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AMERICAN SOCIETY FOR TESTING AND MATERIALS
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Standard Test Methods for Dissolved Oxygen in Water [1]

This standard is issued under the fixed designation D 888; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reapproval.

This standard has been approved for use by agencies of the Department of Defense. Consult the DoD Index of Specifications and Standards for the specific year of issue which has been adopted by the Department of Defense.

1. Scope

1.1 These test methods cover the determination of dissolved oxygen in water. Two test methods are given as follows:

	Range, mg/L	Sections
Test Method A—Titrimetric Procedure–High Level	>1.0	8 to 14
Test Method B—Instrumental Probe Procedure	0.05 to 20	15 to 23

1.2 The precision of Test Methods A and B was carried out using a saturated sample of reagent water. It is the user's responsibility to ensure the validity of the test methods for waters of untested matrices.

1.3 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.* For a specific precautionary statement, see Note 17.

2. Referenced Documents

2.1 *ASTM Standards:*

D 1066 Practice for Sampling Steam[2]

D 1129 Terminology Relating to Water[2]

D 1193 Specification for Reagent Water[2]

D 2777 Practice for Determination of Precision and Bias of Applicable Methods of Committee D-19 on Water[2]

D 3370 Practices for Sampling Water from Closed Conduits[2]

E 200 Practice for Preparation, Standardization, and Storage of Standard and Reagent Solutions for Chemical Analysis[3]

3. Terminology

3.1 *Definitions*—For definitions of terms used in these test methods, refer to Terminology D 1129.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *amperometric systems,, n*—those instrumental probes that involve the generation of an electrical current from which the final measurement is derived.

3.2.2 *instrumental probes,, n*—devices used to penetrate and examine a system for the purpose of relaying information on its properties or composition. The term probe is used in these test methods to signify the entire sensor assembly, including electrodes, electrolyte, membrane, materials of fabrications, etc.

3.2.3 *potentiometric systems,, n*—those instrumental probes in which an electrical potential is generated and from which the final measurement is derived.

4. Significance and Use

4.1 Dissolved oxygen is required for the survival and growth of many aquatic organisms, including fish. The concentration of dissolved oxygen may also be associated with corrosivity and photosynthetic activity. The absence of oxygen may permit anaerobic decay of organic matter and the production of toxic and undesirable esthetic materials in the water.

5. Purity of Reagents

5.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society. [4] Other grades may be used if it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.1.1 Reagent grade chemicals, as defined in Practice E 200, shall be used unless otherwise indicated. It is intended that all reagents conform to this standard.

5.2 Unless otherwise indicated, reference to water shall be understood to mean reagent water conforming to Type II of Specification D 1193.

6. Sampling

6.1 Collect the samples in accordance with Practices D 1066 and D 3370.

[1] These test methods are under the jurisdiction of ASTM Committee D-19 on Water and are the direct responsibility of Subcommittee D19.05 on Inorganic Constituents in Water.

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[2] *Annual Book of ASTM Standards*, Vol 11.01.

[3] *Annual Book of ASTM Standards*, Vol 15.05.

[4] *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

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6.2 For higher concentration of dissolved oxygen, collect the samples in narrow mouth glass-stoppered bottles of 300-mL capacity, taking care to prevent entrainment or solution of atmospheric oxygen.

6.3 With water under pressure, connect a tube of inert material to the inlet and extend the tube outlet to the bottom of the sample bottle. Use stainless steel, Type 304 or 316, or glass tubing with short neoprene connections. Do not use copper tubing, long sections of neoprene tubing, or other types of polymeric materials. The sample line shall contain a suitable cooling coil if the water being sampled is above room temperature, in which case cool the sample 16 to 18°C. When a cooling coil is used, the valve for cooling water adjustment shall be at the inlet to the cooling coil, and the overflow shall be to a point of lower elevation. The valve for adjusting the flow of sample shall be at the outlet from the cooling coil. The sample flow shall be adjusted to a rate that will fill the sampling vessel or vessels in 40 to 60 s and flow long enough to provide a minimum of ten changes of water in the sample vessel. If the sampling line is used intermittently, flush the sample line and cooling coil adequately before using.

6.4 Where samples are collected at varying depths from the surface, a special sample bottle holder or weighted sampler with a removable air tight cover should be used. This unit may be designed to collect several 250 or 300 mL samples at the same time. Inlet tubes extending to the bottom of each bottle and the water after passing through the sample bottle or bottles displaces air from the container. When bubbles stop rising from the sampler, the unit is filled. Water temperature is measured in the excess water in the sampler.

6.5 For depths greater than 2 m, use a Kemmerer-type sampler. Bleed the sample from the bottom of the sampler through a tube extending to the bottom of a 250 to 300 mL biological oxygen demand (BOD) bottle. Fill the bottle to overflowing and prevent turbulence and the formation of bubbles while filling the bottle.

