see Fig. 3-17); and (5) an arbitrary, long period of time

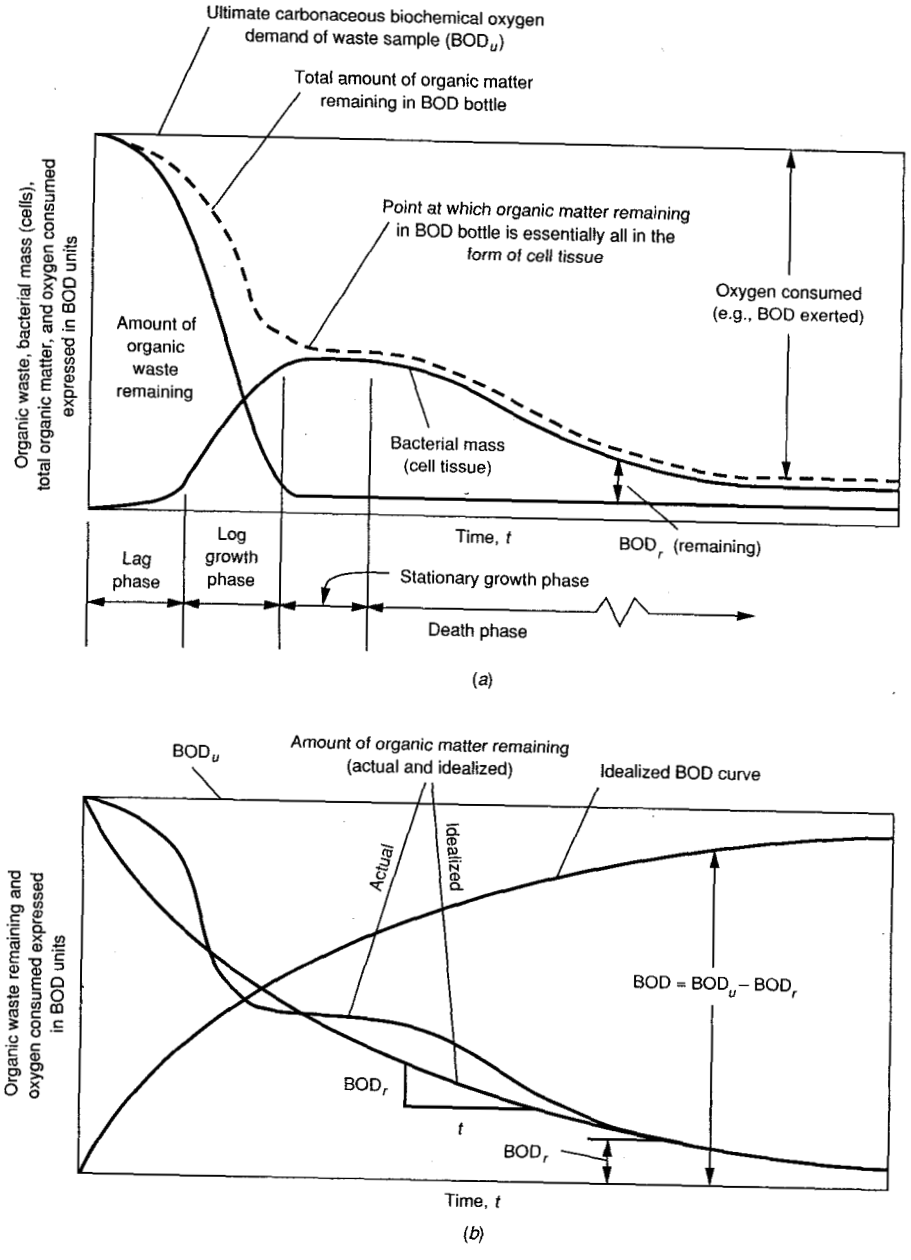


FIGURE 3-17
Functional analysis of the BOD test: (*a*) interrelationship of organic waste, bacterial mass (cell tissue), total organic waste, and oxygen consumed in BOD test and (*b*) idealized representation of the BOD test [23].

required to obtain results. Of the above, perhaps the most serious limitation is that e 5-day period may or may not correspond to the point where the soluble organic atter that is present has been used. The lack of stoichiometric validity at all times duces the usefulness of the test results.

