



Designation: D5543 – 21

# Standard Test Method for Low-Level Dissolved Oxygen in Water<sup>1</sup>

This standard is issued under the fixed designation D5543; 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 reappraisal. A superscript epsilon ( $\epsilon$ ) indicates an editorial change since the last revision or reappraisal.

## 1. Scope

1.1 This test method covers the rapid determination of low-level ( $<100 \mu\text{g/L}$ ) dissolved oxygen in thermal-cycle steam condensate, deaerated boiler feedwater, boiler water, and deaerated deionized water. Color comparators allow the estimation of concentrations ranging from 0 to  $100 \mu\text{g/L}$  (ppb) oxygen.

1.2 This test method may be applicable to electronic-grade, pharmaceutical-grade, and other high-purity waters, although these were not addressed in the collaborative study.

1.3 It is the user's responsibility to ensure the validity of this test method for waters of untested matrices.

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

1.5 *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.*

1.6 *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:*<sup>2</sup>

[D1066 Practice for Sampling Steam](#)

[D1129 Terminology Relating to Water](#)

[D1193 Specification for Reagent Water](#)

<sup>1</sup> 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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<sup>2</sup> For referenced ASTM standards, visit the ASTM website, [www.astm.org](http://www.astm.org), or contact ASTM Customer Service at [service@astm.org](mailto:service@astm.org). For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

- [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](#)
- [D5463 Guide for Use of Test Kits to Measure Inorganic Constituents in Water](#)
- [D5540 Practice for Flow Control and Temperature Control for On-Line Water Sampling and Analysis](#)

## 3. Terminology

3.1 *Definitions:*

3.1.1 For definitions of terms used in this standard, refer to Terminology [D1129](#).

## 4. Summary of Test Method

4.1 The tip of a partially evacuated sealed ampoule is broken while submerged in a flowing water sample. The sample is drawn into the ampoule where it reacts instantaneously with the oxygen-sensitive indicator (leuco form of Rhodazine D) to produce a reddish violet color whose intensity is proportional to the concentration of dissolved oxygen.<sup>3</sup>

## 5. Significance and Use

5.1 Dissolved oxygen is detrimental in certain boiler and steam cycles because it may accelerate corrosion. Concentrations above  $10 \mu\text{g/L}$  are unacceptable in many high-pressure boiler systems. The efficiency of dissolved oxygen removal from boiler feedwater by chemical or mechanical means, or both, is determined by measuring the concentration before and after the process. The measurement is also made to check for air leakage into the boiler system.

5.2 The oxygen treatment method for boiler corrosion reduction requires injection of oxygen into the boiler feedwater. The resulting oxygen level is monitored for control purposes.

## 6. Interferences

6.1 Color, turbidity, and oxidizing impurities interfere in this test method to yield high results. If the sample is colored

<sup>3</sup> Spokes, G. N., *Dissolved Oxygen in Water Measurement and Standardization*, EPRI PWR Plant Chemists' Meeting, San Diego, CA, Nov. 17–20, 1992. Copies obtainable from CHEMetrics Inc., 4295 Catlett Rd., Midland, VA 22728, <https://www.chemetrics.com>.

or turbid or contains oxidizing impurities, the amount of interference that may be contributed by such effects must be determined independently prior to using this test method.

6.2 Easily reduced metal ions may interfere in this test method to cause high results. For example, 100 µg/L (ppb) Cu<sup>+2</sup> may appear as 5 µg/L (ppb) dissolved oxygen, and 100 µg/L Fe<sup>+3</sup> may appear as 7 µg/L dissolved oxygen. However, less than 50 µg/L Cu<sup>+2</sup> or Fe<sup>+3</sup> cause less than 1-µg/L interference.

6.3 Hydrogen peroxide alone in concentrations up to 200 µg/L does not affect the measurement of 1.5 µg/L of dissolved oxygen. Above 200 µg/L hydrogen peroxide, there is a positive interference of 3.3 µg/L dissolved oxygen per 100 µg/L excess over 200 µg/L hydrogen peroxide.

6.4 The following interferences occur in the presence of 2200 mg/L boron present as boric acid: (1) at pH levels below pH 6, recovery can be as low as 80 %; (2) added hydrogen peroxide at a concentration of 0.1 mg/L yields a positive interference of 10 µg/L dissolved oxygen; and (3) added hydrogen peroxide in a concentration range from 0.5 to 650 mg/L yields a positive interference of 20 to 25 µg/L.

NOTE 1—Measurements of 0 to 100 µg/L of dissolved oxygen are unaffected by the presence of 2200 mg/L boron present as boric acid at pH 6 and above in the absence of hydrogen peroxide.