7. Preservation of Samples

7.1 Do not delay the determination of dissolved oxygen. Samples for Test Method A may be preserved 4 to 8 h by adding 0.7 mL of concentrated sulfuric acid (sp gr 1.84) and 1.0 mL of sodium azide solution (20 g/L) to the bottle containing the sample in which dissolved oxygen is to be determined. Biological activity will be inhibited and the dissolved oxygen retained by storing at the temperature of collection or by water sealing (inverting bottle in water) and maintaining at a temperature of 10 to 20°C. Complete the determination as soon as possible, using the appropriate procedure for determining the concentration of dissolved oxygen.

TEST METHOD A—TITRIMETRIC PROCEDURE —HIGH LEVEL

8. Scope

8.1 This test method is applicable to waters containing more than 1000 μg/L of dissolved oxygen such as stream and sewage samples. It is the user's responsibility to ensure the validity of the test method for waters of untested matrices.

8.2 This test method, with the appropriate agent, is usable with a wide variety of interferences. It is a combination of the Winkler Method, the Alsterberg (Azide) Procedure, the Rideal-Stewart (permanganate) modification, and the Pomeroy-Kirshman-Alsterberg modification.

8.3 The precision of the test method was carried out using a saturated sample of reagent water.

9. Interferences

9.1 Nitrite interferences are eliminated by routine use of sodium azide. Ferric iron interferes unless 1 mL of potassium fluoride solution is used, in which case 100 to 200 mg/L can be tolerated. Ferrous iron interferes, but that interference is eliminated by the use of potassium permanganate solution. High levels of organic material or dissolved oxygen can be accommodated by use of the concentrated iodide-azide solution.

10. Apparatus

10.1 *Sample Bottles*, 250 or 300 mL capacity with tapered ground-glass stoppers. Special bottles with pointed stoppers and flared mouths are available from supply houses, but regular types (tall or low form) are satisfactory.

10.2 *Pipets*, 10-mL capacity, graduated in 0.1-mL divisions for adding all reagents except sulfuric acid. These pipets should have elongated tips of approximately 10 mm for adding reagents well below the surface in the sample bottle. Only the sulfuric acid used in the final step is allowed to run down the neck of the bottle into the sample.

11. Reagents

11.1 *Alkaline Iodide Solutions*:

11.1.1 *Alkaline Iodide Solution*—Dissolve 500 g of sodium hydroxide or 700 g of potassium hydroxide and 135 g of sodium iodide or 150 g of potassium iodide (KI) in water and dilute to 1 L. Chemically equivalent potassium and sodium salts may be used interchangeably. The solution should not give a color with starch indicator when diluted and acidified. Store the solution in a dark rubber-stoppered bottle. This solution may be used if nitrite is known to be absent and must be used if adjustments are made for ferrous ion interference.

11.1.2 *Alkaline Iodide-Sodium Azide Solution I*—This solution may be used in all of these submethods except when adjustment is made for ferrous ion. Dissolve 500 g of sodium hydroxide or 700 g of potassium hydroxide and 135 g of sodium iodide or 150 g of potassium iodide in water and dilute to 950 mL. To the cooled solution add 10 g of sodium azide dissolved in 40 mL of water. Add the NaN_3 solution slowly with constant stirring. Chemically equivalent potassium and sodium salts may be used interchangeably. The solution should not give a color with starch indicator solution when diluted and acidified. Store the solution in a dark rubber-stoppered bottle.

11.1.3 *Alkaline Iodide-Sodium Azide Solution II*—This solution is useful when high concentrations of organic matter are found or when the dissolved oxygen concentration exceeds 15 mg/L. Dissolve 400 g of sodium hydroxide in 500 mL of freshly boiled and cooled water. Cool the water slightly and dissolve 900 g of sodium iodide. Dissolve 10 g of sodium azide in 40 mL of water. Slowly add, with stirring, the azide solution

to the alkaline iodide solution, bringing the total volume to 1 L.

11.2 *Manganous Sulfate Solution*—Dissolve 364 g of manganous sulfate in water, filter, and dilute to 1 L. No more than a trace of iodine should be liberated when the solution is added to an acidified potassium iodide solution.

11.3 *Potassium Biiodate Solution* (0.025 *N*)—Dissolve 0.8125 g of potassium biiodate in water and dilute to 1 L in a volumetric flask.

NOTE 1—If the bottle technique is used, dissolve 1.2188 g of biiodate in water and dilute to 1 L to make 0.0375 *N*.

11.4 *Phenylarsine Oxide Solution* (0.025 *N*)—Dissolve 2.6005 g of phenylarsine oxide in 110 mL of NaOH solution (12 g/L). Add 800 mL of water to the solution and bring to a pH of 9.0 by adding HCl (1 + 1). This should require about 2 mL of HCl. Continue acidification with HCl (1 + 1) until a pH of 6 to 7 is reached, as indicated by a glass-electrode system. Dilute to 1 L. Add 1 mL of chloroform for preservation. Standardize against potassium biiodate solution.

