

DETERMINATION OF ULTIMATE CARBONACEOUS BOD
AND THE SPECIFIC RATE CONSTANT (K_1)

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ABSTRACT

Ultimate carbonaceous biochemical oxygen demand (BOD_u) and the specific rate constant (K_1) at which the demand is exerted are important parameters in designing biological wastewater treatment plants and in assessing the impact of wastewater on receiving streams. An analytical method is presented which uses time-series concentrations of BOD, defined as the calculated sum of dissolved oxygen (DO) losses at each time of measurement, for determining BOD_u and K_1 . Time-series DO measurements are obtained from a water sample that is incubated in darkness at 20 degrees Celsius in the presence of nitrapyrin, a chemical nitrification inhibitor. Time-series concentrations of BOD that approximate first order kinetics can be analyzed graphically or mathematically to compute BOD_u and K_1 .

INTRODUCTION

Reliable biochemical oxygen demand (BOD) data are not only essential but the principal tool available for the rational design of biological wastewater-treatment plants and for assessing the impact of wastewater on receiving streams. However, the standard 5-day BOD, which is determined by subtracting the final concentration of dissolved oxygen (DO) from the initial concentration of DO after incubation of a sample for 5 days, does not provide the necessary information for making design decisions or for assessing the impact of wastewater on receiving streams. The cause and effect relationship cannot be defined. The needed information can be obtained from determinations of the ultimate carbonaceous BOD (BOD_u) and the specific rate constant (K_1) at which it is exerted. Stamer and others (1979a) have previously evaluated several methods of BOD_u determination. The determination of reliable BOD_u and K_1 values are important and indispensable parameters in mathematical modeling of DO regimes in rivers and estuaries, an integral part of the U.S. Geological Survey's River-Quality Assessment Program (Hines and others, 1978; Bauer and others, 1978; Stamer and others, 1979b). The purpose of this paper is to present an analytical method for determining BOD_u and K_1 .

DEFINITION OF BOD_u

BOD_u is defined as the total amount of DO consumed by heterotrophic organisms to oxidize decomposable carbonaceous material (Sawyer and McCarty, 1967). Phelps (1944) theorized that the rate at which biochemical oxidation proceeds is proportional to the remaining concentration of unoxidized carbonaceous material. In mathematical form this can be expressed as

$$\frac{dL}{dt} = -K_1 L \quad (1)$$

which may be integrated between the limits L_t and L_o to yield

$$\log_e \frac{L_t}{L_o} = -K_1 t \quad (2)$$

where, t is time, in days,

L_t is the concentration of remaining BOD_u , in milligrams per liter (mg/L) after t days,

L_o is the initial oxidizable concentration of BOD_u at $t=0$, and

K_1 is the specific rate constant, base e , in days⁻¹.

Equation (2) can be rewritten to express the amount of BOD_u exerted, y_t , as

$$y_t = L_o (1 - e^{-K_1 t}). \quad (3)$$

BOD_u and K_1 are determined in the laboratory usually at 20 degrees Celsius ($^{\circ}C$). As with most chemical reactions, K_1 is temperature dependent and can be corrected to in-stream water temperature using the equation (Velz, 1970)

$$(K_1)_T = (K_1)_{20^{\circ}C} 1.047^{(T-20^{\circ}C)} \quad (4)$$

where, $(K_1)_T$ is the specific rate constant at temperature, T , in $^{\circ}C$, and $(K_1)_{20^{\circ}C}$ is the specific rate constant at $T = 20^{\circ}C$.

ANALYTICAL METHOD FOR BOD_u AND K_1 DETERMINATIONS

1. Range of application

1.1 The method can be used to analyze natural waters, municipal wastewater, and some industrial wastewaters containing 0 to 7 mg/L BOD_u. Samples having a BOD_u ranging from about 7-40 mg/L require reaeration during the test. Samples having a BOD_u greater than about 40 mg/L require dilution and possible reaeration during the test.

2. Summary of method

2.1 Values of BOD_u and K_1 are determined on the basis of time-series DO measurements of a water sample. The sample is incubated in darkness at $20^{\circ}C$ in the presence of nitrapyrin, a chemical nitrification inhibitor. Concentrations of DO in the BOD samples are measured using a DO meter with a self stirring BOD bottle probe. The resulting time-series concentrations of BOD, defined as the calculated sum of DO losses at each time of measurement, can be analyzed graphically or mathematically to compute BOD_u and K_1 .

In the graphical technique, described by Lee (1951) and Velz (1970), time-series concentrations of BOD (in mg/L) are plotted on a linear Y-axis, and time (t), in days, is plotted on the X-axis, usually a 25.4-cm (10-in.) scale, which is proportioned according to $(1-e^{-K_1 t})$ for a specific value of K_1 . Time-series concentrations of BOD that decay at that specific rate will plot as a straight line on a graph for that K_1 value. Extrapolation to ultimate B of a best-fit straight line through the time-series concentrations of BOD results directly in the BOD_u value.

In the mathematical technique BOD_u and K_1 are computed using a non-linear least-squares method. The method uses a modified Newton iteration to minimize the sums of the squares of the deviations of the individual time-series concentrations of BOD from equation (3). A detailed derivation of the method is given in the Appendix. The non-linear least-squares method is ideally suited to machine computation and produces directly the optimum values of BOD_u and K_1 . Most desk-top computing systems have some means for displaying graphical results; this means should be used for comparing the observed and computed time-series concentrations of BOD.

3. Interferences

3.1 Wastewater discharges often contain residual chlorine, which can inhibit or cause a lag in the process of biochemical oxidation. Samples containing residual chlorine should be treated at the time of collection. (See step 6.1)

3.2 High concentrations of heavy metals, which include chromium, copper, lead, or mercury and other constituents such as iron, arsenic, or cyanide can inhibit the process of biochemical oxidation. Samples containing one or more of these constituents may require dilution or treatment.

3.3 Industrial wastewater discharges which are very acidic or alkaline can inhibit the process of biochemical oxidation.

4. Apparatus

4.1 Oxygen meter, (Yellow Springs Instrument Co.)^a, Model No. 54 or 57, equipped with Model No. 5720 self-stirring BOD bottle probe, or equivalent.

4.2 Barometer (altimeter), capable of being read to at least the nearest 5 millimeters of mercury, (Thommen Everest), Model No. 3011, or equivalent.

4.3 BOD bottle, 300 milliliters (mL) with ground-glass stopper, (Wheaton) "800", or equivalent. Bottles should be washed thoroughly before each test in an Alconox solution or equivalent, and rinsed with distilled water.

4.4 Overcap, plastic, for BOD bottles, to prevent evaporation of water seal during incubation, (Wheaton) No. 227720, or equivalent.

