THE DISSOLVED OXYGEN ANALYZER (Weston & Stack Inc., Model 300-B) METHOD FOR THE DETERMINATION OF THE BOD OF INCINERATOR QUENCH WATER

A Division of Research and Development
Open-File Report (RS-03-68-17)

U.S. DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
Public Health Service

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written by
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Public Health Service
Environmental Health Service
Bureau of Solid Waste Management
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PREFACE

In publishing an analytical method which employs specific brands of laboratory supplies and instrumentation, the U.S. Public Health Service does not imply that other commercial products could not be utilized with appropriate modifications in the procedure.

INTRODUCTION

The analysis of an aerated, diluted sample for its BOD involves the determination of its dissolved oxygen content before and after an incubation period. The difference between the initial dissolved oxygen and the final oxygen content represents the oxygen demand of the sample.

The oxygen demand of incinerator quench water* (or similarly polluted water) is exerted by three classes of materials: (a) carbonaceous organic material usable as a food source by aerobic organisms; (b) oxidizable nitrogen derived from nitrite, ammonia, and organic nitrogen compounds which serve as food for specific bacteria (e.g. Nitrosomonas and Nitrobacter); and (c) certain chemical reducing compounds (e.g. ferrous iron, sulfite, and sulfide) which will react with molecularly dissolved oxygen. Since the oxidation of nitrogeneous materials may proceed at a variable rate, the nitrification process is inhibited, thus restricting the BOD determination to the organic carbon present. The water sample is acidified to pH 2 to 3 and subsequently neutralized to accomplish the inhibition of the nitrification.

Complete stabilization of a given sample may require an overly long incubation period for practical purposes. The 5-day incubation period has been accepted as standard. For certain industrial wastes, however, it may be advisable to determine the oxidation curve . Conversion of data from one incubation period to another can only be made if such special studies are carried out. Studies in recent years have shown that the exponential rate of carbonaceous oxidation at 20C rarely has a value of 0.1, but may

*Quench water refers to water which has been employed to cool the non-combustibles after emergence from the furnace.

vary from less than one-half to more than twice this value. This fact usually makes it impossible to calculate the ultimate carbonaceous demand of a sample from 5-day BOD values unless the exponential rate value has been determined on the contaminated water under consideration.

Since incinerator quench water may contain many variables which affect the Winkler Method of analysis, the Dissolved Oxygen Analyzer Method is recommended for BOD analysis of all quench water sample. The Alsterberg (Azide) Modification of the Winkler Method is recommended for standardization of the Analyzer using the relatively pure dilution water. Preliminary tests, which show the validity of the Winkler DO value, are discussed in the section on the Winkler Method.

The sampling location at each site is very important in the evaluation of the data. The sampling site should be chosen on the basis of obtaining the most representative sample.

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DISCUSSION

The Weston and Stack Dissolved Oxygen Analyzer utilizes a specially designed probe to measure accurately and quickly the amount of dissolved oxygen in gas streams and liquids. The probe is constructed of cast-epoxy and is separated from the sample by a semipermeable membrane.

The Analyzer is powered by A.C. or internal batteries and is ruggedly constructed and moisture-proof to facilitate laboratory or field use. Interferences in water or gas samples are minimal with this instrument. Hydrogen sulfide does not interfere, but will eventually corrode the lead anode. The probe will then require cleaning. Dissolved or suspended solids will not affect the probe provided the analyzer is calibrated using a similar type of sample to account for partial pressure changes. Laboratory tests have reaffirmed that this probe is not affected by ferrous or ferric iron, sulfite, or nitrite.

Since temperature affects the rate of diffusion of dissolve oxygen through the Teflon® membrane, the probe output for a given concentration of dissolved oxygen is a function of the temperature. A secondary resistance to oxygen diffusion exists at the Teflon®-aqueous sample interface. The interfacial resistance is of minor significance when the sample is vigorously agitated to produce a high degree of turbulence. Also, a high degree of turbulence is imperative for the temperature compensation to function satisfactorily.

Temperature compensation in the Weston and Stack Analyzer is accomplished by an operational amplifier. A thermistor (resistor whose resistivity varies intensely with temperature) and resistance network introduced in the feedback circuit for the amplifier provides suitable multiplication so that temperature effect on the probe is limited to ± 2% over the temperature range of 0 to 50C when suitable turbulence is provided.

The probe must be calibrated by the Winkler Method to enable the analyst to read the true ppm DO directly off the instruments scale. This calibration, although normally needed only once a month, preferably should be checked at the beginning and ending of each 5-day incubation period.

Although a probe output can be obtained for any element or compound which diffuses through the semipermeable (Teflon®) membrane and is reduced at a potential of -0.578 volts or less, interferences of this nature appear to be infrequent. Sulfite, nitrite, ferrous and ferric iron, and other reducing and oxidizing substances which normally interfere with the Winkler Method, apparently do not affect the output of this probe. There are a few substances, however, which affect the probe's sensitivity over a period of time. Hydrogen sulfide and chlorine, although not detected by the probe, will react with the lead anode and cause a decline in sensitivity. Greases and oils will coat the semipermeable memberane, increase the diffusion resistance and decrease the probe output. Variations in dissolved solids will alter the partial pressure of

oxygen in the aqueous samples and hence the probe output. The calibration and utilization of the instrument should be accomplished with these facts in mind.

APPARATUS

Requirements

1. Analyzer, Weston and Stack, Model 300-B: 0-15, 0-1.5 ppm, temperature compensation and temperature readout. A.C. powered with internal combination power supply battery charger.
2. Probe, Weston and Stack, Model A-30 BOD agitator-thermistor assembly.
3. Accessory Kit: membranes, electrolyte, syringe, manual, recorder, plug.
4. Extra membranes: Teflon®, 1/2 mil thick, 3" square; 24 per package.
5. Graduates: 50 ml, 1 liter, and 2 liter.
6. Beakers: 250 ml, 2 liter, and 3 liter.
7. Siphon tubing.
8. Rubber bands.
9. BOD bottles, 300 ml capacity.
10. Analytical balance.
11. Volumetric flasks: 100 ml, 500 ml, and 5 - one liter.
12. pH paper: range 2 through 9.
13. Air incubator or waterbath, thermostatically controlled at 20C ± 1C.
14. Carboy, polyethylene nalgene, wide mouth, two - 2 gallon (7 liters or more).
15. Test tube with 14 mm I.D.
16. Magnetic stirrer with Teflon®- coated stirring bar.
17. Stopwatch or accurate watch with second hand.
18. Pipets, graduated or volumetric, two - 2ml.