NOTE 2—Phenylarsine oxide is more stable than sodium thiosulfate. However, sodium thiosulfate may be used. The analyst should specify which titrant is used. For a stock solution (0.1 *N*), dissolve 24.82 g of $Na_2S_2O_3 \cdot 5H_2O$ in boiled and cooled water and dilute to 1 L. Preserve by adding 5 mL of chloroform. For a dilute standard titrating solution (0.005 *N*) transfer 25.00 mL of 0.1 *N* $Na_2S_2O_3$ to a 500-mL volumetric flask. Dilute to the mark with water and mix completely. Do not prepare more than 12 to 15 h before use.

NOTE 3—If the full bottle technique is used, 3.9007 g must be used to make 0.0375 *N*.

NOTE 4—If sodium thiosulfate is used, prepare and preserve a 0.1 *N* solution as described in Note 1. Determine the exact normality by titration against 0.025 *N* potassium biiodate solution. Dilute the appropriate volume (nominally 250 mL) of standardized 0.1 *N* $Na_2S_2O_3$ solution to 1 L. One millilitre of 0.025 *N* thiosulfate solution is equivalent to 0.2 mg of oxygen. If the full bottle technique is followed, use 37.5 mL of sodium thiosulfate solution and standardize to 0.0375 *N*.

11.5 *Starch Solution*—Make a paste of 6 g of arrowroot starch or soluble iodometric starch with cold water. Pour the paste into 1 L of boiling water. Then add 20 g of potassium hydroxide, mix thoroughly, and allow to stand for 2 h. Add 6 mL of glacial acetic acid (99.5 %). Mix thoroughly and then add sufficient HCl (sp gr 1.19) to adjust the pH value of the solution to 4.0. Store in a glass-stoppered bottle. Starch solution prepared in this manner will remain chemically stable for one year.

NOTE 5—Powdered starches such as thyodene have been found adequate. Some commercial laundry starches have also been found to be usable.

NOTE 6—If the indicator is not prepared as specified or a proprietary starch indicator preparation is used, the report of analysis shall state this deviation.

11.6 *Sulfuric Acid* (sp gr 1.84)—Concentrated sulfuric acid. One millilitre neutralizes about 3 mL of the alkaline iodide reagent.

NOTE 7—Sulfamic acid (3 g) may be substituted.

11.7 *Potassium Fluoride Solution* (400 g/L)—Dissolve 40 g of potassium fluoride in water and dilute to 100 mL. This solution is used in the procedure for eliminating ferric ion interference. Store this solution in a plastic bottle.

11.8 *Potassium Oxalate Solution* (20 g/L)—Dissolve 2 g of potassium oxalate in 100 mL of water. One millilitre of this solution will reduce 1.1 mL of the $KMnO_4$ solution. This solution is used in the procedure for eliminating ferrous ion interference.

11.9 *Potassium Permanganate Solution* (6.3 g/L)—Dissolve 6.3 g of potassium permanganate in water and dilute to 1 L. With very high ferrous iron concentrations, solution of $KMnO_4$ should be stronger so that 1 mL will satisfy the demand. This solution is used in the procedure for eliminating ferrous ion interference.

12. Procedure

12.1 *Elimination of Ferrous Ion Interference, if necessary*:

12.1.1 Add to the sample (collected as in 6.2) 0.70 mL of H_2SO_4, followed by 1.0 mL of $KMnO_4$ solution. Where high iron is present, also add 1.0 mL of KF solution. Stopper and mix by inversion. The acid should be added with a 1-mL pipet graduated in 0.1-mL divisions. Add sufficient $KMnO_4$ solution to maintain a violet tinge for 5 min. If the color does not persist for 5 min, add more $KMnO_4$ solution, but avoid excess. In those cases where more than 5 mL of $KMnO_4$ solution is required, a stronger solution of this reagent may be used to avoid dilution of the sample.

12.1.2 After 5 min, completely destroy the permanganate color by adding 0.5 to 1.0 mL of $K_2C_2O_4$ solution. Mix the sample well, and allow it to stand in the dark. Low results are caused by excess oxalate so it is essential to add only sufficient oxalate to completely decolorize the permanganate without having an excess of more than 0.5 mL. Complete decolorization should be obtained in 2 to 10 min. If the sample cannot be decolorized without a large excess of oxalate, the dissolved oxygen results will be of doubtful value.