4.5 BOD incubator, (Precision) Model 815, or equivalent. The BOD incubator selected should meet the following general requirements:

Maintain a uniform temperature of $20^{\circ}\text{C} \pm 0.5^{\circ}\text{C}$.

Have a blower which will circulate air within the incubator.

Be thermostatically controlled.

Nominal capacity should be about 0.45 cubic meter to hold 300 BOD bottles.

4.6 Aquarium pump, (Silent Giant), or equivalent; plastic air tubing, air diffusion stones, and gang valve. The aquarium pump selected should be capable of driving about 10 air diffusion stones.

4.7 Thermometer, Celsius, with a range of about $5-50^{\circ}\text{C}$ with 0.5°C divisions, (H-B Instrument Co.) catalog No. 21223 1/2, or equivalent.

4.8 Aeration tube, plastic, about 8 centimeters long, tapered on both ends to fit a standard 300 mL bottle. The tapered tube can be produced easily by most machine shops from 2.54-centimeter outside diameter plastic

^aThe use of brand names in this report is for identification purposes only and does not imply endorsement by the U.S. Geological Survey.

pipe. The aeration tube is convenient for reaerating BOD samples of wastewater effluent during incubation when the DO in the BOD sample is near depletion. These samples generally foam during reaeration, and use of the aeration tube minimizes loss of sample volume as compared to reaerating with an aquarium pump equipped with air diffusion stones.

4.9 Glass beads, borosilicate, solid spherical, 5 millimeters in diameter, (Corning) 7268 or equivalent. The glass beads should be washed thoroughly in an Alconox solution or equivalent, and rinsed with distilled water before use.

4.10 Graduated cylinder, borosilicate, 250 mL volume with 2 mL subdivisions, (Corning) 3050, or equivalent.

4.11 Pipets, volumetric, borosilicate, capacities of 1-50 mL (Corning) 7100, or equivalent. Grind off about 3-4 millimeters of the tip to reduce errors associated with subsampling.

4.12 Spatula, micro, stainless, Fisher catalog No. 20-401-18, or equivalent.

5. Reagents

5.1 Nitrapyrin, 2 chloro-6 (trichloromethyl) pyridine, 96-percent pure. Nitrapyrin should be kept in a tightly sealed amber bottle.

5.2 Sodium sulfite-cobalt chloride solution: Dissolve 1 g of sodium sulfite (Na_2SO_3) and 1 small crystal (a few mg) of cobalt chloride (CoCl_2) in 1 liter of distilled water.

5.3 Sulfuric acid (1N): Add 28 mL of concentrated sulfuric acid (H_2SO_4) to about 900 mL of distilled water, mix and dilute to 1 liter.

5.4 Sodium hydroxide (1N): Add 40 g of sodium hydroxide (NaOH) to about 900 mL of distilled water, mix until dissolved, cool to about 20°C, and dilute to 1 liter.

5.5 Sodium sulfite solution (0.025N): Dissolve 1.575 g of anhydrous sodium sulfite (Na_2SO_3) in 1,000 mL of distilled water. The solution is not stable and should be prepared daily or as needed.

5.6 Dilution water: Native stream water of high quality should be used as dilution water for BOD_u test of wastewaters and natural waters containing high concentrations of BOD_u. Native stream water of high quality implies that: The water has a ready-made bacterial "seed" acclimated to the types of wastewater entering the stream, lake, or estuary; the concentration of BOD_u is low (less than about 2-3 mg/L); and the water contains no known interferences. Dilution water should be acclimated as given in step 5.7.

5.7 Collect several liters of dilution water, aerate to saturation at 20°C, and incubate at 20°C. Measure DO concentrations daily for about 3-5 days to insure that the BOD_u is low. The dilution water is then ready for use.

Procedure

6.1 If sample contains interferences, pretreat as described by the oxygen demand (biochemical) method (507) in "Standard Methods" (1975).

6.2 A decision must be made as to whether 300 mL or a lesser volume of sample is to be analyzed. The decision is based on estimates of the BOD_u , K_1 , and the desired frequency of making DO measurements on the sample. For example, no sample dilution would be required if the sample contained less than about 40 mg/L BOD_u , K_1 was less than about 0.14 day^{-1} , and DO measurements were made when $t = 0, 0.5, 1, 2, 3, 4, 5, 6, 8, 10, 12, 16,$ and 20 days. Figure 1 illustrates some general guidelines for sample dilutions based on a range of values of BOD_u and K_1 . Minimize sample dilution such that at least 4.0 mg/L of DO are depleted over the course of the test. When sample dilutions are required, make two dilutions, differing by a factor of 3 (for example, sample volumes of 50 and 150 mL).

6.3 Warm samples to $20^\circ\text{C} \pm 0.5^\circ\text{C}$. Insert air diffusion stone into the container and aerate sample, or deaerate sample if the sample is super-saturated, for about 10-15 minutes. Remove air diffusion stone and allow several minutes for excess air bubbles to dissipate.

6.4 For samples that do not require dilution, proceed to step 6.8.

6.5 Measure the amount of sample to be used in the determination using a volumetric pipet for sample volumes less than 50 mL or a graduated cylinder for sample volumes greater than 50 mL. Pour the sample from the graduated cylinder or drain the sample from the pipet carefully down the inside of a 300 mL BOD bottle.

6.6 Fill the remainder of the BOD bottle to the neck with dilution water, carefully pouring the dilution water down the inside of the BOD bottle. Avoid entrapment of air bubbles under the neck of the BOD bottle. If air bubbles become entrapped, tap the outside of the BOD bottle.

6.7 Prepare in triplicate BOD bottles containing only dilution water. Proceed to step 6.9.

6.8 Pour the sample carefully down the inside of a BOD bottle and fill to neck of bottle. Avoid entrapment of air bubbles under neck of the BOD bottle. If air bubbles become entrapped, tap the outside of the BOD bottle.

6.9 The DO meter with probe should be turned on for at least one hour before calibration, but not the stirring motor.

6.10 Calibrate the DO meter using a wet-all method as described in the instructions manual of the Yellow Springs Instrument Co.

6.10a Insert the probe into a BOD bottle containing about 50 mL of distilled water. Probe, BOD bottle, and distilled water should all be at room temperature.

6.10b Turn on the stirring motor.

6.10c Switch to the temperature position and read the temperature.