19. Reagent bottles, resistant glass, narrow mouth with ground glass stoppers, 1 liter capacity, at least one amber in color.
20. Sample collection bottles, polyethylene (or similar non-breakable bottle) with narrow mouth and tightly fitting caps, about 1 liter (or one quart) capacity, sterile.
21. Regulator, 2-stage, with cylinder valve outlet for nitrogen (CGA No. 580).
22. Ice chest, capable of holding several one liter sample collection bottles and maintaining a 5C temperature for 24 hours.

Preparation and Maintenance

Probe. Membrane Installation. Since the performance of the probe is dependent upon a properly installed membrane, the analyst should exercise great care in performing the following instructions:

Procedure	Comments
1. Remove the probe shield and thermistor housing, electrolyte fill screw, and old membrane from the probe.	1. See Figure 1 for identification of probe components.
2. Wrap a rubber band around a test tube, having a 14 mm I.D.	2. See Figure 2(a-f) for the diagrammatic representation of steps #2, 6, 7, 9, 10 and 12.
3. Hold the test tube in an upright position by encircling it with the fingers and thumb of one hand.	3. The open end of the test tube should be flush with the forefinger.
4. Place one membrane sheet over the top of the test tube and fist.	

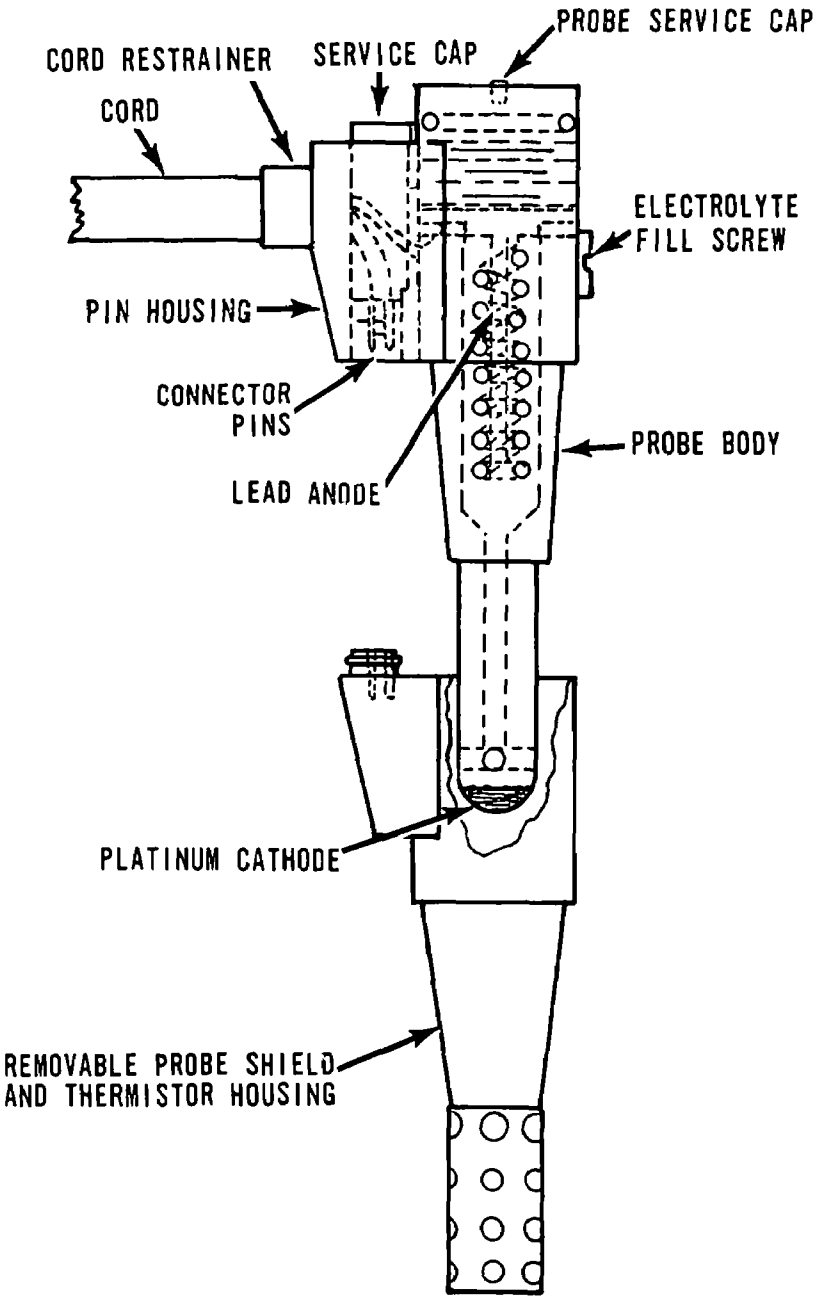
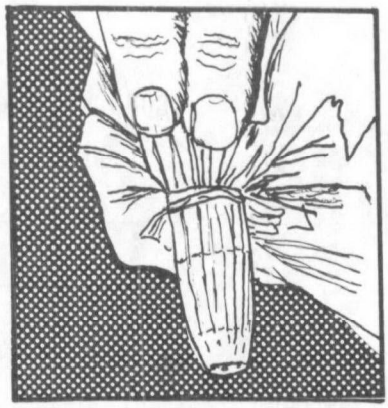
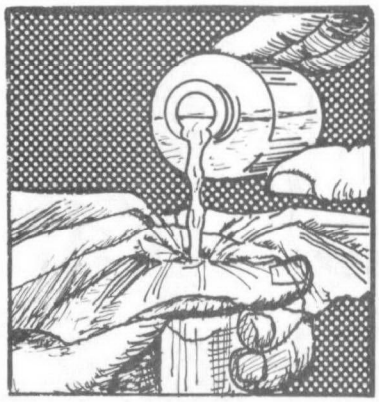


Figure 1. THE PROBE.
(Reproduced with the permission of Weston and Stack, Inc.)