12.2 Add 2.0 mL of $MnSO_4$ solution to the sample as collected in a sample bottle, followed by 2.0 mL of alkaline iodide-sodium azide solution well below the surface of the liquid (see Note 8 and Note 9). Be sure the solution temperature is below 30°C to prevent loss due to volatility of iodine. Carefully replace the stopper to exclude air bubbles and mix by inverting the bottle several times. Repeat the mixing a second time after the floc has settled, leaving a clear supernatant solution. Water high in chloride requires a 10-min contact period with the precipitate. When the floc has settled, leaving at least 100 mL of clear supernatant solution, remove the stopper, and add 2.0 mL of H_2SO_4, allowing the acid to run down the neck of the bottle. Restopper and mix by inversion until the iodine is uniformly distributed throughout the bottle. Titrate without delay 203 mL of original sample. A correction is necessary for the 4 mL of reagents added (2 mL of $MnSO_4$ solution and 2 mL of alkaline iodide-sodium azide solution: $200 \times [300/(300 - 4)] = 203$ mL (see Note 10)).

NOTE 8—Take care to use the correct alkaline iodide solution (11.1.1) if no nitrite is present or ferrous ion was oxidized, (11.1.2) for normal use, or (11.1.3) if there is a high organic or dissolved oxygen concentration.

NOTE 9—Two millilitres of the alkaline iodide-sodium azide solution are used to ensure better contact of the iodide-azide solution and sample with less agitation. With 250-mL bottles, 1 mL of the iodide-azide solution may be used if desired. In this procedure, as in the succeeding ones, all reagents except the H_2SO_4 are added well below the surface of the liquid.

NOTE 10—In the case where ferrous ion interference has been eliminated, a total of 6.7 mL of reagents were added (0.7 mL of acid, 1 mL of $KMnO_4$ solution, 2 mL of $MnSO_4$ solution, and 3 mL of alkaline iodide solution). The volume of sample for titration is 203 mL. A slight error occurs due to the dissolved oxygen of the $KMnO_4$ solution, but rather than complicate the correction further, this error is ignored.

12.3 Rapidly titrate the 203 mL of sample with 0.025 *N* titrating solution to a pale, straw yellow color. Add 1 to 2 mL of starch indicator. Continue the titration to the disappearance of the blue color.

NOTE 11—If the full bottle technique is used, transfer the entire contents of the bottle, 300 ± 3 mL, to a 500-mL Erlenmeyer flask and titrate with 0.0375 *N* titrating solution.

NOTE 12—At the correct end point, one drop of 0.025 *N* $KH(IO_3)_2$ solution will cause the return of the blue color. If the end point is overrun, continue adding 0.025 *N* $KH(IO_3)_2$ solution until it reappears, noting the volume required. Subtract this value, minus the last drop of $KH(IO_3)_2$ (0.04 mL) from the volume of 0.025 *N* titrating solution used. Disregard the late reappearance of the blue color, which may be due to the catalytic effect of organic material or traces of uncomplexed metal salts.

13. Calculation

13.1 Calculate the dissolved oxygen content of the sample as follows:

$$\text{Dissolved oxygen, mg/L} = \frac{T \times 0.2}{200} \times 1000 \quad (1)$$

where:

T = 0.025 *N* titrating solution required for titration of the sample, mL.

13.2 Use Eq. 2 to convert to a standard temperature and pressure measurement.

$$\text{Dissolved oxygen, mg/L} = \frac{A}{0.698} \quad (2)$$

where:

A = oxygen at 0°C and 760 mm Hg, mL.

NOTE 13—Each millilitre of 0.0375 *N* titrant is equivalent to 1 mg/L O_2 when the full bottle technique is used.

NOTE 14—If the percentage of saturation at 760-mm atmospheric pressure is desired, the dissolved oxygen found is compared with solubility data from standard solubility tables,[5] making corrections for barometric pressure and the aqueous vapor pressure, when necessary. See Appendix X1.

14. Precision and Bias [6]

14.1 The precision of the test method was determined by six operators in three laboratories, running three duplicates each (not six laboratories as required by Practice D 2777 – 86) using a saturated sample of reagent water. The mean concentration was 9.0 mg/L, and the pooled single operator precision in these samples was 0.052 mg/L.

[5] Carpenter, J. H., "New Measurement of Oxygen Solubility in Pure and Natural Water," Limnology and Oceanography, Vol 11, No. 2, April 1966, pp. 264–277.

[6] Supporting data for the precision statement have been filed at ASTM Headquarters. Request RR: D19 – 1070.

TEST METHOD B—INSTRUMENTAL PROBE PROCEDURE

15. Scope

15.1 This test method is applicable to waters containing dissolved oxygen in the range from 50 to 20 000 µg/L. It is the user's responsibility to ensure the validity of this test method for waters of untested matrices.

15.2 This test method describes procedures that utilize probes for the determination of dissolved oxygen in fresh water and in brackish and marine waters that may contain dissolved or suspended solids. Samples can be analyzed in situ in bodies of water or in streams, or samples can be collected and analyzed subsequent to collection. The probe method is especially useful in the monitoring of water systems in which it is desired to obtain a continuous record of the dissolved oxygen content.