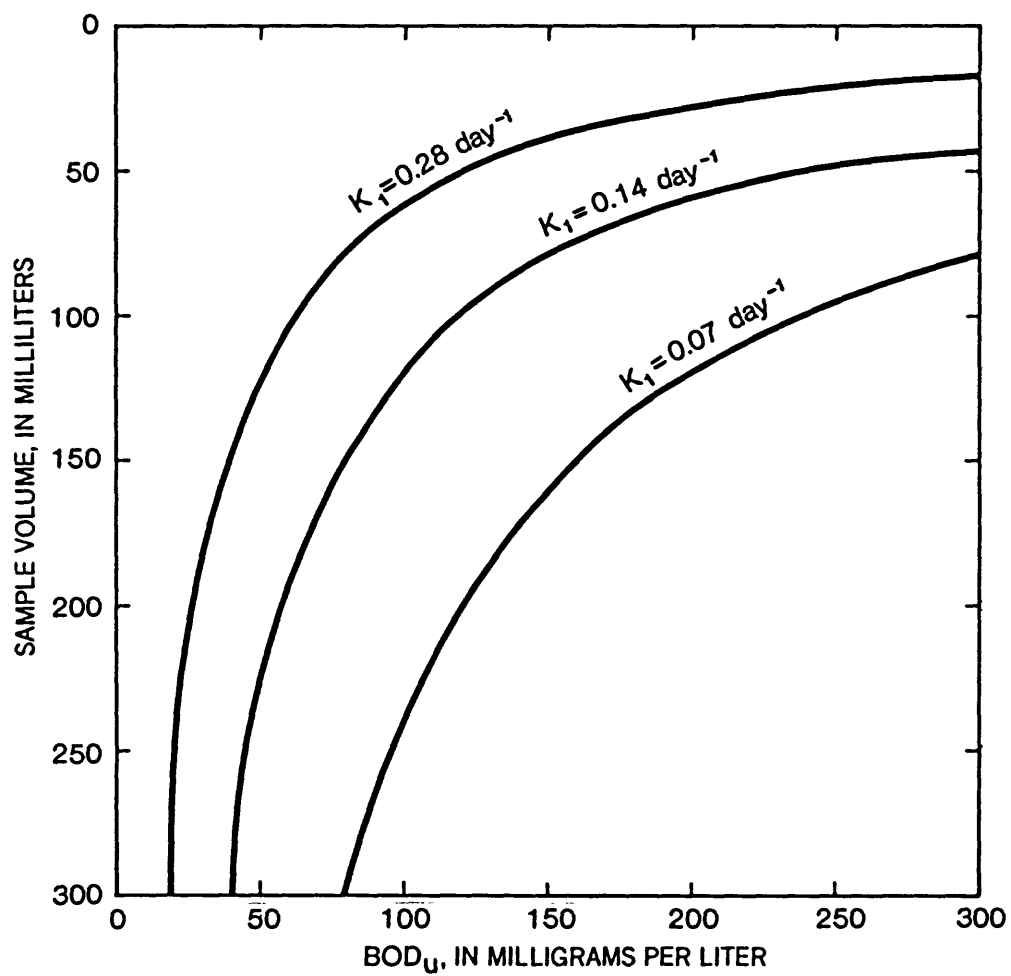


Figure 1.--Recommended sample volume to be added to a standard BOD bottle based on estimates of BOD_u and K_1 .

6.10d Determine the barometric pressure using the barometer.

6.10e Determine the solubility of oxygen, based on the temperature and barometric pressure from an oxygen-solubility table. (Manufacturer's instruction manual contains a table of oxygen solubilities at various temperatures and barometric pressures.)

6.10f Switch to calibration and position the needle to the correct DO reading using the calibration knob.

6.10g Turn off the stirring motor before removing the probe from the BOD bottle.

6.11 To measure concentration of DO of a sample, carefully insert the self-stirring probe into a BOD bottle to avoid entrapment of air.

6.12 Turn on the stirring mechanism.

6.13 Allow about 1-2 minutes for DO reading to stabilize.

6.14 Record the date, time, and DO concentration (in column titled "DISS O₂") on a form similar to that shown in table 1.

6.15 Turn off the stirring mechanism, remove the probe and rinse with distilled water.

6.16 Add about 3-5 small crystals of nitrapyrin to the BOD sample. Do not add further nitrapyrin during the incubation period.

6.17 Carefully insert the glass stopper and tip the BOD bottle to one side to check for trapped air. If an air bubble exists, remove the glass stopper and add just enough glass beads to displace it. Replace the glass stopper and check again for trapped air. If the bubble remains, add additional glass beads. If no bubble exists, create a water seal using distilled water and place overcap on the BOD bottle. Incubate the sample (in darkness) at $20^{\circ}\text{C} \pm 0.5^{\circ}\text{C}$.

6.18 After the initial DO reading, measure the DO concentration 10-12 times during the incubation period. Suggested incubation periods and measurements are: (1) 20-day incubation period with DO measurements made at $t = 0, 0.5, 1, 2, 3, 4, 5, 6, 8, 10, 12, 16,$ and 20 days and (2) 5-7 day incubation period with DO measurements at 12-15 hour intervals provided that the BOD reaction is proceeding normally (that is, no initial lag because of the presence of a substance toxic to the bacteria).

6.19 After each incubation period, remove the BOD bottle from the incubator, remove the plastic overcap, pour off the water seal, remove the ground-glass stopper and measure the DO concentration following steps 6.9 through 6.17.

Note - Carefully insert the calibrated DO probe (step 6.10a) into a BOD bottle during sequential measurements of DO concentrations to minimize loss of sample volume.

Table 1.--An example of a BOD work sheet

SAMPLE SOURCE			YEAR	MONTH	DAY	TIME	BOTTLE NO.	SAMPLE VOLUME	
Wastewater Plant No. 3			1979	02	27	1400	163	300 mL	
MONTH	DAY	TIME	ACCUMULATED TIME, IN DAYS	DISS. O ₂	REAERATION	DO LOSS	ACCUMULATED DO LOSS	TIME-SERIES BOD	
02	27	1620		9.0					
02	28	0905	0.7	5.8		3.2	3.2	3.2	
02	28	1840	1.1	4.0		1.8	5.0	5.0	
03	01	0900	1.7	1.7	8.6	2.3	7.3	7.3	
03	02	1125	2.8	4.8	8.0	3.8	11.1	11.1	
03	03	0900	3.7	5.1	8.2	2.9	14.0	14.0	
03	04	0855	4.7	5.4		2.8	16.8	16.8	
03	05	0900	5.7	2.7	8.4	2.7	19.5	19.5	
03	07	0730	7.6	4.7		3.7	23.2	23.2	
03	08	0500	8.5	3.4	8.5	1.3	24.5	24.5	
03	09	0505	9.5	7.4		1.1	25.6	25.6	
03	11	1010	11.7	5.4		2.0	27.6	27.6	

6.20 If the BOD sample does not require reaeration, (DO concentration will not fall below 2 mg/L by the next reading), then replace it in the incubator (as in step 6.17).

6.21 If the BOD sample requires reaeration (DO concentration may fall below 2 mg/L by next reading), use a reaeration tube as indicated in steps 6.22 to 6.24.