hemical Oxygen Demand. The COD test is used to measure the content of ganic matter of both wastewater and natural waters. The oxygen equivalent of ıe organic matter that can be oxidized is measured by using a strong chemical xidizing agent in an acidic medium. Potassium dichromate has been found to be xcellent for this purpose. The test must be performed at an elevated temperature. A atalyst (silver sulfate) is required to aid the oxidation of certain classes of organic ompounds. Since some inorganic compounds interfere with the test, care must be ıken to eliminate them. The principal reaction using dichromate as the oxidizing gent may be represented in a general way by the following unbalanced equation:

$$\text{Organic matter } (C_aH_bO_c) + Cr_2O_7^{-2} + H^+ \xrightarrow[\text{heat}]{\text{catalyst}} Cr^{+3} + CO_2 + H_2O \qquad (3\text{-}23)$$

The COD test is also used to measure the organic matter in industrial and ıunicipal wastes that contain compounds that are toxic to biological life. The COD ıf a waste is, in general, higher than the BOD because more compounds can be hemically oxidized than can be biologically oxidized. For many types of wastes, it s possible to correlate COD with BOD. This can be very useful because the COD an be determined in three hours, compared with five days for the BOD. Once the orrelation has been established, COD measurements can be used to good advantage or treatment-plant control and operation.

Total Organic Carbon. Another means for measuring the organic matter present in water is the TOC test, which is especially applicable to small concentrations of organic matter. The test is performed by injecting a known quantity of sample into a high-temperature furnace or chemically-oxidizing environment. The organic carbon is oxidized to carbon dioxide in the presence of a catalyst. The carbon dioxide that is produced is quantitatively measured by means of an infrared analyzer. Acidification and aeration of the sample prior to analysis eliminates errors due to the presence of inorganic carbon. If VOCs are known to be present, the aeration step is omitted to eliminate their removal by stripping. The test can be performed very rapidly and is becoming more popular. Certain resistant organic compounds may not be oxidized, however, and the measured TOC value will be slightly less than the actual amount present in the sample. Typical TOC values for wastewater are reported in Table 3-16 in Sec. 3-5.

Theoretical Oxygen Demand. Organic matter of animal or vegetable origin in wastewater is generally a combination of carbon, hydrogen, oxygen, and nitrogen. The principal groups of these elements present in wastewater are, as previously noted, carbohydrates, proteins, fats, and products of their decomposition. The biological decomposition of the substances is discussed in Chap. 8. If the chemical formula of the organic matter is known, the ThOD may be computed, as illustrated in Example 3-4.

Example 3-4 Calculation of ThOD. Determine the ThOD for glycine ($CH_2(NH_2)COOH$) using the following assumptions:

1. In the first step, the organic carbon and nitrogen are converted to carbon dioxide (CO_2) and ammonia (NH_3), respectively.
2. In the second and third steps, the ammonia is oxidized sequentially to nitrite and nitrate.
3. The ThOD is the sum of the oxygen required for all three steps.

Solution

1. Write balanced reaction for the carbonaceous oxygen demand.

$$CH_2(NH_2)COOH + \tfrac{3}{2}O_2 \rightarrow NH_3 + 2CO_2 + H_2O$$

2. Write balanced reactions for the nitrogenous oxygen demand.

(*a*) $$NH_3 + \tfrac{3}{2}O_2 \rightarrow HNO_2 + H_2O$$

(*b*) $$HNO_2 + \tfrac{1}{2}O_2 \rightarrow HNO_3$$

$$NH_3 + 2O_2 \rightarrow HNO_3 + H_2O$$

3. Determine the ThOD.

$$\begin{aligned} \text{ThOD} &= (\tfrac{3}{2} + \tfrac{4}{2}) \text{ mol } O_2/\text{mol glycine} \\ &= 3.5 \text{ mol } O_2/\text{mol glycine} \times 32 \text{ g/mol } O_2 \\ &= 112 \text{ g } O_2/\text{mol glycine} \end{aligned}$$

Correlation Among Gross Measures of Organic Content. Establishment of constant relationships among the various measures of organic content depends primarily on the nature of the wastewater and its source. Of all the measures, the most difficult to correlate to the others is the BOD_5 test, because of the problems cited previously (see BOD discussion). For typical untreated domestic wastes, however, the BOD_5/COD ratio varies from 0.4 to 0.8, and the BOD_5/TOC ratio varies from 1.0 to 1.6. It should also be noted that these ratios vary considerably with the degree of treatment the wastewater has undergone. Because of the rapidity with which the COD, TOC, and related tests can be conducted, it is anticipated that more use will be made of these tests in the future.

Inorganic Matter

Several inorganic components of wastewaters and natural waters are important in establishing and controlling water quality. The concentrations of inorganic substances in water are increased both by the geologic formation with which the water comes in contact and by the wastewaters, treated or untreated, that are discharged to it [17,20]. The natural waters dissolve some of the rocks and minerals with which they come in contact. Wastewaters, with the exception of some industrial wastes, are seldom