15.2.1 This test method is recommended for measuring dissolved oxygen in waters containing materials that interfere with the chemical methods, such as sulfite, thiosulfate, polythionate, mercaptans, oxidizing metal ions, hypochlorite, and organic substances readily hydrolyzable in alkaline solutions.

15.3 Dissolved oxygen probes are practical for the continuous monitoring of dissolved oxygen content in natural waters, process streams, biological processes, etc., when the probe output is conditioned by a suitably stable electronic circuit and recorded. The probe must be standardized before use on samples free of interfering materials, preferably with the azide modification of Test Method A.

16. Summary of Test Method

16.1 The most common instrumental probes for determination of oxygen dissolved in water are dependent upon electrochemical reactions. Under steady-state conditions, the current or potential can be correlated with dissolved oxygen concentrations.

NOTE 15—Steady-state conditions necessitate the probe being in thermal equilibrium with the solution, this typically taking 20 min for nonlaboratory conditions.[7]

16.1.1 Probes that employ membranes normally involve metals of different nobility immersed in an electrolyte that is retained by the membrane. The metal of highest nobility (the cathode) is positioned at the membrane. When a suitable potential exists between the two metals, reduction of oxygen to hydroxide ion occurs at the cathode surface. An electrical current is developed that is directly proportional to the rate of arrival of oxygen molecules at the cathode.

16.1.2 The thallium probe, which does not utilize a membrane, exposes a thallium electrode to the water sample. Reaction of oxygen with the thallium establishes a potential between the thallium electrode and a reference electrode. The potential is related logarithmically to dissolved oxygen concentration. The cell output decreases (theoretically 59 mV/decade at 25°C) with increased oxygen concentration.

[7] D'Aoust, B. G., Clark, M. J. R., "Analysis of Supersaturated Air in Natural Waters and Reservoirs," *Transactions of the American Fisheries Society*, Vol 109, 1980, pp. 708–724.

NOTE 16—The thallium probe has utility in waste treatment monitoring systems; it has limited application under conditions of high dissolved oxygen (>8 mg/L) and low temperature (<10°C).

16.1.3 The electronic readout meter for the output from dissolved oxygen probes is normally calibrated in convenient scales (0 to 10, 0 to 15, or 0 to 20 mg/L) with a sensitivity of approximately 0.05 mg/L. More sensitive dissolved oxygen ranges are practical through amplification in the electronic readout (including μg/L readings in boiler feed waters).

16.2 Interfacial dynamics at the probe-sample interface are a factor in probe response. Turbulence should be constant or above some minimum level as recommended by the instrument manufacturer.

16.3 Response rates of dissolved oxygen probes are relatively rapid, often as fast as 99 % in 15 s. Probe outputs may be recorded for continual monitoring or utilized for process control (see Note 15).

17. Interferences

17.1 Dissolved organic materials normally encountered in water are not known to interfere in the output from dissolved oxygen probes.

17.2 Dissolved inorganic salts are a factor in the calibration of dissolved oxygen probe.

17.2.1 Solubility of oxygen in water at a given oxygen partial pressure changes with the kind and concentration of dissolved inorganic salts. Conversion factors for seawater and brackish waters may be calculated from dissolved oxygen saturation versus salinity data if internal compensation is not included in the instrument. Conversion factors for specific inorganic salts may be developed experimentally. Broad variations in the kinds and concentrations of salts in samples can make the use of a membraned probe difficult.

17.2.2 The thallium probe measures ionic activity instead of concentration as do all ion selective electrodes. Gross changes in the concentration of dissolved salts will affect the activity coefficient of the thallous ion and thus shift the span (see 19.2.1). The thallium probe may be calibrated and operated in water of any conductivity above 100 μS, but a ten-fold change in conductivity will produce an error of approximately 20 %. Since the thallium requires a conducting path through the sample to the reference electrode, the response will become sluggish at very low conductivity. It is therefore desirable to calibrate the sensor in solutions having a conductivity greater than 100 μS.

17.3 Reactive compounds can interfere with the output or the performance of dissolved oxygen probes.

17.3.1 Membraned probes are sensitive to reactive gases that may pass through the membrane. Chlorine will depolarize the cathode and cause a high probe output. Long-term exposure to chlorine can coat the anode with the chloride of the anode metal and may eventually desensitize the probe. Hydrogen sulfide will interfere with membraned probes if the applied potential is greater than the half-wave potential of the sulfide ion. If the applied potential is less than the half-wave potential, an interfering reaction will not occur, but coating of the anode metal can occur.

17.3.2 The thallium probe is affected by interference from soluble sulfur compounds, such as hydrogen sulfide or mercaptans. Ten milligrams of hydrogen sulfide per litre of water will produce a negative error corresponding to approximately 1 mg/L of dissolved oxygen. Free halogens also will interfere with the thallium probe if present in appreciable concentrations, such as above 2 mg of chlorine per litre of water.

