Designation: ~~D5462 – 13~~ D5462 – 21

Standard Test Method for On-Line Measurement of Low-Level Dissolved Oxygen in Water[1]

This standard is issued under the fixed designation D5462; 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.

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 µg/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~~ The values given in parentheses after SI units are provided for information only and are not considered 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, health, and environmental practices and determine the applicability of regulatory limitations prior to use.* For specific hazards statements, see 6.5.

1.4 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

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 Flowing Process Streams
D3864 Guide for On-Line Monitoring Systems for Water Analysis

3. Terminology

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

3.1.1 For definitions of terms used in this standard, refer to Terminology D1129.

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[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~~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 µg/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~~ 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.

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

5.2 ~~Guidelines for feedwater to high-pressure boilers with~~ Feedwater chemistry guidelines for high-pressure boilers generally require specific feedwater DO concentrations: 5 µg⁄L or less for reducing all volatile treatment ~~generally require~~[AVT(R)]; 5–10 µg ~~a feedwater DO concentration below 5 µg/L~~⁄L for oxidizing all volatile treatment [AVT(O)]; 50–200 µg⁄L for oxygenated treatment [OT] (3).

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

5.3 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~~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~~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.)

TABLE 1 Solubility of Oxygen (mg/L) at Various Temperatures and Elevations (Based on Sea Level Barometric Pressure of 760 mmHg) (~~5~~4)

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

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 suppressant as well as the type of electrochemical cell used. The probe ~~manufacturer's~~manufacturer's cautions and limitations should be considered.

6.8 New sample lines require conditioning to achieve equilibrium conditions. See Practices D3370 to avoid sampling interferences.

6.9 Iron oxides and other deposits accumulate in slow-flowing horizontal sample lines and can develop chromatograph-like retention of dissolved species, resulting in very long delay times. Precautions are described in Section 9~~9.~~.

6.10 The response time can be slow for large decreases in DO. This is especially true of measurements below 10 µg/L following air calibration, which corresponds to a concentration decrease of 3 to 4 orders of magnitude. Hours may be required for all traces of oxygen to diffuse out of the probe and to achieve accurate measurements at low µg/L levels.

7. Apparatus

7.1 *Measuring Instrument:*

7.1.1 The instrument should have both µg/L (ppb) and mg/L (ppm) range capability. It must have a span calibration adjustment to match the readout to the sensitivity of a particular probe.

7.1.2 The direct readout of DO concentration requires temperature compensation for effects of the following: (*1*) oxygen solubility in water; (*2*) electrochemical cell output; and (*3*) when necessary, diffusion rate of oxygen through the membrane. During air calibration, the instrument must disable the oxygen solubility portion of the compensation to respond only to partial pressure.

7.1.3 If included, electrical output signal(s) from the instrument must be isolated from the probe measuring circuit and from earth ground in order to prevent ground loop problems when the instrument is connected to grounded external devices.

7.2 *Probe:*

7.2.1 Diffusion-type probes use galvanic or polarographic systems, with a noble metal cathode and oxidizable anode immersed in an electrolyte and separated from the sample with a polyethylene or fluorocarbon gas-permeable membrane.

7.2.2 Equilibrium-type probes are similar to polarographic probes, except that both the anode and cathode are platinum and the anode is not oxidized.

7.2.3 A sealed flow-through probe configuration must be used to prevent contamination from the atmosphere, as described in 6.1. The flowrate must be maintained within the ~~manufacturer's~~manufacturer's recommendations. The probe must be capable of withstanding the flowrate, temperature, and pressure conditions of the installation. The probe must incorporate an integral precision temperature sensor to ensure that it senses the sample temperature at which the DO is being detected in order to ensure accurate temperature compensation with fast response.

7.2.4 Diffusion-type probes must have their electrodes, electrolyte, and membrane serviced or replaced according to the ~~manufacturer's~~manufacturer's recommendations. Equilibrium-type probes do not require internal maintenance.

7.2.5 Probe membranes must be cleaned in accordance with the ~~manufacturer's~~manufacturer's recommendations. The cleaning frequency is determined by experience with the particular sample and must be sufficient to maintain acceptable accuracy with diffusion-type probes (see 6.3). The cleaning of equilibrium-type probes is not necessary unless a heavy coating increases response time or becomes biologically active (see 6.5).