6.22 Place one end of the reaeration tube into the top of a clean empty BOD bottle, and place the other end into the top of the BOD sample bottle to be reaerated.

6.23 Hold the bottles, one in each hand, and vigorously shake the bottles back and forth for about 30 seconds.

6.24 Set the two bottles down, with the BOD sample bottle upright and allow time for the sample to drain back into original BOD sample bottle.

6.25 Allow time for the air bubbles in the sample to dissipate.

6.26 Measure the DO concentration (reaeration) and record results according to steps 6.9 through 6.17.

7. Calculations

7.1 Determine carbonaceous BOD_u and K_1 using either the graphical or mathematical techniques. Either technique provides concentrations of 5- and 20-day BODs.

7.2 To use the mathematical technique, proceed to step 7.12.

7.3 Calculate the accumulated time of incubation for each DO reading to the nearest 0.1 day in column titled "ACCUMULATED TIME, IN DAYS" (table 1) with accuracy to the nearest tenth of a day.

7.4 Calculate the "ACCUMULATED DO LOSS" equal to the oxygen demand exerted in the BOD bottle. See example in table 1. If dilution water was not used, these are the BOD values used to determine the specific rate constant, K_1 .

7.5 Calculate the "BOD of dilution water". If dilution water was used, these are the average values taken from the three BOD tests on dilution water only (see step 6.7).

7.6 Calculate the time-series concentrations of BOD of the sample when dilution water has been used from

$$BOD_s = \frac{300 BOD_B - (300 - V_s) BOD_D}{V_s}$$

where,

BOD_S = BOD of sample, in mg/L,

BOD_B = BOD of bottle, in mg/L,

V_S = Volume of sample used in bottle, in mL,

and, BOD_D = BOD of dilution water in mg/L.

Record the value in column "TIME-SERIES BOD" in table 1 and use these to determine the values of BOD_u and .

7.7 BOD_u and K_1 are determined using methods described by Lee (1951) and Velz (1970). The Lee (1951) grid is constructed with BOD concentration on a linear Y-axis and t (in days) on the X-axis (usually 25.4 cm), which is proportioned according to $(1 - e^{-K_1 t})$. For example, the plotting position of t on a 25.4-cm scale for $K_1 = 0.14 \text{ day}^{-1}$ is equal to 3.32 cm for $t = 1.0$ day, 12.79 cm for $t = 5.0$ days, 19.14 cm for $t = 10$ days, etc.

7.8 Prepare a series of the Lee (1951) grids in intervals of K_1 values of 0.10, 0.14, 0.18, and 0.22 day^{-1} should be suitable for most purposes.

7.9 Plot the time-series BOD concentrations from the BOD work sheet (table 1) on selected K_1 value for the data set is the grid on which the plotted data most nearly approximate a straight line. A plot that bends downward indicates that the K_1 selected is too low, and a plot that bends upward indicates that the K_1 selected is too high. Draw the best-fit straight line through the data points.

7.10 Extrapolate the best-fit straight line to ultimate t to determine BOD_u . Figure 2 shows a time-series plot (after Lee, 1951) of BOD concentrations as shown in the BOD work sheet.

7.11 Extrapolation of the line of best-fit toward zero t indicates whether the BOD reaction has proceeded normally from initial incubation. For example, an intercept on the X-axis indicates a lag, which could result from the presence of a toxin. An intercept on the Y-axis at zero indicates an immediate oxygen demand, which could result from excessive algal respiration or readily oxidizable substrates during the first days of incubation. In the case of a lag in the reaction, the value of the observed BOD_u does not change, but the course of the reaction is adjusted by drawing a straight line from the origin to the intersection of ultimate time and the observed BOD_u (C. J. Velz, written commun., 1980) (fig. 3). The time of each BOD observation is thereby adjusted by the period of time lag. Values of 5- and 20-day BODs can be read directly from the adjusted line. In the case of an immediate oxygen demand, the BOD_u is adjusted by drawing a straight line from the origin to ultimate t parallel to the line of best fit (fig. 4). BOD_u is determined from where the adjusted line intersects ultimate t . Values of 5- and 20-day BODs can be read directly from the adjusted line.