17.4 At dissolved oxygen concentrations below 2 mg/L, pH variation below 4 and above 10 interfere with the performance of the thallium probe (approximately ±0.05 mg/L dissolved oxygen per pH unit). The performance of membraned probes is not affected by pH changes.

17.5 Dissolved oxygen probes are temperature sensitive and temperature compensation is normally provided by the manufacturer. The thallium probe has a temperature coefficient of 1.0 mV/°C, membraned probes have a temperature coefficient of 4 to 6 %/°C dependent upon the membrane employed.

17.6 Insoluble organic or inorganic materials that can coat the surface of dissolved oxygen probes will affect the performance of either the thallium or membraned probes.

18. Apparatus

18.1 *Amperometric Probes*—Oxygen-sensitive probes of the amperometric type are normally composed of two solid metal electrodes of different nobility in contact with a supporting electrolyte that is separated from the test solution by a selective membrane. The current generated by the reduction of oxygen at the cathode is measured through an electronic circuit and displayed on a meter. Typically, the anode is constructed of metallic silver or lead and the cathode of gold or platinum. Probes are generally not affected by hydraulic pressure and can be used in the temperature range from 0 to 50°C.

18.1.1 *Semipermeable Membranes of Polyethylene or TFE-fluorocarbon* permit satisfactory oxygen diffusion and limit interference from most materials.

18.1.2 *Accessory Equipment* may involve apparatus to move the sample past the probe and to provide suitable turbulence at the membrane-sample interface.

18.2 *Potentiometric Probes*—The commonly used potentiometric probe employs a thallium-measuring electrode and a suitable reference half cell such as a saturated calomel. At 25°C and 0.1 mg/L of dissolved oxygen, the cell establishes a negative potential of approximately 817 mV. The potential decreases logarithmically in absolute value with increased dissolved oxygen concentration (theoretically, 59 mV/decade change in dissolved oxygen concentration) to approximately 688 mV at 15 mg/L of dissolved oxygen. An external millivoltage source that opposes the output of the electrometer is used to adjust the net readout of output to the desired range.

NOTE 17—Thallium and its salts are toxic. Avoid contact with the skin.

19. Apparatus Standardization

19.1 Under equilibrium conditions, the partial pressure of oxygen in air-saturated water is equal to that of the oxygen in the water-saturated air. Consequently, a probe may be calibrated in air as well as water. Consider carefully the manufacturer's recommended procedure. If it is necessary to zero the instrument, immerse the probe in water containing 1 g

of sodium sulfite and two drops of saturated cobalt chloride solution (as deoxygenation catalyst) per litre of water and adjust the instrument to read zero. If a water-saturated air calibration is necessary, follow the manufacturer's directions for its preparation.

19.2 To calibrate the probe in water, carefully obtain approximately 1 L of the type of water to be tested and saturate it with oxygen from the atmosphere by passing clean air through it. Carefully draw three replicate samples from the well mixed sample and immediately determine the dissolved oxygen concentration by Test Method A in duplicate. In the third replicate sample, immerse the probe and provide for suitable turbulence in the sample. Standardize the probe by adjusting the meter reading to the dissolved oxygen value as determined by the chemical procedure. If substances that interfere with the chemical method are present in the natural water or wastewater sample, standardize the probe using reagent water or a synthetic sample as indicated below.

19.2.1 *Fresh Water Samples* (less than 1000 mg/L of dissolved salts)—If chemical interferences are absent, use a test sample as indicated above. If interferences are present, use reagent water for membraned probes. With thallium probes, the greatest accuracy can be obtained from calibrating in a sample of the water to be tested or a synthetic sample similar to the test sample.

19.2.2 *Salt Water Samples and Membraned Probes* (greater than 1000 mg/L of dissolved salts)—Use a sample of clean water having the same salt content as the test material. If a sample free from substances that interfere with the azide method is not available, prepare a synthetic standardization sample by adding the same salts contained in the sample until the two solutions have the same electrical conductance within 5 %. High concentrations of dissolved salts are not a problem with the thallium probe.

19.3 *Temperature Coefficient*—Systems are available with automatic temperature compensation that permit direct measurements in milligrams per litre of dissolved oxygen. The temperature compensation of membraned probes corrects for changes in membrane characteristics including boundary-layer effects at the membrane-water interface and the changes in solubility of oxygen in water. The temperature compensation of thallium probes corrects for the changes characteristic of oxidation/reduction systems (see Note 15). It is necessary that the probe is in thermal equilibrium with the solution to be measured for satisfactory temperature correction.

19.3.1 For those instrumental systems using membraned probes that are not temperature-compensated, the following procedure is recommended to obtain the temperature coefficient. Measure the oxygen content in water samples for five temperatures over a ±10°C range greater and less than the expected sample temperature. By a least-squares procedure, or graphically in a semilog plot of Y versus T, calculate the slope and intercept constant as follows:

$$\text{Log}\, y = B/T + A \tag{3}$$

where:

y = scale factor, milligrams of dissolved oxygen per litre per microampere of electrode current,
B = slope constant,
T = temperature, °C, and
A = intercept constant.