8. Reagents

8.1 *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, where such specifications are available.[4] Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

8.2 *Purity of Water*—References to water shall be understood to mean water that meets or exceeds the quantitative specifications for type III reagent water conforming to 1.1 of Specification D1193~~, Section 1.1.~~.

8.3 *Hydrochloric Acid (1 + 44)*—Add 1 volume of concentrated HCl (sp gr 1.19) to 44 volumes of water and mix.

8.4 *Sodium Hypochlorite (10 mg/L)*—Add approximately 0.05 mL (1 drop) of 5 % NaOCl solution (commercial bleach is satisfactory for this purpose) to 250 mL of water.

8.5 *Cobalt Chloride Solution, Saturated*—Dissolve 4.5 g of cobalt chloride ($CoCl_2$) in 10 mL of water.

8.6 *Sodium Sulfite Zero Solution (10 g/200 mL)*—Dissolve 10 g of sodium sulfite (Na_2SO_3) in 200 mL of water.

NOTE 1—To attain zero DO more rapidly, add two drops of saturated cobalt chloride solution to the sodium sulfite zero solution.

9. Sampling

9.1 Design and operate the sample lines to maintain sample integrity and fast response. Follow the applicable sampling precautions in Practices D1066~~,~~ and D3370, and Guide D3864.

9.2 The preferred permanent material for sample lines is 316SS. Higher alloys in sample coolers may be required for high chloride cooling waters. PVDF and Nylon can be used for portable or patch panel applications as long as the integrity of connections is verified by the user. Most other plastic and rubber tubing materials are gas permeable and allow significant oxygen diffusion into the sample. A discussion of suitable plastic sampling materials for this purpose is given by Carr (**~~6~~5**). Do not use copper because it can oxidize and consume oxygen.

9.3 Maintain a continuous, stable flowrate to enable the sample line to reach equilibrium with the sample conditions. Measurements following changes to the sample flowrate or temperature may not represent actual process conditions during the period of time required to recover from transient effects.

9.4 Seal the sample from the atmosphere to prevent oxygen absorption. Leakage of the equivalent of only one 2-mm-diameter air bubble/min into a sample flowing at 100 mL/min adds approximately 11 µg/L oxygen to the sample. Test the sample line integrity by observing the measurement under steady state conditions of DO and increasing the sample flowrate approximately 50 %, but not exceeding the ~~manufacturer's~~manufacturer's recommendations. A significant decrease in DO reading is usually an indication of air leakage since the higher flowrate dilutes the leak. (An *increase* in DO reading could be observed with a diffusion-type probe and indicates that the original flowrate was too low, as described in 6.2. The flowrate must then be increased until a stable plateau of response is reached.)

9.5 In power plant installations in which iron oxide and other solids occur in pure water samples, control flowrates to minimize the accumulation of deposits, which could delay the transport of dissolved materials greatly. A water sample flow velocity of 1.8 m/s (6 ft/s) in sample lines has been found optimum. Additional sample line design criteria have been documented in Refs (**~~7~~-6-~~9~~8**).

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[4] ~~*Reagent Chemicals, American Chemical Society Specifications,*~~*ACS Reagent Chemicals, Specifications and Procedures for Reagents and Standard-Grade Reference Materials,* American Chemical Society, Washington, DC. For ~~Suggestions~~suggestions on the testing of reagents not listed by the American Chemical Society, see ~~*Annual*~~*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.

10. Calibration

10.1 *Measuring Instrument*—Evaluate the measuring instrument calibration and performance using substitute resistors in place of the probe, or by other means as recommended by the manufacturer.

10.2 *Temperature Measurement Circuit*—Because of the high-temperature coefficient of the solubility of oxygen in water (see Table 1), verify the temperature measurement accuracy within ±1°C. Some temperature measurement circuits require precise temperature calibration after installation in order to compensate for leadwire resistance and ensure accurate temperature compensation. Calibrate the temperature measurement according to the ~~manufacturer's~~manufacturer's recommendations where applicable.

10.3 *Probe:*

10.3.1 Air standardization uses the consistent composition of the atmosphere at 20.9 % oxygen with barometric pressure correction to provide a universally available and reliable partial pressure standard for span adjustment. With diffusion-type probes, follow the ~~manufacturer's~~manufacturer's recommendations for drying the outside of the membrane to prevent water drops from affecting the oxygen diffusion rate. Expose the probe membrane to water-saturated air and wait for the reading to stabilize fully. Adjust the instrument span control in accordance with the ~~manufacturer's~~manufacturer's procedure.