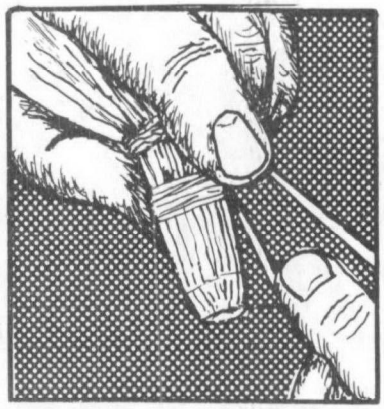
a. Step #2: Position of the rubber band on the test tube.



d. Step #9: Drawing up the membrane to provide a snug fit across the face of the platinum tip.

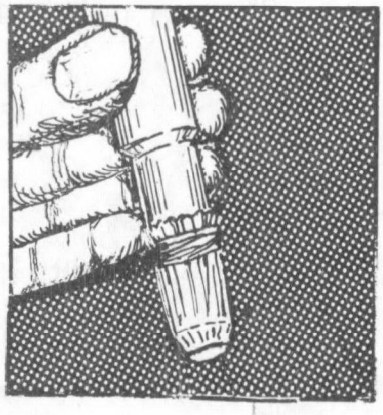


b. Step #6: Pouring the electrolyte into the depressed membrane.



e. Step #10: Wrapping a second rubber band around the probe just above the small holes.

c. Step #7: Pressing the membrane down into the tube with the probe.



f. Step #12: The probe after the removal of the upper rubber band and the trimming of the membrane.

Figure 2. MEMBRANE INSTALLATION PROCEDURE.
(Drawings reproduced with the permission of Weston and Stack, Inc.)

Procedure	Comments
5. Gently depress the membrane about one inch into the tube.	
6. Pour electrolyte into the depression.	6. See preparation of electrolyte.
7. Press the membrane down into the tube with the probe.	7. Do this carefully so the membrane is not damaged. Keep air bubbles from being trapped between the probe and membrane.
8. Slip the rubber band off the tube and over the membrane to a point 1/2 inch above the holes near the tip of the probe.	8. Remove the tube.
9. Carefully draw up the membrane to provide a snug fit.	9. It is necessary to have a close, smooth fit over the platinum electrode without stretching or tearing the membrane.
10. Wrap a second rubber band as tightly as possible just above the holes.	10. Apply securely to prevent leakage of electrolyte from membrane.
11. Remove the first (top) rubber band.	
12. Trim membrane close to and above the second rubber band.	

Procedure	Comments
13. Use the syringe to completely fill the cavity in the probe with electrolyte.	13. The probe should be held upright.
14. Shake and tap the probe so that air bubbles will escape from the fill hole.	14. Thumb is held over fill hole during shaking.
15. Replace the fill screw and probe shield.	
16. Connect the probe to the readout instrument and turn the meter to the "ON" position and the selector switch to "DO-MULT 1" position.	16. See Figure 3 for the location of components of the instrument.
17. Hold the probe with platinum electrode up and shake it vigorously.	17. If the meter needle oscillates, air bubbles are present and steps #14 through #17 must be repeated.

Detection of Membrane Perforation. When a hole developes in the membrane, the response rate of the probe decreases as the electrolyte is diluted and the cathode is poisoned. To assure the proper performance of the probe, frequent inspections of the membrane should be performed:

Procedure	Comments
1. Hold the membrane end of the probe in a beaker containing clear water.	1. If the membrane was installed recently, the probe should be rinsed thoroughly to remove electrolyte which may be trapped in the folds of the membrane.

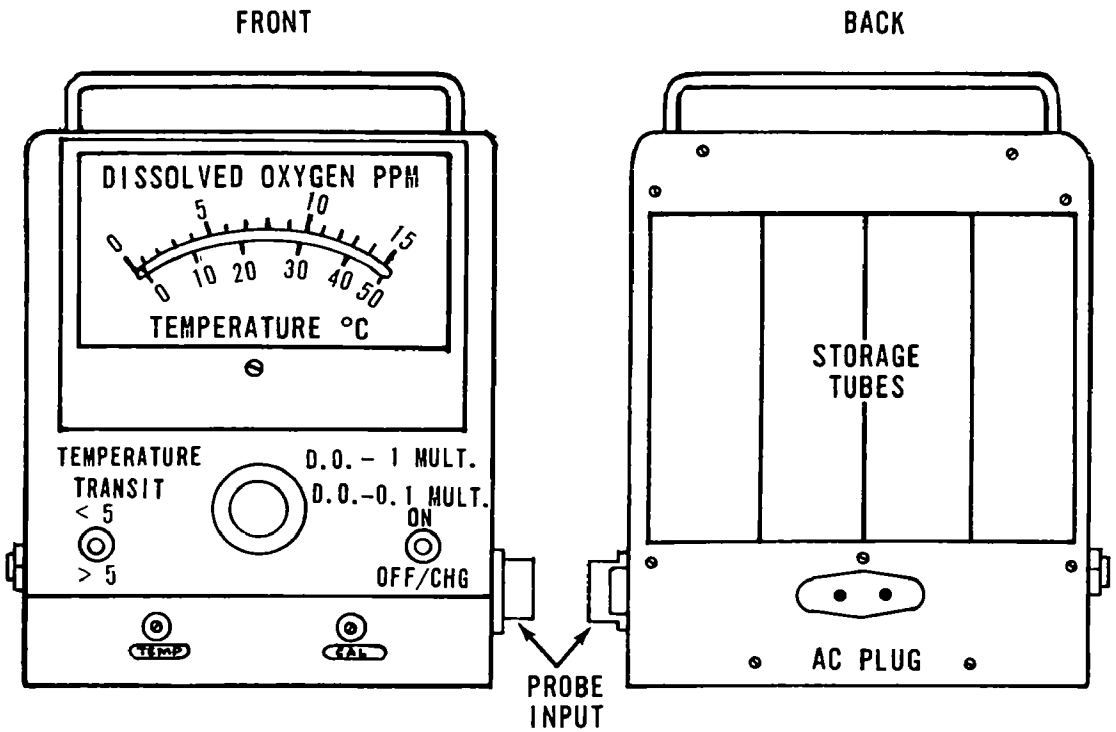


Figure 3. FRONT AND BACK VIEWS OF THE ANALYZER.
(Reproduced with the permission of Weston and Stack, Inc.)

2. While looking through the water towards a light source search for a small stream (diffused light) of electrolyte floating through a hole in the membrane.	2. If a hole is detected a new membrane must be installed.