This relationship is linear on a semilog plot only over a range of ±10°C. Over larger ranges an equation of higher degree is necessary to reflect the curvature of the relationship.

19.3.2 If the thallium probe is utilized in a circuit without temperature compensation, the observed output in millivolts must be corrected for the temperature sensitivity of the measuring cell that has a temperature coefficient of 1.0 mV/°C. The measuring cell's output will increase (apparent dissolved oxygen concentration decrease) with an increase in temperature,

$$MV_R = MV_0 - 1.0\,(T_o - T_R) \tag{4}$$

where:

MV_R = millivolts of output at reference temperature,
MV_0 = millivolts of output observed,
T_R = reference temperature, °C, and
T_o = temperature at the observed output, °C.

19.4 *Correction for Content of Dissolved Salts*—If the concentration of salts is above 1000 mg/L, it will be necessary to correct for the effect of the salts in the relationship between oxygen partial pressure and concentration and also for the activity of thallium ion. For any given salt, a series of experimental data should be obtained in which solutions are prepared by dissolving varying weights of the salt in reagent water in the range of interest. The solutions plus a reagent water control are aerated at constant temperature until oxygen saturation is achieved. Determine the oxygen concentration of each solution by the chemical method and, at the same time, obtain probe readings. Determine the ratio A for each solution as follows:

$$A = O/R \tag{5}$$

where:

O = actual dissolved oxygen concentration, mg/L, as determined by Test Method A, and
R = reading of the probe meter.

For the reagent water control to which the probe is calibrated, the value of A is 1.0. Prepare a plot with salt concentration as abscissa and the ratio A as ordinate. Use the developed curve for calculation of the dissolved oxygen content of salt waters.

20. Sampling

20.1 *Bottle Samples*—Collect a bottle sample by the procedure described in Practice D 1066 or Practices D 3370. Collect the samples in 300-mL BOD bottles or other suitable glass-stoppered bottles, preventing entrainment or solution of atmospheric oxygen. If analysis is delayed beyond 15 min, cool the sample below 5°C and hold at this temperature until analyzed. Make the dissolved oxygen determination without further temperature adjustment using the appropriate temperature coefficient. It will be necessary to have the probe

at the temperature of the sample or otherwise compensate for instability due to heat flow from probe to sample.

20.2 *In Situ Samples*—An effective use of the instrumental probes is for the direct, in situ determination of dissolved oxygen. By this means, sample handling problems are avoided, and data may be obtained quickly at various locations in a body of water without concern for the change in oxygen during storage or handling.

21. Procedure

21.1 Consider carefully the manufacturer's recommendations on the use of equipment to obtain satisfactory operation.

21.2 Provide for suitable turbulent flow past the membrane of membraned probes or past the thallium probe. This may, under some circumstances, be achieved adequately in flowing streams. However, in large bodies of water, it may be necessary to employ mechanical stirring or pumping of water past the probe. For accurate results, it is important that comparable degrees of turbulence be employed both for calibration and utilization.

21.3 If the probe is not automatically compensated for temperature changes, record the temperature of the water at the sample probe at the time of dissolved oxygen measurement. To avoid heat-flow effects, it is important that temperature equilibrium be established between sample and probe.

21.4 Recalibrate the probe whenever the comparison with reference samples (19.2) indicates an absolute error of more than ±0.2 mg/L of dissolved oxygen or other value that is compatible with the desired accuracy.

21.4.1 Careful handling is required with membraned probes to avoid rupturing the thin membrane.

21.4.2 Recalibrate the probe after replacing the membrane or cleaning the probe in accordance with the manufacturer's directions. For a period of a few hours after a membrane replacement, the probe output may drift, and frequent recalibration may be required.

21.5 Probes can become fouled by oil, grease, biological growths, etc., and cleaning may be required. Some of the techniques currently in use include air-blasting, brush cleaning, and ultrasonic cleaning systems.

21.6 The probe may be utilized in situ or the sample may be transferred to a sampling station that houses the probe and associated equipment.

21.6.1 In situ placement of the probe is preferable from the consideration that sample handling is not involved. However, in situ installations may be impractical because of problems with vandalism, severe climate conditions (freezing, etc.), and difficulty in probe recovery for maintenance.

21.6.2 The use of sample transfer systems is practical when proper consideration is given to design features such as line size, rates of transfer, kind of pump and location, practicality for cleaning the transfer system, and other maintenance.

21.6.3 Examine unattended probes at least once per week and recalibrate when required depending upon condition and service. Recalibration may be accomplished by using a portable probe that has been placed into position next to the unattended probe and that has been properly calibrated as outlined in 19.2.