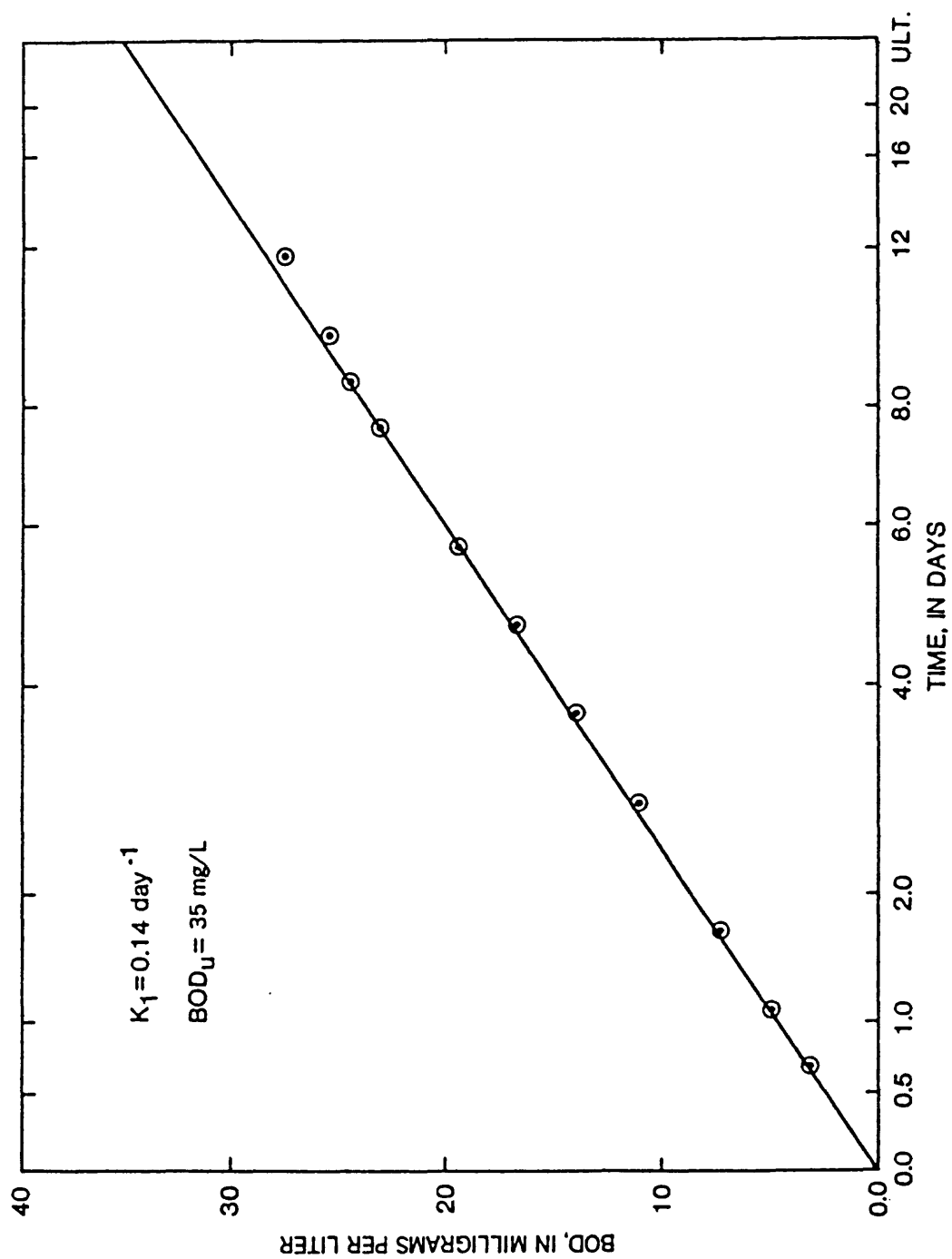


Figure 2. Time-series plot (after Lee, 1951) of BOD concentrations as shown in BOD work sheet.

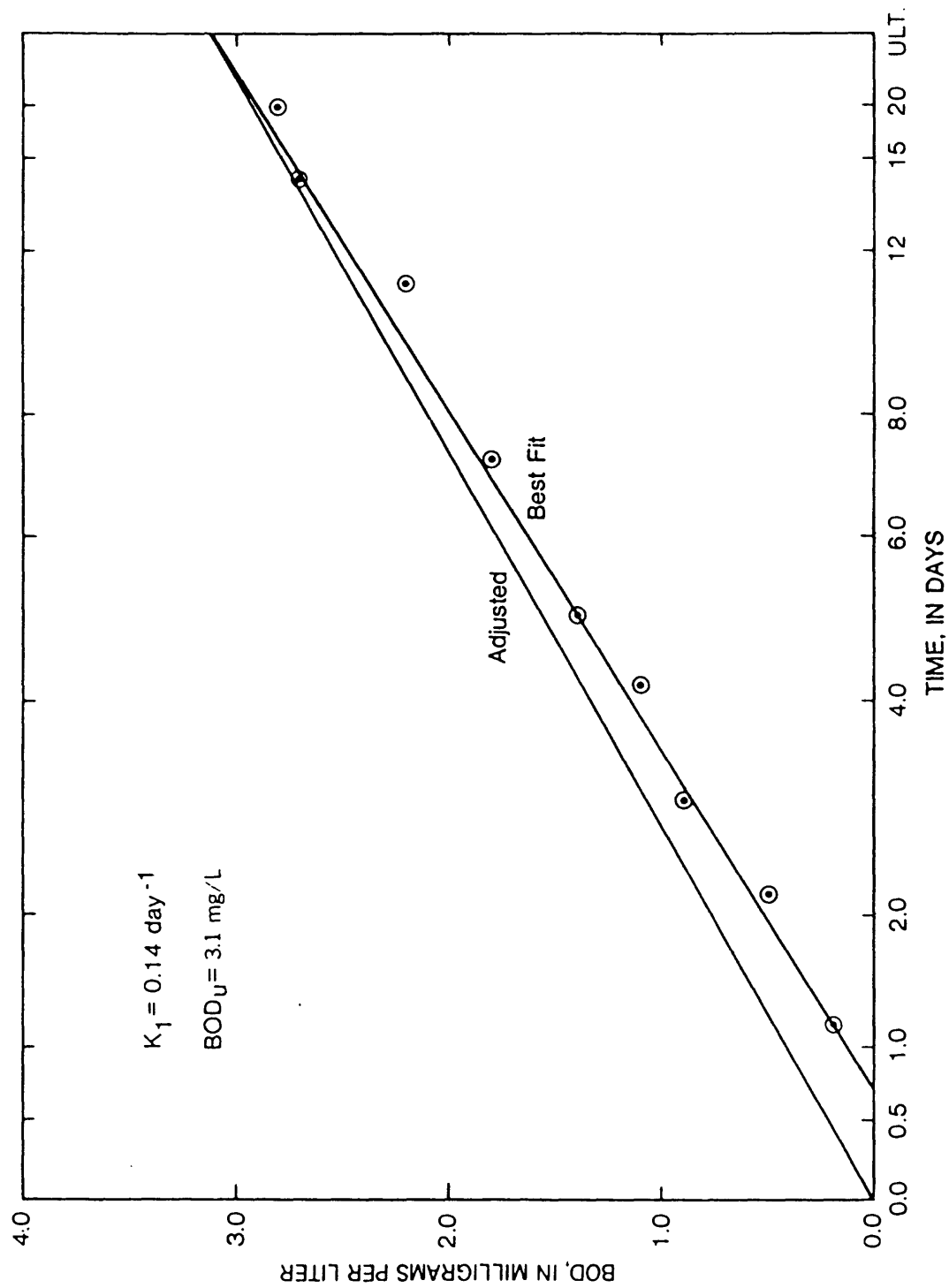


Figure 3.--Time-series plot (after Lee, 1951) of BOD concentrations showing a lag in the reaction.