Servicing a Contaminated Probe. Upon setting for a few months with electrolyte, the inner parts of the probe become contaminate and may not allow any calibration adjustment to be made or readout needle drifting downwards. The procedure for cleaning a probe is as follows:

Procedure	Comments
1. Remove the probe shield and thermistor housing, membrane, electrolyte fill screw, and probe service cap screw (may use quarter coin).	1. See Figure 1 for identification of probe parts.
2. Turn probe upside down and shake out the lead anode.	
3. Clean the lead anode by immersing it in warm 10 percent NaOH (or HCl) solution, then rinse thoroughly with distilled water.	3. All the yellow deposit must be removed.
4. Clean the platinum electrode and the inside of the probe body with 6N(1:1)HCl, then rinse thoroughly with distilled water.	4. The lead anode will not seat properly or make contact if the lead ring inside the probe is not completely clean.

5. Polish the platinum cathode with a soft tissue.	
6. Reassemble lead anode and probe service cap.	6. Use a small amount of silicon grease on the threads and the "O" ring.
7. Install a new membrane as previously directed.	7. See section on Membrane Installation.

Glass and Plastic Apparatus. Sampling bottles, tubing, containers, and the like must be thoroughly cleaned (sterile) to assure the removal of materials capable of exerting a BOD. Detergents may be used if cleaning is followed by thorough rinsing with distilled water.

Recharging Batteries. The Weston and Stack Dissolved Oxygen Analyzer, Model 300-B, is provided with an internally combined AC power supply and battery charger. The instrument can be operated in the laboratory directly on 110 AC or in the field using the rechargeable nickel cadmium batteries. When the instrument is employed in the field, a record of the hours of amplifier usage should be maintained. Before each standardization of the instrument in the laboratory or utilization in the field, the analyst should then check his record. If the amplifier usage $\geq$ 20 hours, the batteries should be recharged, as follows:

Procedure	Comments
1. While operating the instrument on 110 AC, place the selector switch in the "DO-Mult 1" position.	1. See Figure 3 for the location of the components of the instrument.
2. Turn the power switch to the "OFF/CHG" position.	

3. Determine if a charge is coming from the batteries.	3. The meter needle should respond and possibly oscillate. If no response occurs check the 12V batteries and connections. Replace components if necessary.
4. Place selector switch in the "Transit" position and recharge the batteries for a maximum of 10 hours.	4. Rechargeable batteries last about three years.

NOTE: The 30 V battery is not rechargeable and last about six months.

REAGENTS

Chemical Requirements

The following chemicals are ACS, Reagent Grade:

1. Potassium iodide
2. Sodium sulfite
3. Sodium hydroxide
4. Hydrochloric acid, concentrated
5. Sulfuric acid, concentrated
6. Phosphate buffer solution, pH 7.2 (or prepared)
7. Potassium phosphate, monobasic
8. Potassium phosphate, dibasic
9. Sodium phosphate, dibasic, heptahedrate, crystal
10. Ammonium chloride
11. Magnesium sulfate, crystal
12. Calcium chloride, anhydrous

13. Ferric chlroide, lumps
14. Manganese(ous) sulfate, monohydrate
15. Potassium hydroxide
16. Nitrogen, 99.9 percent pure.

Preparation of Solutions

The water employed in the preparation of solutions must be distilled from a block tin or all-glass still, contains less than 0.01 mg/liter copper, and be free of chlorine, chloramines, caustic alkalinity, organic materials, and acids.

Solutions are prepared as follows:

1. Electrolyte solution: Dissolve 50.0 g of potassium iodide in distilled water and dilute with same to 100 ml. Store solution in a dark brown bottle. (8 oz. bottles of this solution may be purchased from either the Weston and Stack Company, 1426 Lewis Lane, West Chester, Pennsylvania, 19380 or their Ohio representative, Henry P. Thompson Co., 4866 Cooper Road, Cincinnati, Ohio, 45242).
2. Sodium sulfite solution: Dissolve about five grams of sodium sulfite in 500 ml of distilled water.
3. Sodium hydroxide solution, approximately 1N: Dissolve 41.6 grams NaOH in distilled water and dilute with same to one liter.
4. Sulfuric acid solution, approximately 1N: Cautiously add 28 ml of concentrated H_2SO_4 to distilled water and dilute with same to one liter.

5. "Dilution Water": To one liter of distilled water at 20C, add 1 ml of each of the following solutions: Phosphate buffer solution, pH 7.2; magnesium sulfate solution (22.5 g Mg $SO_4 \cdot 7H_2O$ per liter of solution); calcium chloride solution (27.5 g anhydrous $CaCl_2$ per liter of solution); ferric chlroide solution (0.25 g $FeCl_3 \cdot 6H_2O$ per liter of solution).
6. Sodium hydroxide solution, 10% (w/v): Dissolve 10.0 g NaOH in distilled water and dilute with same to 100 ml.
7. Phosphate buffer solution, pH 7.2 may be purchased already prepared or prepared as such: Dissolve 8.5 g KH_2PO_4, 21.75 g K_2HPO_4, 33.4 g $Na_2HPO_4 \cdot 7H_2O$, and 1.7 g NH_4Cl in 500 ml distilled water and dilute with same to one liter. The pH of this buffer should be 7.2 without further adjustment.
8. Hydrochloric acid solution, 10 percent (v/v): Cautiously add 10 ml concentrated HCl (sp. gr. 1.19) to 75 ml distilled water and dilute with the latter to 100 ml.
9. Hydrochloric acid solution, 5N: Cautiously add 42.8 ml concentrated HCl (sp. gr. 1.19) to 40 ml distilled water and dilute with the latter to 100 ml.
10. Manganous sulfate solution, 0.25 M: Dissolve 21.13 g $MnSO_4 \cdot H_2O$ in distilled water and dilute with same to 500 ml.
11. Potassium hydroxide solution, 0.5M: Dissolve 14.03 g KOH in distilled water and dilute with same to 500 ml.

SAFETY PRECAUTIONS

Follow general laboratory safety rules. This method has no pronounced safety hazards.

