



Designation: D 5543 – 94 (Reapproved 2005)

Standard Test Methods for Low-Level Dissolved Oxygen in Water¹

This standard is issued under the fixed designation D 5543; 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 These test methods cover the determination of low-level (<100 μ g/L) dissolved oxygen in thermal-cycle steam condensate, deaerated boiler feedwater, boiler water, and deaerated deionized water. The following test methods are included:

Test Method	Range, μ g/L	Sections
Test Method A—Color Comparator Test Method Using Self-Filling Glass Ampoules	0 to 100	8 to 17
Test Method B—Instrument Test Method Using Self-Filling Glass Ampoules	0 to 100	18 to 26

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

1.3 Test Method A is a colorimetric procedure applicable to dissolved oxygen in water in the range from 0 to 100 μ g/L.

1.4 Test Method B is an instrumented colorimetric procedure applicable to dissolved oxygen in water in the range from 0 to 100 μ g/L.

1.5 It is the user's responsibility to ensure the validity of these test methods for waters of untested matrices.

1.6 The values stated in SI units are to be regarded as the standard.

1.7 *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.*

2. Referenced Documents

2.1 *ASTM Standards:*²

D 1066 Practice for Sampling Steam

D 1129 Terminology Relating to Water

¹ These test methods are under the jurisdiction of ASTM Committee D19 on Water and are the direct responsibility of Subcommittee D19.03 on Sampling of 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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Originally approved in 1994. Last previous edition approved in 1999 as D 5543 – 94 (1999) ^{ϵ 1}.

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.

D 1192 Specification for Equipment for Sampling Water and Steam in Closed Conduits³

D 1193 Specification for Reagent Water

D 2777 Practice for Determination of Precision and Bias of Applicable Methods of Committee D19 on Water

D 3370 Practices for Sampling Water from Closed Conduits

3. Terminology

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

4. Significance and Use

4.1 Dissolved oxygen is detrimental in certain boiler and steam cycles because it may accelerate corrosion. Concentrations above 10 μ 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.

4.2 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.

5. Reagents

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

5.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water as defined by Type II of Specification D 1193.

6. Precautions

6.1 Users must exercise caution by using finger cots, in accordance with the manufacturer's instructions, when handling the mixing of sample and reagent in the glass ampoules.

7. Sampling

7.1 Sampling is the most critical part of any dissolved oxygen test. The sample stream must be completely leak-free,

³ Withdrawn.

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.

7.2 Collect the samples in accordance with Practices **D 1066** and **D 3370** and Specification **D 1192**.

7.3 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 or tube. 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 room temperature, the sample line shall contain a suitable cooling coil to cool it to approximate room temperature.

TEST METHOD A—COLOR COMPARATOR TEST METHOD USING SELF-FILLING GLASS AMPOULES

8. Scope

8.1 This test method covers the rapid, routine determination of dissolved oxygen in steam condensate, deaerated boiler feedwater, and deaerated deionized water. Color comparators allow the estimation of concentrations ranging from 0 to 100 µg/L (ppb) oxygen.

8.2 This test method was tested in steam condensate, deaerated boiler feedwater, and deaerated deionized water. It is the user's responsibility to ensure the validity of the test method for waters of untested matrices.

9. Summary of Test Method

9.1 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 to produce a reddish violet color whose intensity is proportional to the concentration of dissolved oxygen.⁴

10. Interferences

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

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

10.3 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.

10.4 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.

10.5 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.

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

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

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

11. Apparatus

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

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

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

11.4 *Sampling Tube*. See Fig. 1.

12. Reagents and Materials

12.1 Sealed, evacuated glass ampoules containing oxygen-sensitive indicator.

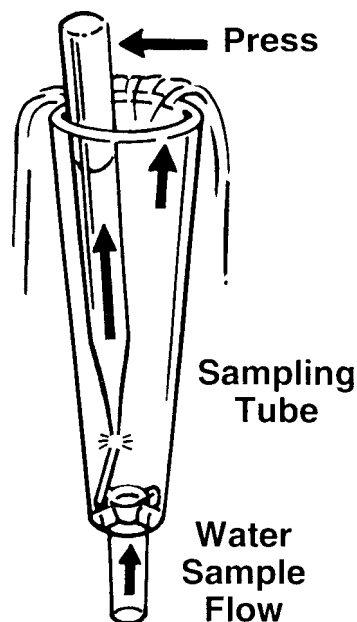


FIG. 1 Sampling Tube for Use with Ampoules to Measure Dissolved Oxygen in a Flowing Water Sample

⁴ 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., Route 28, Calverton, VA 22016.

13. Sampling

13.1 Attach the feedwater source to the plastic sampling tube as described in 7.3. 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.

14. Calibration and Standardization

14.1 No calibration is required.

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

14.2 A dissolved-oxygen-in-water standard may be generated by following the procedures given in Appendix X1.

15. Procedure

15.1 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.

15.2 Gently press the ampoule toward the wall of the sampling tube to snap off the tip, and remove the ampoule, keeping the tip down, immediately after filling is complete.

15.3 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.

15.4 Use the color comparator as illustrated in Fig. 2 to

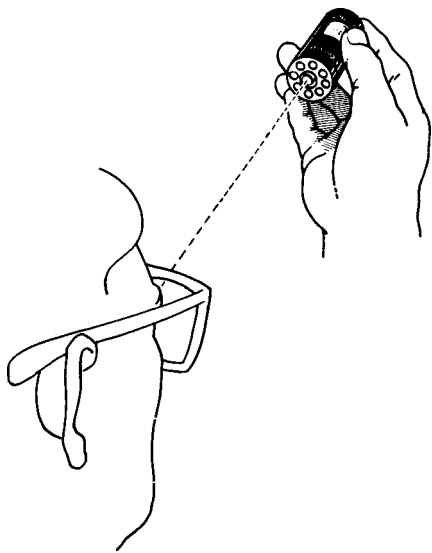


FIG. 2 Use of the Comparator—Test Method A

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.

15.4.1 Find the analytical result from the concentration value of the closest matching color standard as designated on the comparator label. Estimate the concentration to within a half color standard interval.

16. Calculation

16.1 The dissolved oxygen content of the sample is the value obtained in 15.4. Use the average of the two resulting values if two ampoules are used.

17. Precision and Bias ⁵

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

17.2 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.

17.2.1 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.

17.2.1.1 The data in the following table were obtained using 0 to 20-µg/L (ppb) range ampoules and comparators. ⁶ 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

17.2.1.2 The data in the following table were obtained using 0 to 40-µg/L (ppb) range ampoules and comparators. ⁷ A total

⁵ Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR: D19-1153.

⁶ 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, 4295 Catlett Road, Calverton, VA 20138. 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 ¹, which you may attend.

⁷ 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.