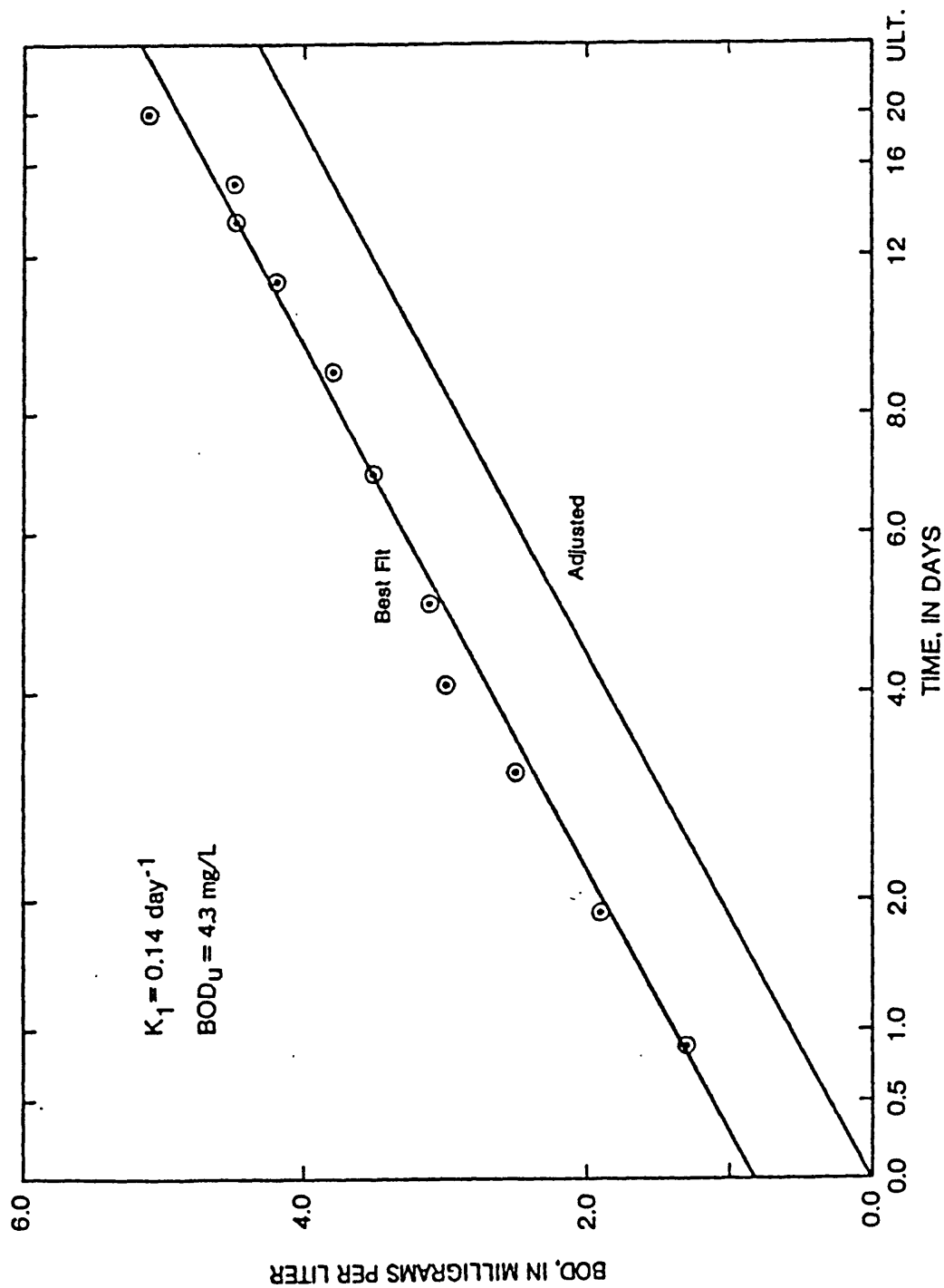


Figure 4. Time-series plot (after Lee, 1951) of BOD concentrations showing an immediate oxygen demand.

7.12 The mathematical technique derived in the Appendix is very stable but converges slowly (using as many as 200 iterations) and requires evaluation of several cumbersome summations. The technique is, therefore, probably not suitable for solution by hand-held calculator. However, it can be easily programmed for execution by a desk-top calculator and is ideally suited for solution by a larger computer in the interactive mode. The program can be made to accept the basic data, the month, day, time, dilutions, concentrations of DO before and after reaeration, and compute the series of measurement times and the corresponding time-series concentrations of BOD to be used in obtaining the optimized values of BOD_u (L_o) and K_1 . The obvious advantage of the technique is the speed at which the computations, such as accumulated time and DO losses, and plotting of the time-series concentrations of BOD can be executed. The danger lies in thoughtless application of the technique; that is, in blindly accepting the results of the fitting process without inspecting the data. Figure 5 shows an example of a non-linear least-squares fit of the time-series concentrations of BOD using the data shown in the BOD work sheet (table 1).

7.13 The abnormalities discussed in step 7.11 are usually manifested within the first two days of the BOD test. In the mathematical technique, equivalent results to the graphical technique can be obtained by omitting the first, then the second, and subsequent sets of DO measurements from the computation and fitting equation (3) to the remaining data. Based on equation (3), all fittings will yield the same values of K_1 but different values of L_o . Because this process simply shifts the origin for fitting, the "true" BOD_u can be obtained following each fitting exercise by simply multiplying the optimized values of L_o by $e^{K_1 \Delta t}$ where Δt is the amount of time the temporary origin was shifted away from the start of the incubation time. The solid lines of figures 6 and 7 were drawn using parameters obtained from non-linear least-squares fits to the data shown in figures 3 and 4, respectively.

7.14 When applying the mathematical technique, the best way to benefit from the above discussion is as follows: Apply the fitting procedure to all the data, then repeat the process omitting the first point, then the first two points, then the first three. If three of the best-fit values of K_1 so obtained are within 0.04 of each other, extrapolate to find the "true" BOD_u . If the value of K_1 are not consistent, continue omitting data points until a consistent pattern emerges; extrapolate to obtain the "true" BOD_u , or discard the data set. If the desk-top calculator or interactive system has a plotter, plot the final relationship along with the data to verify the fit.