CALIBRATION

Zero Adjustment of Amplifier

To insure the proper amplification of the temperature-compensated signal from the probe, the output of the amplifier should first be adjusted to zero while the probe is inserted in a solution containing no dissolved oxygen. The procedure is as follows:

Procedure	Comments
1. Set the selector switch to "Transit" and power switch to "OFF/CHG".	1. See Figure 3 for the location of components of the instrument.
2. Using the unmarked screw on the meter face, set the meter needle to zero.	2. Adjustment may not be necessary.
3. Place the probe in the sodium sulfite solution for 2 minutes or longer	3. Use regular BOD bottle to contain the solution.
4. Set the selector switch to "DO-Mult 1" and turn the Analyzer "ON" for a period of at least 2 minutes.	4. The agitator should be employed.
5. Adjust the meter reading to zero using the zero-adjustment screw, marked "zero", on the front of the instrument case.	

6. Remove the probe from the sulfite solution and rinse the membrane thoroughly with distilled water.	6. Keep the probe in BOD bottle of clean distilled water when not in use.

Temperature Compensation of the Probe's Output

A thermistor (resistor whose resistivity varies intensely with temperature) and resistance network introduced into the feedback circuit of an operational amplifier provides the temperature compensation of the probe's output. The compensation is accurate to ± 2 percent over a sample temperature range of 0 to 50C. However, an adjustment is necessary if sample temperature varies more than 5C from the temperature of the probe. The adjustment is as follows:

Procedure	Comments
1. If the probe and sample are not essentially the same temperature (within 5C) then move front-left-switch (marked >5 & <5) to the >5 position.	1.a) See Figure 3 for the location of the switch. b) Analyzer may be used to check temperatures of room and sample. (see Sample Analysis).
2. If the probe and sample are near the same temperature (within 5C) then move above switch to the <5 position.	2. Normally this step is applied.

Temperature Scale

Regular Adjustment of the Bridge Potential. The temperature scale of the instrument is calibrated at the factory and in normal operation should not require re-calibration. The thermometer circuit is, however, designed as an unbalanced bridge, whose potential is supplied by a 30 volt-battery. Regular (each day of use) adjustments of the bridge potential should, therefore, be performed as follows:

Procedure	Comments
1. Turn the selector switch to "Temperature."	1. See Figures 3 and 4 for the location of the switch and other components of these instructions.
2. Press the "Temp Test" button.	2. The resistor's activity is equivalent to the thermistor's resistance at 50C.
3. While pressing the "Temp Test" button, adjust the potentiometer by turning the "Temp Adj. Screw" until the needle indicates exactly 50C.	3. If the needle can not be adjusted to 50C, the probe may need cleaning or the 30 volt-battery may need replacement.
4. Release the "Temp Test" button.	4. The Analyzer is now indicating temperature correctly.

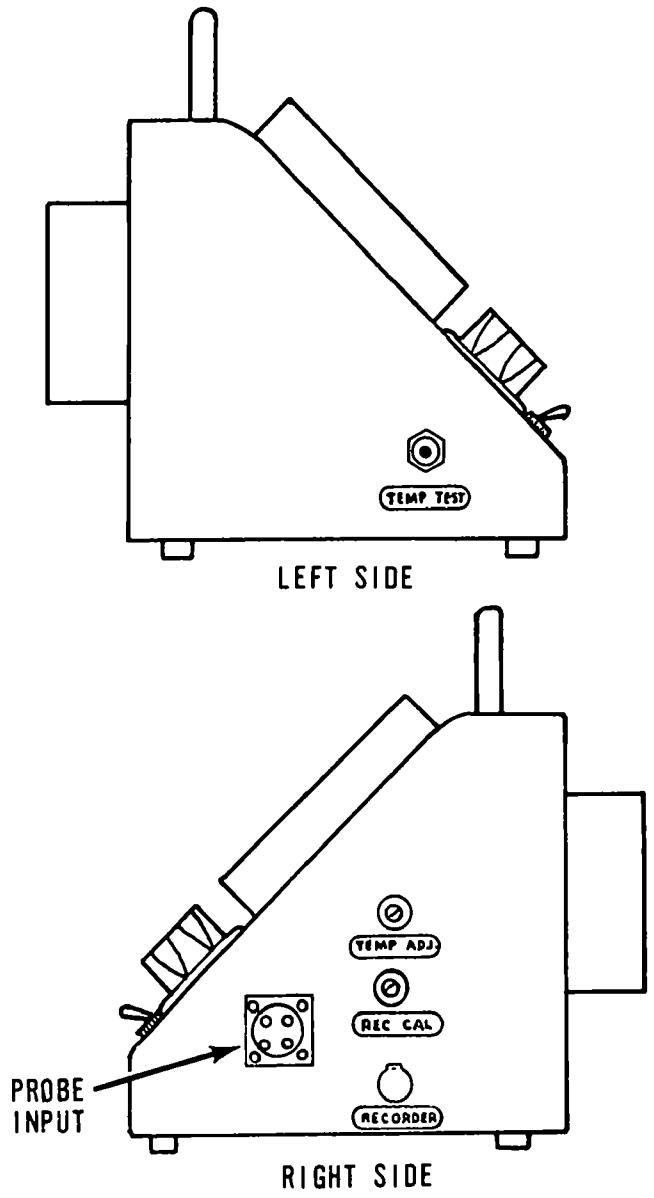


Figure 4. SIDE VIEWS OF ANALYZER. (Reproduced with the permission of Weston and Stack, Inc.)

Special Adjustment of the Bridge Potential. When a resistance component in the temperature bridge is replaced, the temperature scale must be recalibrated. The special potentiometer adjustments are as follows:

Procedure	Comments
1. With the power switch in the "OFF/CHG" position and the selector switch in the "Transit" position, adjust the meter to zero using the unlabeled screw on the meter face.	1. See Figures 3 and 4 for the location of the components of the instrument.
2. Assemble probe and thermistor housing.	
3. Connect the probe cable to connector.	3. Connector located on right side of instrument case.
4. Remove the back cover of the instrument by removing all eight screws.	
5. Locate the three potentiometer adjustment screws inside the unit.	5. Facing the back of the unit, four small screws, aligned in a horizontal line, are immediately beneath the handle attachment. The multiplier adjustment screw is the one on the far left, the others are the potentiometer screws.

6. Immerse the probe into a 0 C bath consisting of distilled water and finely crushed ice, then agitate the probe assembly.

6.a) The temperature of the bath should be checked with an accurate thermometer.

b) Equilibrium should be reached after 5 to 10 minutes.

7. Still agitating the probe, turn the potentiometer screw which is farthest to the right (facing the back of the Analyzer) until a reading of 0 C is obtained on the meter.