22. Calculation

22.1 For uncompensated probes, correct the observed meter reading for the difference of the observed temperature from the standardization temperature by the factors developed in 19.3.

22.2 For wastewaters with varying salt contents, make corrections utilizing the data developed in 19.4.

23. Precision and Bias

23.1 The precision of this test method was determined by six operators in three laboratories running three duplicates each (not six laboratories as required by Practice D 2777 – 86) using a saturated sample of reagent water. The mean concentration was 9.0 mg/L, and the pooled single-operator precision in these samples was 0.029 mg/L.

24. Keywords

24.1 analysis; dissolved; oxygen; probe; titrimetric; water

APPENDIX

(Nonmandatory Information)

X1. OXYGEN SATURATION VALUES

X1.1 *Oxygen Saturation Values in Water and Elevations*—The solubility of oxygen in water at various temperatures and elevations under an atmospheric pressure of 760 mm is shown in Table X1.1.

X1.2 *Oxygen Saturation Values in Water and Salt Waters*—The solubility of oxygen in water exposed to water saturated air under an atmospheric pressure of 760 mm is shown in Table X1.2 at several temperatures and concentrations of sea water to illustrate the effects of salt concentration and temperature. The solubility versus dissolved salt concentration can vary considerably with the nature of the salts in solution.

TABLE X1.1 Solubility of Oxygen (mg/L) at Various Temperatures and Elevations (Based on Sea Level Barometric Pressure of 760 mm Hg) [12]

Temperature, °C	Elevation, Feet above Sea Level						
	0	1000	2000	3000	4000	5000	6000
0	14.6	14.1	13.6	13.2	12.7	12.3	11.8
2	13.8	13.3	12.9	12.4	12.0	11.6	11.2
4	13.1	12.7	12.2	11.9	11.4	11.0	10.6
6	12.4	12.0	11.6	11.2	10.8	10.4	10.1
8	11.8	11.4	11.0	10.6	10.3	9.9	9.6
10	11.3	10.9	10.5	10.2	9.8	9.5	9.2
12	10.8	10.4	10.1	9.7	9.4	9.1	8.8
14	10.3	9.9	9.6	9.3	9.0	8.7	8.3
16	9.9	9.7	9.2	8.9	8.6	8.3	8.0
18	9.5	9.2	8.7	8.6	8.3	8.0	7.7
20	9.1	8.8	8.5	8.2	7.9	7.7	7.4
22	8.7	8.4	8.1	7.8	7.7	7.3	7.1
24	8.4	8.1	7.8	7.6	7.3	7.1	6.8
26	8.1	7.8	7.6	7.3	7.0	6.8	6.6
28	7.8	7.5	7.3	7.0	6.8	6.6	6.3
30	7.5	7.2	7.0	6.8	6.5	6.3	6.1
32	7.3	7.1	6.8	6.6	6.4	6.1	5.9
34	7.1	6.9	6.6	6.4	6.2	6.0	5.8
36	6.8	6.6	6.3	6.1	5.9	5.7	5.5
38	6.6	6.4	6.2	5.9	5.7	5.6	5.4
40	6.4	6.2	6.0	5.8	5.6	5.4	5.2

TABLE X1.2 Solubility of Oxygen (mg/L) at Various Temperatures and Chlorinity (Based on Sea Level Barometric Pressure of 760 mm Hg) [12]

Temperature,° C	Chlorinity, %					
	0	4.0	8.0	12.0	16.0	20.0
0	14.6	13.9	13.2	12.5	11.9	11.3
2	13.8	13.2	12.5	11.9	11.4	10.8
4	13.1	12.5	11.9	11.3	10.8	10.3
6	12.4	11.8	11.3	10.8	10.3	9.8
8	11.8	11.3	10.8	10.3	9.8	9.4
10	11.3	10.8	10.3	9.8	9.4	9.0
12	10.8	10.3	9.8	9.4	9.0	8.6
14	10.3	9.9	9.4	9.0	8.6	8.3
16	9.9	9.4	9.0	8.6	8.3	8.0
18	9.5	9.1	8.7	8.3	8.0	7.6
20	9.1	8.7	8.3	8.0	7.7	7.4
22	8.7	8.4	8.0	7.7	7.4	7.1
24	8.4	8.1	7.7	7.4	7.1	6.9
26	8.1	7.8	7.5	7.2	6.9	6.6
28	7.8	7.5	7.2	6.9	6.6	6.4
30	7.5	7.2	7.0	6.7	6.4	6.2
32	7.3	7.0	6.7	6.5	6.2	6.0
34	7.1	6.8	6.5	6.3	6.0	5.8
36	6.8	6.6	6.3	6.1	5.8	5.6
38	6.6	6.4	6.1	5.9	5.6	5.4
40	6.4	6.2	5.9	5.7	5.4	5.2

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