8. Report

8.1 Report BOD_u concentrations to two significant figures.

8.2 Report values of K_1 to the log base e to the nearest 0.01 day⁻¹.

9. Precision

9.1 No precision data are available.

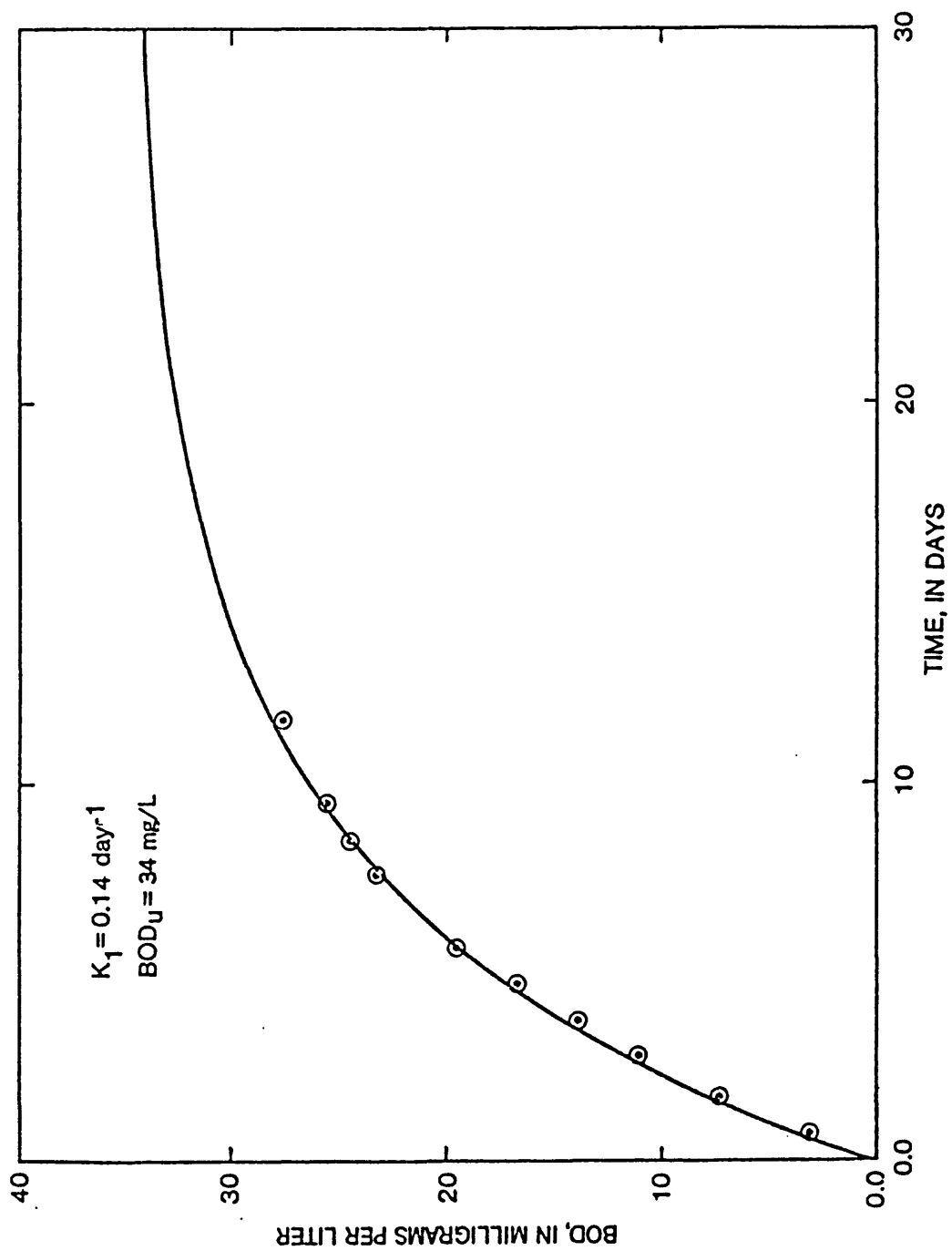


Figure 5. An example of a non-linear least-squares fit of the data from the BOD work sheet.

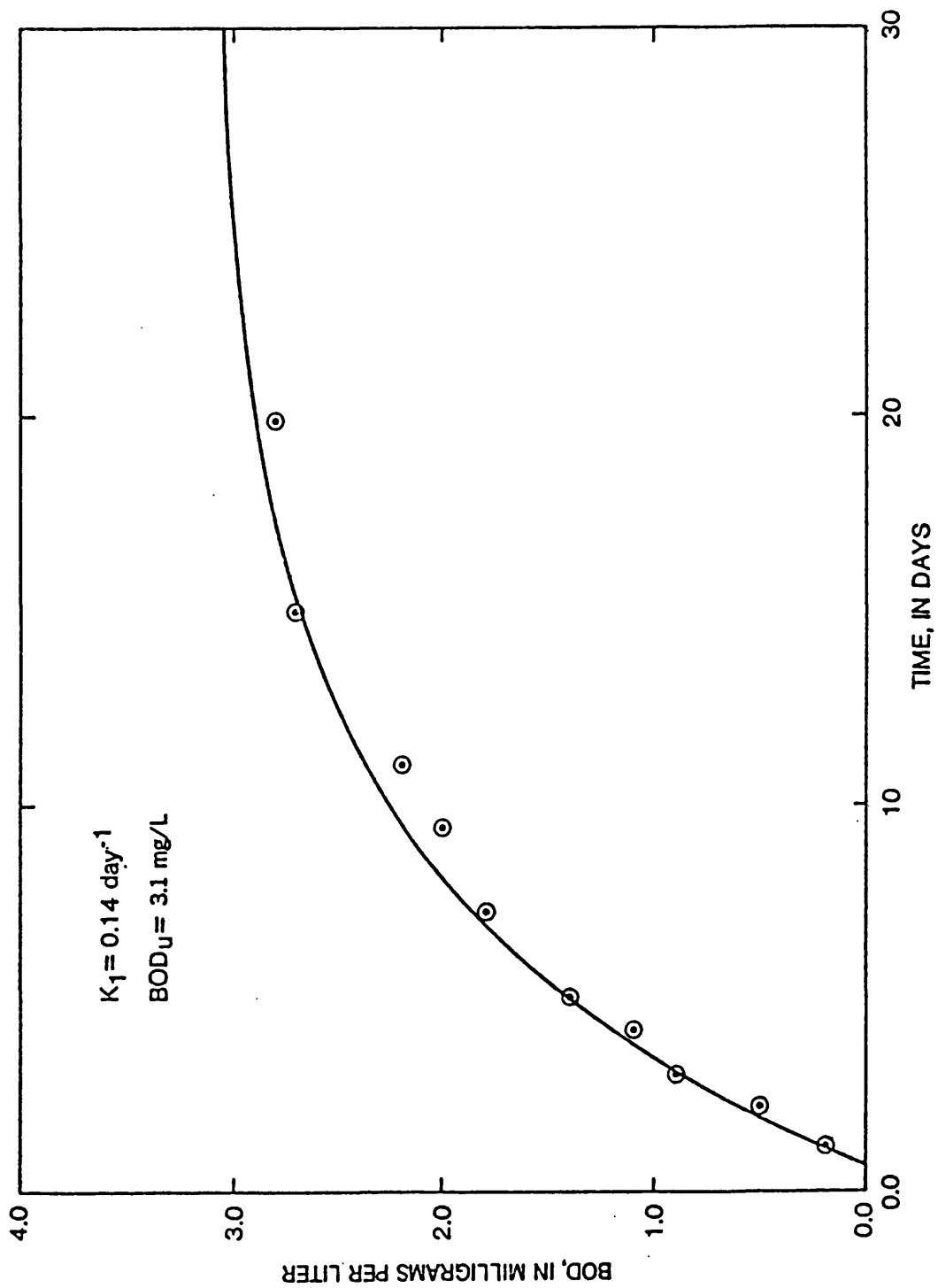


Figure 6. An example of a non-linear least-squares fit of the data shown in figure 3.