8. Repeat the procedure with a water bath at 50C and the meter reading adjustments with the "Temp Adj." screw only.

8. "Temp Adj" screw is located on the left side (Figure 4) of the instrument case.

9. While pushing on the "Temp Test" button, turn the second from right (facing the back of the Analyzer) potentiometer screw until the meter reads 50C.

10. Using a 25C water bath, compare the meter temperature reading to an accurate thermometer. If there is an error, readjust potentiometer adjustment screw farthest to right (facing the back of the Analyzer).

10. The third potentiometer adjustment screw, which is located right of the multiplier adjustment screw, should never be turned.

Probe

Various DO Saturation Levels. Before employing the Analyzer and preferably each day it is used (never longer than three weeks), the analyst should calibrate the probe with samples whose DO concentration have been determined by the Alsterberg (Azide) Modification of the Winkler Method.

The dissolved oxygen probe is a partial pressure device; this means that the transfer of dissolved oxygen through the semi-permeable membrane is a function of the ratio of dissolved oxygen concentration to dissolved oxygen concentration at saturation. For example, when a salt solution is saturated with oxygen at 20C, it may contain only 3 ppm of dissolved oxygen; water, however, when saturated with oxygen at 20C will contain 9.2 ppm of dissolved oxygen. Since the rate of oxygen transfer through the membrane would be the same in both cases, the probe output would be the same. The probe must therefore be calibrated using a liquid similar to the sample to be analyzed. Since "quench water" is greatly diluted with "dilution water" before analysis, the calibration of the probe, before analyzing general "quench water" samples, should be performed with "dilution water". The probe must be calibrated each day it is used. If the membrane has been replaced the calibration of the probe will change slowly for a period of about 24 hours before becoming stabilized. If the probe is used during the period, frequent calibration checks will be required.

The probe must be calibrated to the specific turbulence of the system. Since the Weston & Stack BOD Agitator is used, the agitation is built into the probe assembly. Therefore, when calibration is performed, it is applicable for any container or use to which the BOD Agitator may be applied.

NOTE: The Modified Winkler Method must be established before the probe can be calibrated.

Procedure	Comments
1. Saturate a liter of "dilution water" with oxygen.	1. This may be done by pouring the water forth and back from a graduate to a beaker at least three times.
2. Siphon the aerated water from the beaker into each of 3 BOD bottles.	2. During the siphoning, the water should be continuously stirred using a magnetic mixer and a Teflon®-coated magnetic bar.
3. Using the Analyzer and probe, determine the DO and temperature of one of these aerated samples.	3. See "Determination of the DO Concentration."
4. Adjust the calibration screw so the Analyzer reads the same ppm DO as observed in Table 1 for the sample temperature.	4.a) See Figure 3 for the location of "Cal" screw. b) An exact DO concentration at 20C and zero chloride concentration is 9.1%.

Table 1. SOLUBILITY OF OXYGEN IN WATER EXPOSED TO WATER-SATURATED AIR*

Temp. °C	Chloride Concentration in Water—mg/l					Difference per 100 mg Chloride
	0	5,000	10,000	15,000	20,000	
	Dissolved Oxygen—mg/l (ppm)					
0	14.6	13.8	13.0	12.1	11.3	0.017
1	14.2	13.4	12.6	11.8	11.0	0.016
2	13.8	13.1	12.3	11.5	10.8	0.015
3	13.5	12.7	12.0	11.2	10.5	0.015
4	13.1	12.4	11.7	11.0	10.3	0.014
5	12.8	12.1	11.4	10.7	10.0	0.014
6	12.5	11.8	11.1	10.5	9.8	0.014
7	12.2	11.5	10.9	10.2	9.6	0.013
8	11.9	11.2	10.6	10.0	9.4	0.013
9	11.6	11.0	10.4	9.8	9.2	0.012
10	11.3	10.7	10.1	9.6	9.0	0.012
11	11.1	10.5	9.9	9.4	8.8	0.011
12	10.8	10.3	9.7	9.2	8.6	0.011
13	10.6	10.1	9.5	9.0	8.5	0.011
14	10.4	9.9	9.3	8.8	8.3	0.010
15	10.2	9.7	9.1	8.6	8.1	0.010
16	10.0	9.5	9.0	8.5	8.0	0.010
17	9.7	9.3	8.8	8.3	7.8	0.010
18	9.5	9.1	8.6	8.2	7.7	0.009
19	9.4	8.9	8.5	8.0	7.6	0.009
20	9.2	8.7	8.3	7.9	7.4	0.009
21	9.0	8.6	8.1	7.7	7.3	0.009
22	8.8	8.4	8.0	7.6	7.1	0.008
23	8.7	8.3	7.9	7.4	7.0	0.008
24	8.5	8.1	7.7	7.3	6.9	0.008
25	8.4	8.0	7.6	7.2	6.7	0.008
26	8.2	7.8	7.4	7.0	6.6	0.008
27	8.1	7.7	7.3	6.9	6.5	0.008
28	7.9	7.5	7.1	6.8	6.4	0.008
29	7.8	7.4	7.0	6.6	6.3	0.008
30	7.6	7.3	6.9	6.5	6.1	0.008
31	7.5					
32	7.4					
33	7.3					
34	7.2					
35	7.1					
36	7.0					
37	6.9					
38	6.8					
39	6.7					
40	6.6					
41	6.5					
42	6.4					
43	6.3					
44	6.2					
45	6.1					
46	6.0					
47	5.9					
48	5.8					
49	5.7					
50	5.6					

*At a total pressure of 760 mm, Hg. Under any other barometric pressure, P (mm, or P', in.), the solubility, S' (mg/l), can be obtained from the corresponding value in the table by the equation:

$$S' = S\frac{P-p}{760-p}$$

in which S is the solubility at 760 mm (29.92 in.) and p is the pressure (mm) of saturated water vapor at the temperature of the water. For elevations less than 3,000 ft and temperatures below 25°C, p can be ignored. The equation then becomes:

$$S' = S\frac{P}{760} = S\frac{P'}{29.92}$$

Dry air is assumed to contain 20.90 per cent oxygen. (Calculations made by Whipple and Whipple).