6.5 Benzoquinone, an oxidation product of hydroquinone, interferes with this test method. One hundred micrograms per litre of benzoquinone may appear as 33 µg/L dissolved oxygen.

6.6 Reducing agents such as hydrazine and sulfite do not interfere at 5-mg/L (ppm) levels in the sample.

6.7 Ampoules must be protected from light to prevent darkening. Follow the manufacturer's storage recommendations.

6.8 Color comparator tubes must be protected from light to prevent fading. Follow the manufacturer's storage recommendations.

## 7. Apparatus

7.1 *Color Comparator*, for 0, 2, 4, 6, 8, 12, 16, and 20 µg/L (ppb) of oxygen.

7.2 *Color Comparator*, for 0, 5, 10, 15, 20, 25, 30, and 40 µg/L (ppb) of oxygen.

7.3 *Color Comparator*, for 0, 10, 20, 30, 40, 60, 80, and 100 µg/L (ppb) of oxygen.

7.4 *Sampling Tube*. See Fig. 1.

## 8. Reagents and Materials

8.1 This test method does not require the preparation of any reagents. All the necessary analytical reagents are provided by the manufacturer in sealed ampoules.

8.2 *Purity of Water*—Reference to water shall mean water that meets or exceeds the quantitative specifications for Type II reagent water of Specification D1193, Section 1.1.

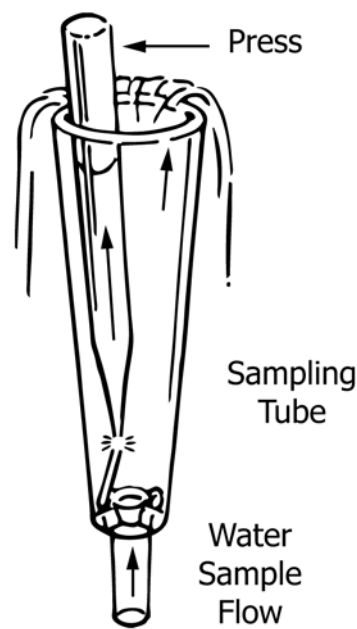


FIG. 1 Sampling Tube for Use with Ampoules to Measure Dissolved Oxygen in a Flowing Water Sample

## 9. Precautions

9.1 Users should review the manufacturer's kit instructions before use.

## 10. Sampling

10.1 Collect the samples in accordance with Practices D5540, D1066, and D3370.

10.2 Sampling is the most critical part of any dissolved oxygen test. The sample stream must be completely leak-free, since even the smallest leak can elevate the oxygen level in the sample and cause large errors in the results. New or intermittently used sampling systems must be purged for a minimum of 4 h. Sample streams that are used routinely may require only a few minutes of purging.

10.3 With water under pressure, connect a tube of inert material to the inlet and extend the tube outlet to the bottom of the plastic sampling tube. Clamps may be attached to the tube to hold it vertical, or it can be attached to a vertical rod or pipe above a sink, drain, or bucket. 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 elastomeric polymeric materials. If the water being sampled is above ambient temperature, the sample line shall contain a suitable cooling coil to cool it to ambient temperature to prevent introduction of atmospheric oxygen into the test ampoule at the time of analysis. Establish a flow rate ranging from 500–1000 mL per minute to prevent the introduction of atmospheric oxygen during sampling.

## 11. Calibration and Standardization

11.1 No calibration is required.

NOTE 2—The color comparator standards are precalibrated by the manufacturer for measurement of dissolved oxygen in water.

11.2 A dissolved-oxygen-in-water standard may be generated by following the procedures given in [Appendix X1](#).

## 12. Procedure

12.1 Insert the ampoule into the sampling device, with the pointed end down. Allow the sample to flow at least 5 min. A 15-min wait time may be necessary to achieve the best accuracy for samples with below 20 µg/L of dissolved oxygen.

12.2 Gently press the ampoule toward the wall of the sampling tube to snap off the tip ([Fig. 1](#)), and remove the ampoule, keeping the tip down, immediately after filling is complete.

12.3 Using a protective rubber finger cot, place a finger over the broken tip. (**Warning**—Glass may be sharp.) Invert the ampoule several times to mix the contents, allowing the bubble to travel from end to end each time. Wipe all liquid from the exterior of the ampoule.

NOTE 3—A small bubble of inert gas will remain in the ampoule to facilitate mixing.

NOTE 4—Due to the possibility of air leaking in during this step, it is advisable to run tests in duplicate. It should be noted, however, that some variation in observed concentrations may be due to changes in system conditions.

