



Standard Test Method for On-Line Measurement of Low-Level Dissolved Oxygen in Water¹

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1. Scope

1.1 This test method covers the on-line determination of dissolved oxygen (DO) in water samples primarily in ranges from 0 to 500 $\mu\text{g/L}$ (ppb), although higher ranges may be used for calibration. On-line instrumentation is used for continuous measurements of DO in samples that are brought through sample lines and conditioned from high-temperature and high-pressure sources when necessary.

1.2 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

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 specific hazards statements, see 6.5.

2. Referenced Documents

2.1 ASTM Standards:²

- D1066 Practice for Sampling Steam
- D1129 Terminology Relating to Water
- D1193 Specification for Reagent Water
- D2777 Practice for Determination of Precision and Bias of Applicable Test Methods of Committee D19 on Water
- D3370 Practices for Sampling Water from Closed Conduits
- D3864 Guide for On-Line Monitoring Systems for Water Analysis

3. Terminology

3.1 *Definitions*—For definitions of terms used in this test method, refer to Terminology D1129.

¹ This test method is under the jurisdiction of ASTM Committee D19 on Water and is the direct responsibility of Subcommittee D19.03 on Sampling Water and Water-Formed Deposits, Analysis of Water for Power Generation and Process Use, On-Line Water Analysis, and Surveillance of Water.

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² For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

3.2 Definitions of Terms Specific to This Standard:

3.2.1 *diffusion-type probes, n*—galvanic or polarographic sensors that depend on the continuous influx of oxygen through the membrane to develop the electrical signal.

3.2.2 *equilibrium-type probes, n*—modified polarographic sensing probes that have a negligible influx of oxygen through the membrane except during changes of sample DO concentration.

3.2.2.1 *Discussion*—Oxygen consumption and regeneration balance each other within the probes under stable conditions, and the net flux through the membrane is insignificant.

3.2.3 *galvanic systems, n*—sensing probes and measuring instruments that develop an electrical current from two electrodes inside the probe from which the final measurement is derived.

3.2.4 *partial pressure (of oxygen), n*—the volume fraction of oxygen multiplied by the total pressure.

3.2.4.1 *Discussion*—The partial pressure of oxygen is the actual parameter detected by DO probes, whether in air or dissolved in water.

3.2.5 *polarographic systems, n*—sensing probes and measuring instruments that include circuitry to control the operating voltage of the system, usually using a third (reference) electrode in the probe.

4. Summary of Test Method

4.1 Dissolved oxygen is measured by means of an electrochemical cell separated from the sample by a gas-permeable membrane. Behind the membrane and inside the probe, electrodes immersed in an electrolyte develop an electrical current proportional to the oxygen partial pressure of the sample.

4.2 The partial pressure signal is temperature compensated automatically to account for variations with temperature of the following: oxygen solubility in water; electrochemical cell output; and, when necessary, diffusion rate of oxygen through the membrane. This yields a direct readout in concentration of $\mu\text{g/L}$ (ppb) or mg/L (ppm).

4.3 Diffusion-type probes rely on a continuous diffusion of oxygen through the membrane. Immediately inside the membrane, oxygen is reduced at the noble metal cathode, usually platinum or gold. An electrical current is developed

that is directly proportional to the arrival rate of oxygen molecules at the cathode, which is in turn dependent on the diffusion rate through the membrane. The less noble anode, usually silver or lead, completes the circuit and is oxidized in proportion to the current flow. At steady state, the resulting current signal is then proportional to the oxygen partial pressure of the sample. Thorough descriptions of diffusion-type probes are given by Hitchman (1)³ and Fatt (2).

4.4 Equilibrium-type probes rely on oxygen diffusion through the membrane only until equilibrium between the inside and outside is achieved. Oxygen is reduced at the noble metal cathode, as with diffusion-type probes. However, the measuring circuit forces electrical current to flow through the noble metal anode equal and opposite to that at the cathode, and the resulting oxidation reaction produces oxygen. This is the exact reverse of the reaction at the cathode, so there is no net consumption of oxygen by the probe. It reaches equilibrium in constant DO samples, and no net oxygen diffuses through the membrane. Accuracy is not dependent on membrane surface condition or sample flowrate.

5. Significance and Use

5.1 DO may be either a corrosive or passivating agent in boiler/steam cycles and is therefore controlled to specific concentrations that are low relative to environmental and wastewater treatment samples. Out-of-specification DO concentrations may cause corrosion in boiler systems, which leads to corrosion fatigue and corrosion products—all detrimental to the life and efficient operation of a steam generator. The efficiency of DO removal from boiler feedwater by mechanical or chemical means, or both, may be monitored by continuously measuring the DO concentration before and after the removal process with on-line instrumentation. DO measurement is also a check for air leakage into the boiler water cycle.

5.2 Guidelines for feedwater to high-pressure boilers with all volatile treatment generally require a feedwater DO concentration below 5 µg/L (3).

5.3 Boiler feedwater with oxygenated treatment is maintained in a range of 50 to 300 µg/L DO (4).

5.4 In microelectronics production, DO can be detrimental in some manufacturing processes, for example, causing undesirable oxidation on silicon wafers.

6. Interferences

6.1 The leakage of atmospheric air into samples is sometimes difficult to avoid and detect. Although sample line fittings and connections to flow chambers may be water tight, it is still possible for air to diffuse through the water film of a joint to contaminate a low-µg/L sample. Sample flow through fittings, valves and rotometers can create a venturi effect, which draw ambient air into the sample. Section 9 provides further details on this non-obvious interference.

6.2 Diffusion-type probes consume oxygen and will deplete it from the sample in immediate contact with the membrane

surface unless an adequate, turbulent sample flow is maintained. The manufacturer's minimum flowrate recommendations must be met or exceeded in order to prevent erroneously low readings.

6.3 Diffusion-type probes are subject to negative errors from the buildup of coatings such as iron oxides, which impede the diffusion rate of oxygen. (Equilibrium-type probes are not subject to errors from flowrate or coating.)

6.4 Calibration must be corrected for barometric pressure according to the manufacturer's recommendations at atmospheric conditions that deviate from a nominal range of 745 to 775 mmHg. See Table 1 for altitude corrections. Calibration under low-pressure conditions without compensation would result in positive measurement errors.

6.5 The growth of bacteria in sample lines and flow chambers and on probe membranes can consume oxygen and cause negative errors. Chemical sterilization with hydrochloric acid (1 + 44) or sodium hypochlorite solution (10 mg/L) should be performed if errors from bacteria growth are suspected. (**Warning**—Do not mix hydrochloric acid and sodium hypochlorite since hazardous chlorine gas would be released rapidly.)

6.6 The passage of high-temperature samples containing both DO and an oxygen scavenger through hot sample lines can allow continued reaction of the two. With long sample lines, the DO measured at the probe may be significantly below that at the sample point. Short sample lines and cooling near the source are recommended.

6.7 Volatile oxygen scavengers or suppressants, such as hydrazine, amines, and hydrogen, that pass through the probe membrane may cause unwanted reactions at the electrodes and negative errors. The magnitude of errors depends on the relative concentrations of DO and the oxygen scavenger or

TABLE 1 Solubility of Oxygen (mg/L) at Various Temperatures and Elevations (Based on Sea Level Barometric Pressure of 760 mmHg) (5)

| Temperature, ° C | Elevation, ft 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 |

³ The boldface numbers in parentheses refer to the list of references at the end of this test method.