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5. Determine the DO of the same sample using the Modified Winkler Method.	5. See Modified Winkler Method (Bibliography).
6. Using the Analyzer and probe, determine the DO of the second aerated sample.	
7. Considering the difference between the Analyzer and Modified Winkler Method with the first aerated sample, adjust the calibration screw.	
8. Determine the DO of the same sample using the Modified Winkler Method.	
9. The third aerated sample is used as a re-check of the calibration point. If the calibration screw needs more adjustments, then more aerated sample should be prepared and analyzed until the calibration screw does not need adjustment.	9. After calibration the probe should always be kept in a BOD bottle filled with distilled water to prevent air bubbles from entering the probe.

Having performed the above calibration procedure, the probe has now been calibrated at the upper and lower (zero adjustment of amplifier) DO saturation limits. The Analyzer's DO measurements are linear between

these limits; however, the analyst may wish to verify the DO readings between these limits. This may be done by performing the probe calibration as just described except allowing pure nitrogen to bubble, for about 15 to 30 minutes, through the aerated samples before the DO analysis. This treatment with nitrogen gas will lower the saturated oxygen concentration to about 3 to 4 ppm. The nitrogen gas will not interfere with the Modified Winkler's DO analysis.

System of Known DO Depletion Capability. The calibration procedures described thus far are usually employed only in the laboratory. The following method is applicable both in the laboratory and in the field where regular calibration procedures would be difficult to perform. This method utilizes a system of known oxygen depletion capability to evaluate indirectly the probe's response below the saturation level. It is not a true probe calibration method. The probe or Analyzer must first be calibrated by comparison to the Modified Winkler Method then, while being operated in the field, can easily be checked for performance by the following method.

Procedure	Comments
1. Prepare 3 BOD bottles of aerated water samples as previously described in the probe calibration procedures.	
2. Using the Analyzer and probe, determine the DO of one of these aerated samples.	2. See "Determination of the DO Concentration."
3. Remove the probe and rinse it with distilled water.	3. When the probe is not being used, keep it in a BOD bottle which is filled with distilled water.

4. To the same BOD bottle, using a volumetric pipet, add 2 ml of 0.25 M manganous sulfate solution.	4. The tip of the pipet should be placed beneath the surface of the sample.
5. Immediately initiate the addition of 2 ml of 0.5 M potassium hydroxide solution; record the exact time of initiation.	5.a) Use a volumetric pipet. b) Use a stopwatch or other accurate device to measure exactly the 10-minute reaction period.
6. After the KOH has been added, stopper the bottle and mix the contents by repeated inversions.	
7. After not more than 8 minutes have elapsed, insert the probe into the BOD bottle.	7. Equilibrium is attained in about two minutes.
8. After exactly 10 minutes have elapsed since the addition of the KOH solution, record the DO concentration.	
9. Repeat steps #2 through #8 with the other two prepared BOD bottles.	
10. Determine the depletion of DO for each sample by substracting the final ppm DO from the initial observation.	10. The average depletion should be 3.60 $\pm$ 0.25 ppm. If the depletion is not this value, re-check calibrations; the instrument may have to be returned to the manufacturer.

ANALYSIS OF SAMPLES

Sample Collection

Site Selection. When the BOD of quench water is measured to determine the amount of oxidizable wastes that will be discharged to a sewerage system serving an incinerator facility or a drainage system associated with the residue disposal area, the site of sample collection must be chosen with due consideration. Settlement tanks, surface pools, sewers, and other areas immediately adjacent to the sewage or drainage system are preferable collection sites.

Sample Size and Container. Normally 50 ml of sample is needed to perform the BOD analysis; however, since various dilutions may be needed and a larger sample size may be more representative, it is recommended to collect one liter quench water sample.

The samples should be collected in sterile, non-breakable bottles with narrow mouths and caps which can be tightly fitted. The sample bottle should be completely filled. All containers must be thoroughly rinsed, especially if cleaned with a detergent, before they can be reused.

Samples should not be collected on Monday or Tuesday unless the analysts are to work on Saturday or Sunday (5-day BOD).

Sample Preservation and Shipment

If the sample analysis is to be initiated within four hours after collection, sample preservation measures are not absolutely necessary. However, if initiation of the analysis will be started after four hours, samples, soon after collection, should be placed in an ice chest (or similar container) so that the samples are maintained in the dark at 5C. The bottle caps must be tightly fitted to prevent an increase in oxygen solubility with the reduction in temperature.

Sample shipment to the laboratory should be immediate and via air freight if necessary to insure the initiation of BOD analysis in the laboratory within 24 hours of sample collection. Samples received more than 24 hours old should not be analyzed.

Since the Analyzer requires calibration, the laboratory personnel should be informed at least two days before the arrival of samples. Because samples require some preparation before the actual analysis and the exact dilution requirements may not be known, samples (not at 5C) should be shipped to the laboratory so that they are received at least two hours before the end of the normal working day. Samples shipped in an ice chest (5C) and refrigerated may be analyzed the following day provided the analysis can be initiated before the samples are 24 hours old.

Sample (and Blank) Preparation

Adjustment for Nitrification Process. Prior to analysis each sample (and "dilution water" blank) is treated as follows to inhibit the nitrification process:

Procedure	Comments
1. Place 50 ml of a thoroughly mixed quench water sample in a 250 ml beaker.	1. The exact volume of quench water sample depends upon the dilution requirements. See "Dilution and Aeration."
2. Using pH paper, check the pH of the sample.	2. Usually the pH is about 11.
3. Using 1N NaOH or 1N H_2SO_4, adjust the pH of the sample to a range of 2 to 3; maintain pH for 15 minutes.	3. Omit if the sample already has a pH of 2 to 3.
4. Then neutralize the sample to a pH of 6.5 to 8.3.	4. Employ the same 1N solutions as in step 3.

Adjustment for Residual Chlorine. Chlorine, at concentrations normally found in chlorinated water and sewage effluent, does not influence the probe output nor the determination of oxygen. Chlorine will react with lead and hence cause the probe sensitivity to decrease after long exposure. Since residual chlorine dissipates when samples stand for 1 to 2 hours or they are well aerated, no adjustments are therefore recommended.