12.4 Use the color comparator as illustrated in [Fig. 2](#) to determine the level of dissolved oxygen in the sample. Place the ampoule in the center (empty) tube of the comparator, with the flat end downward. Direct the top of the comparator toward a source of bright, white light while viewing from the bottom. Hold the comparator in a nearly horizontal position, and rotate it until the color standard below the ampoule shows the closest match. Complete this color matching procedure in less than 30 s after snapping the tip in the sample.

NOTE 5—The color intensity may continue to increase after the rapid initial color reaction. However, it is the initial color reaction that is complete within 30 s, and to which the system calibrations apply.

12.4.1 Find the analytical result from the concentration value of the closest matching color standard as designated on

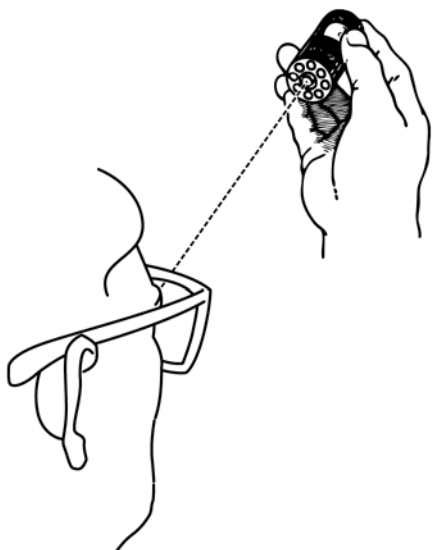


FIG. 2 Use of the Comparator

the comparator label. Estimate the concentration to within a half color standard interval.

## 13. Calculation

13.1 The dissolved oxygen content of the sample is the value obtained in [12.4.1](#). Use the average of the two resulting values if two ampoules are used.

## 14. Precision and Bias<sup>4</sup>

14.1 The overall precision and bias of this test method cannot be determined by round-robin testing because of the instability of shipping solutions.

14.2 This test method was evaluated for single-operator precision by eight laboratories, with a total of 15 operators running a total of 200 samples in triplicate. The collaborative test data were obtained on the samples available at the laboratory site locations. These data may not apply for other matrices.

14.2.1 The single-operator precision,  $S_o$ , of this test method was found to be dependent on the ampoule type and to be partly dependent on the dissolved oxygen content of the sample. The data are summarized in the tables that follow.

14.2.1.1 The data in the following table were obtained using 0 to 20-µg/L (ppb) range ampoules and comparators.<sup>5</sup> A total of 66 samples was measured in triplicate by a total of 15 operators in 8 laboratories:

Range, µg/L (ppb)	0 to 0.9	1 to 4.9	5 to 9.9	10 to 14.9	15 to 20
$S_o$	0.20	1.6	2.5	1.4	3.2

14.2.1.2 The data in the following table were obtained using 0 to 40-µg/L (ppb) range ampoules and comparators.<sup>6</sup> A total of 78 samples was measured in triplicate by a total of 14 operators in 7 laboratories:

Range, µg/L (ppb)	0 to 1.9	2 to 9.9	10 to 19.9	20 to 29.9	30 to 40
$S_o$	0.15	1.4	2.8	2.7	2.2

14.2.1.3 The data in the following table were obtained using 0 to 100-ppb range ampoules and comparators.<sup>7</sup> A total of 56 samples was measured in triplicate by a total of 10 operators in 6 laboratories.

Range, µg/L (ppb)	0 to 4.9	5 to 19.9	20 to 39.9	40 to 59.9	60 to 100
$S_o$	0.95	1.1	1.4	5.3	2.9

14.3 Eight independent laboratories (and a total of fifteen operators) participated in this study. Precision testing for this test method conforms to Practice [D2777](#).

<sup>4</sup> Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D19-1153. Contact ASTM Customer Service at [service@astm.org](mailto:service@astm.org).

<sup>5</sup> CHEMetrics Catalog No. K7511 kits or R7511 ampoule with a C7511 comparator. The sole source of supply of the apparatus known to the committee at this time is CHEMetrics, Inc., 4295 Catlett Road, Midland, VA 22728, <https://www.chemetrics.com>. If you are aware of alternative suppliers, please provide this information to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee<sup>1</sup>, which you may attend.

<sup>6</sup> CHEMetrics Catalog No. K7540 kits or R7540 ampoule with C7540 comparator. If you are aware of alternative suppliers, please provide this information to ASTM International Headquarters.

<sup>7</sup> CHEMetrics Catalog No. K7599 kits or R7540 or R7599 ampoule with a C7599 comparator. If you are aware of alternative suppliers, please provide this information to ASTM International Headquarters.