10.3.2 Zero DO standardization consists of immersing the probe into a solution of sodium sulfite for several hours. The reading should be between 0 and 4 µg/L DO. Zero the instrument.

10.3.3 For a check of calibration within the normal measurement range on-line, use a commercially available self-filling colorimetric ampoule test kit. See Appendix X1.

10.3.4 For an off-line standard to verify calibration within the normal measurement range, saturate water with a precisely known oxygen-in-nitrogen gas mixture, as described in Appendix X2.

11. Procedure

11.1 Set up the flow type DO probe, leadwire, and instrument. Where severe fouling is anticipated at startup, divert the sample initially to prevent an accumulation of contaminants in the probe and flow chamber. If using a sample line, establish a flowrate through the cell of 200 mL/min, or according to the ~~manufacturer's~~manufacturer's recommendations, and allow several hours of rinse time for the probe to dissipate all of the oxygen accumulated during storage under atmospheric conditions. Make a check for air leakage, as described in 9.4. Calibrate the instrument span in accordance with 10.3 and the ~~manufacturer's~~manufacturer's recommendations.

11.2 Allow sufficient time for excess oxygen from the calibration to dissipate in accordance with 6.10, and read the DO to the nearest 0.1 µg/L.

12. Precision and Bias

12.1 Methods involving continuous sampling or measurement, such as this one, are specifically exempted from the requirements for collaborative testing as specified in 1.3.3 of Practice D2777.

12.2 Some statistical experience with high-purity DO measurements in power plants has been compiled as part of EPRI project RP2712-3 (~~10~~9).

13. Quality Control

13.1 Depending on the sample stream, the probe membrane will require cleaning and inspection on some regular frequency. After each cleaning, repair or replacement perform the air standardization in accordance with ~~Section~~ 10.3.1 and the zero standardization in accordance with ~~Section~~ 10.3.2.

13.2 Perform the air standardization in accordance with ~~Section~~ 10.3.1 and the zero standardization in accordance with ~~Section~~ 10.3.2 on a minimum monthly basis.

13.3 A written record should be maintained for each cleaning, repair, replacement and standardization performed.

14. Keywords

14.1 dissolved oxygen; galvanic cell; oxygen; polarographic sensor

APPENDIXES

(Nonmandatory Information)

X1. ON-LINE CALIBRATION CHECK

X1.1 For a calibration check with the DO instrument operating on line, use a commercially available self-filling colorimetric ampoule test kit. Make the check under stable DO conditions and without changing the overall sample flowrate in order to prevent the errors noted in 6.10 and 9.3.

X1.2 Follow the test kit ~~manufacturer's~~manufacturer's instructions for sampling and measurement. Agreement between the on-line instrument and test kit determination should be within ±15 % of the average of the two values or ±3 µg/L (ppb), whichever is greater.

X2. DISSOLVED OXYGEN STANDARDS

X2.1 The apparatus and procedures described in this appendix permit the convenient establishment of DO-in-water standards of good quality for off-line checks. Make DO-in-water standards by bubbling oxygen-in-nitrogen gas mixtures through a water sample. Use these standards to calibrate DO instrumentation in the range of measurement.

X2.2 Determine the DO concentration attained by ~~Henry's~~Henry's law (~~11~~10):

$$C = X\left(P - P_w\right)\exp\left(16.9775 - \left(5269 - 1\,004\,200/T\right)/T\right) \quad \text{(X2.1)}$$

where:

C = DO concentration (µg/L),
X = volume fraction of oxygen in the gas mixture (unitless),
P = gas pressure (bar),
T = temperature (K), and
P_w = water vapor pressure (bar) given by (Eq X2.2).

$$P_w = \exp\left(11.86 - \left(3841 + 216\,960/T\right)/T\right) \quad \text{(X2.2)}$$

X2.2.1 Ambient air pressure may be measured with an accurately calibrated barometer. It may also be determined from the barometric pressure recorded by a local weather station or airport, with a correction for the altitude difference between the location of use of the test method and the weather station; 1 bar = 750.1 mmHg.

X2.3 Obtain a compressed cylinder of certified oxygen-in-nitrogen gas mixture to provide the desired DO standard in (Eq X2.1) or Table X2.1.