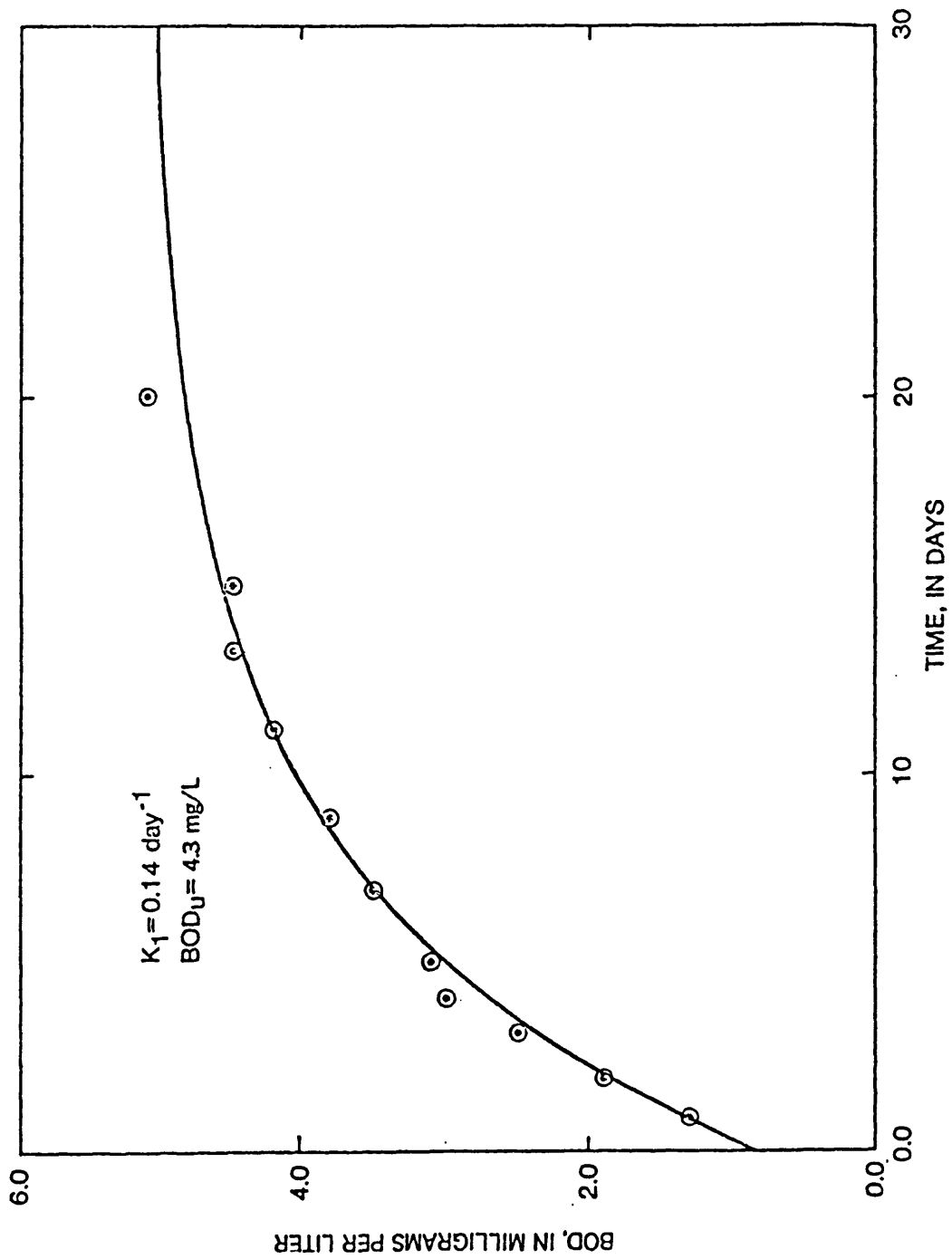


Figure 7. An example of a non-linear least-squares fit of the data shown in figure 4.

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APPENDIX

The mathematical technique is based on the premise that the best overall (optimum) fit of a set of data to a particular equation (model) is obtained by minimizing the sums of the squares of the deviations of the data from the equation. For the model given by equation (3), this is expressed as:

$$L_o \min_{K_1} \sum_{i=1}^n (y_{t_i} - y_{o_i})^2 = F \quad (A-1)$$

where y_{t_i} is the prediction of DO consumed, given by equation 3 for the i-th observation time, t_i , corresponding to the i-th observation y_{o_i} . The total number of observations is n. The above process will yield optimized values of L_o and K_1 .

The minimization (optimization) process in equation (A-1) is accomplished by solving for the values of the parameters L_o and K_1 , which jointly make the gradients of F with respect to these parameters equal to 0. That is solve

$$\frac{\partial F}{\partial L_o} = g = 0 = \sum_{i=1}^n (y_{t_i} - y_{o_i}) (1 - e^{-K_1 t_i}) \quad (A-2)$$

and

$$\frac{\partial F}{\partial K_1} = m = 0 = \sum_{i=1}^n (y_{t_i} - y_{o_i}) t_i e^{-K_1 t_i} \quad (A-3)$$

for L_o and K_1 . Equation (A-2) may be rewritten

$$0 = L_o \sum_{i=1}^n (1 - e^{-K_1 t_i})^2 - \sum_{i=1}^n y_{o_i} (1 - e^{-K_1 t_i}) \quad (A-4)$$

and solved directly for

$$L_o = \frac{\sum_{i=1}^n (1 - e^{-K_1 t_i})}{\sum_{i=1}^n (1 - e^{-K_1 t_i})^2} \quad (A-5)$$

The value given for L_o by equation (A-5) is the optimum value of BOD_u for any particular value of K_1 .

Equation (A-5) is not so readily solved for the remaining parameter K_1 , because it cannot be separated explicitly from the equation. In this situation, Newton Iteration can be used, however, to solve for K_1 . Express the $k + 1$ 'st estimate of $m=0$ as

$$m^{k+1} = 0 = m^k + \frac{\partial m^k}{\partial L_o} \Delta L_o + \frac{\partial m^k}{\partial K_1} \Delta K_1 \quad (\text{A-6})$$

where $\Delta L_o = L_o^{k+1} - L_o^k$, and $\Delta K_1 = K_1^{k+1} - K_1^k$ and the partial derivatives are computed using the values of the k -th estimates of the parameters, L_o^k and K_1^k . Rewriting equation (A-6)

$$K_1^{k+1} = K_1^k - \frac{m^k + \frac{\partial m^k}{\partial L_o} \Delta L_o}{\frac{\partial m^k}{\partial K_1}} \quad (\text{A-7})$$

where m^k is the (not necessarily 0) value obtained by evaluating equation (A-3) using the k -th level estimates of the parameters, and

$$\frac{\partial m^k}{\partial L_o} = \sum_{i=1}^n (1 - e^{-K_1^k t_i}) t_i e^{-K_1^k t_i} \quad (\text{A-8})$$

$$\frac{\partial m^k}{\partial K_1} = L_o \sum_{i=1}^n t_i^2 e^{-K_1^k t_i} (2e^{-K_1^k t_i} - 1) + \sum_{i=1}^n t_i^2 e^{-K_1^k t_i} y_{o_i} \quad (\text{A-9})$$

and ΔL_o is the difference between the value obtained from equation (A-5) and L_o^k .