## 15. Quality Control

15.1 Test kit quality control is the responsibility of the manufacturer. The manufacturer may be requested to furnish supporting quality control data. The user should verify that the final developed color in the snapped ampoule matches the hue of the color standards in the color comparator. If the color matching quality is poor, further investigation should be done to determine whether sample background color or sample matrix effects are a root cause and whether test results should be considered suspect. Refer to Guide [D5463](#) for additional information about using test kits.

15.2 A procedure for generating dissolved oxygen in water standards is described in [Appendix X1](#). However, it is likely that most analysts using the ppb dissolved oxygen test kit will not have gas standards available at their facility. Nonetheless some basic quality control steps that do not involve the use of gas standards are described below that serve to ensure dissolved oxygen test kit results are valid.

### 15.3 *Over-Range Calibration Verification:*

15.3.1 Snap an ampoule in a suitable snapping cup containing 25 mLs of water taken from a municipal drinking water supply or any other clean water supply that is not deaerated (that is, a sample that contains 2–14 ppm level of oxygen). Follow the steps given in [12.3](#) and [12.4](#).

15.3.2 The analytical result should exceed the highest color standard increment on the comparator.

### 15.4 *Under-Range Calibration Verification:*

15.4.1 Prepare 100 mL of a 0.4 M sodium sulfite solution: Dissolve 5 g of anhydrous sodium sulfite ( $\text{Na}_2\text{SO}_3$ ) in 100 mL of reagent water.

15.4.2 Pour 25 mL of this solution in a suitable snapping cup. Allow the sample to sit undisturbed for 10 minutes.

NOTE 6—Failure to allow the  $\text{Na}_2\text{SO}_3$  solution to sit undisturbed or

agitating the sample prior to snapping the ampoule will cause false high bias.

15.4.3 Snap an ampoule in the  $\text{Na}_2\text{SO}_3$  sample. Follow steps [12.3](#) and [12.4](#).

15.4.4 The analytical result should be nearly  $\leq 5$  ppb.

### 15.5 *Initial Demonstration of Laboratory Capability:*

15.5.1 If a laboratory has not performed the test before, or a new analyst is using the test kit, a precision and bias study should be conducted to demonstrate laboratory capability.

NOTE 7—A new analyst should practice snapping ampoules in the sampling device and reading them in the comparator in order to gain confidence with the procedure.

15.5.2 Snap three ampoules in quick succession in a flowing water sample. The three results should agree with one another to within two color standard increments.

### 15.6 *Laboratory Control Sample (LCS):*

15.6.1 Preparation of a LCS is possible only if gas standards are available. Refer to [Appendix X1](#).

### 15.7 *Matrix Spike (MS):*

15.7.1 Dissolved oxygen is not an analyte that can be feasibly spiked into samples.

### 15.8 *Duplicate:*

15.8.1 To check the precision of sample analyses, follow the procedure given in [15.5.2](#).

### 15.9 *Independent Reference Material (IRM):*

15.9.1 Stable standards of dissolved oxygen in the ppb range are not commercially available.

## 16. Keywords

16.1 ampoules; boiler; boiler feedwater; colorimetric analysis; dissolved oxygen; oxygen; oxygen sensitive indicator; steam; steam condensate; petroleum refining; power generation

## APPENDIX

### (Nonmandatory Information)

#### X1. ESTABLISHMENT OF DISSOLVED OXYGEN IN WATER STANDARDS

X1.1 Dissolved oxygen-in-water standards may be made by bubbling oxygen-in-nitrogen gas mixtures through a water sample. The apparatus and procedures described in this appendix permit the inexpensive and easy establishment of dissolved oxygen-in-water standards of good quality. These standards may be used to check the accuracy of the self-filling ampoules and comparators.

X1.1.1 The dissolved oxygen concentration attained is determined by Henry's law:<sup>8</sup>

$$C(\mu\text{g/L}) = X(P - P_w)\text{exp} \quad (\text{X1.1})$$

$$\{16.9775 - (5268.95 - 1004170/T)/T\}$$

The gas pressure is  $P$ (bar), the fraction of oxygen is  $X$ , and the absolute temperature is  $T$  kelvins.  $P_w$ (bar) is the water vapor pressure given by the following:

$$P_w = \text{exp}\{11.857 - (3840.7 + 216961/T)/T\} \quad (\text{X1.2})$$

1-mm Hg pressure is equivalent to 0.001333 bar (0.1333 kPa).

X1.1.2 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

<sup>8</sup> Derived by J. M. Hale from B. B. Benson and D. Krause, Jr., *Limnol. Oceanogr.*, Vol 25, 1980, p. 662.