Dilution and Aeration. Prepared samples must be diluted in order to obtain a measurable depletion (2 ppm to 7 ppm) of oxygen at the end of the 5-day incubation period. Since incinerator quench water usually has a BOD of 100-300 ppm, a suitable or applicable dilution is 50 ml of sample diluted to 2 liters. If the analyst suspects that the BOD of the quench

water differs from the usual value, he should test various dilutions since the analysis cannot be repeated upon the same original sample after the 5-day waiting period. To obtain more reliable results, 3 BOD bottles should be prepared, 3 for the initial DO and the same 3 for the final DO and the final DO values should never be less than 1.0 ppm.

Since the dilution water, employed in the analysis of each quench water, may contain a few oxidizable materials capable of exerting a small BOD, each quench water analysis should include a blank evaluation, i.e., a determination of the BOD of the dilution water. The observed BOD of the quench water can then be corrected by substracting the appropriate proportionate fraction of this blank value.

The dilution and aeration procedures are as follows:

Procedure	Comments
1. Pour the total prepared sample from the 250 ml beaker into a 2 liter graduate and dilute to the mark with "dilution water."	1. Solution still represents 50 ml of original sample.
2. Aerate the sample by pouring it forth and back from the graduate into a 3 liter beaker at least 3 times.	2. Dilution water blank is aerated in like manner.
3. Siphon the diluted aerated sample (or blank) from the beaker and into 3 BOD bottles.	3. The sample should be stirred continuously using a magnetic stirrer and a Teflon® coated magnetic bar.

4. The DO concentration of the sample (or blank) in the 3 BOD bottles should be determined immediately.	4.a) See "Determination of the DO Concentration." b) Only two reasonable DO results are needed. See "Precision."
5. Then put the same 3 BOD bottles in an incubator (or waterbath) and determine their DO content after a 5-day incubation period at 20C.	5.a) During the incubation period the samples should not be exposed to the light. b) See "Determination of the DO Concentration" c) Only two reasonable DO results are needed. See "Precision."

Determination ~~the~~ of the DO Concentration

As shipped, the Analyzer has the components necessary for operation. Before attempting to place the analyzer into service, check to ascertain that: 1) the membrane is free of holes, 2) the needle zeroes correctly, 3) the temperature reading is correct, and 4) the probe is free of air bubbles.

Procedure	Comments
1. Turn the toggle switch located in the lower left hand corner of the front panel to "<5".	1. In most cases the entire body of the probe is essentially at the temperature of the sample. If the probe body temperature varies more than 5°C from the sample temperature, turn the toggle switch ">5".

2. Turn the selector switch to "DO-Mult 1."
3. Turn toggle switch located in front lower right hand corner of case to "ON".
4. Insert probe into BOD bottle.
4. The agitator should be operating.
5. Wait 2 minutes for equilibrium and then read ppm dissolved oxygen directly on top scale.
5.a) Record value.
b) The absolute value of the difference between duplicated readings should not exceed $1.96\sqrt{2}s$, or 0.58 ppm, more than 5% of the time. See "Precision".
6. If temperature of the sample is desired, turn selector switch to "Temp" and read temperature (C) directly on the bottom scale.
6.a) Record value.
b) Accuracy is ± 1C.
7. Turn toggle switch (right hand corner) to "OFF" and selector switch to "TRANSIT".
7. Perform this step if the meter is not to be used for several hours.

CALCULATIONS

BOD of Dilution Water

The following formula should be employed to calculate the BOD of each individual sample of "dilution water."

$$BOD_1 = D_1 - D_2$$

Where: BOD_1 = The biochemical oxygen demand of dilution water

D_1 = The dissolved oxygen content of initial (before incubation) dilution water

D_2 = The dissolved oxygen content of final (after incubation) dilution water

BOD of Quench Water

The initial DO concentration minus the final DO concentration equals BOD of the diluted sample. The BOD of the diluted sample times the dilution factor equals the BOD of the original sample.

The dilution factor is found by dividing the original amount of sample taken into the final dilution as: 50 ml of sample diluted into # 2 liters gives a factor of 40.

The following formula should be employed to calculate the BOD of each indidivual sample of quench water.

$$BOD_2 = F[(D_3 - D_4) - P_1(BOD_1)]$$

Where: BOD_2 = The biochemical oxygen demand of quench water

F = The dilution factor

D_3 = The dissolved oxygen content of initial (before incubation) quench water

D_4 = The dissolved oxygen content of final (after incubation) quench water

P_1 = The decimal fraction of dilution water used in the BOD analysis of the quench water

METHOD EVALUATION

Precision

After analyzing a number of "quench water" samples, in duplicate (three determinations were performed to ensure reasonable duplicate results), the precision of the observations were evaluated by calculating (using Olivetti Programma 101) the pooled standard deviation of all observations, except those obtained on samples collected from dump truck drainage. The results of these calculations are shown in the following table.

Accuracy

There is no standard with which the accuracy of the determination can be measured. The accuracy of the instrument is 1% of the reading and is better than ± 0.1 ppm

Sensitivity

This DO Analyzer method is not applicable to samples with a dilution factor of 40, having a 5-day BOD value of 23.5 ppm or less.

TABLE 2

PRECISION OF THE DO ANALYSIS[a]

Number of Determinations[b]	Pooled Standard Deviation(s)[c]	Confidence Interval $\pm 1.96\sqrt{2}$ (s)[d]
82	0.21	$\pm$ 0.58

PRECISION OF THE BOD ANALYSIS

Number of Determinations	Standard Deviation(s)[e]	Dilution Factor[f]	Confidence Interval $\pm 1.96(40)S$[g]
20	0.30	40	$\pm$ 23.5

[a]Assistance in the statistical analysis was provided by the Statistical Section, Operational Analysis Branch, Division of Technical Operations, BSWM.

[b]Normally at least two initial and three final determinations were made for each sample.

[c]A pooled standard deviation was computed for all determinations. It was assumed that there was no statistically significant difference between initial and final variances, i. e. homogeneity of the variances was assumed.

[d]The absolute value of the difference between duplicated readings should not exceed $1.96\sqrt{2}(s)$, or 0.58 ppm, more than 5% of the time. The covariance between the duplicated readings was ignored.

[e]The standard deviation of the difference between initial and final DO readings, (i.e., $S=\sqrt{(s^2 + s^2)}$. In this calculation it was assumed that the initial and final pooled variances were equal and the covariance term between initial and final readings was ignored.

[f]Dilution factor may vary, but for calculation purposes the normal dilution factor is shown here.

[g]95% confidence limits about a single BOD result, assuming a standard dilution factor of 40 or 2.5 percent dilution.

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