



Designation: D8084 – 17

Standard Test Method for Photoelectrochemical Oxygen Demand of Freshwater Sources for Drinking Water Treatment Plants and Treated Drinking Water¹

This standard is issued under the fixed designation D8084; 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 a protocol for the determination of the photoelectrochemical oxygen demand of freshwater sources for drinking water treatment plants and treated drinking water in the range of 0.7 mg/L to 20 mg/L. Higher levels may be determined by sample dilution.

1.2 Photoelectrochemical oxygen demand is determined using the current generated from the photoelectrochemical oxidation of the sample using titanium dioxide (TiO_2) irradiated with ultraviolet (UV) light from a light-emitting diode (LED).

1.3 This test method does not require the use of the hazardous reagents, such as mercuric sulfate, potassium dichromate and silver sulfate, that are often associated with the determination of chemical oxygen demand (that is, Test Methods [D1252](#)). It can also provide a result rapidly, as samples do not require reflux.

1.4 Determination of photoelectrochemical oxygen demand in freshwater sources for drinking water treatment plants and treated drinking water matrices has important implications for assessing treatment efficacy. Photoelectrochemical oxygen demand can be used as a bulk surrogate measure of natural organic matter, a key target for drinking water treatment. In aerobic biological treatment processes, determination of photoelectrochemical oxygen demand can provide an estimation of the oxygen required by microorganisms to degrade organic matter. This test method is complementary to existing natural organic matter (NOM) monitoring techniques and will help scientists and engineers further the understanding of NOM in water with a rapid oxygen demand test.

1.5 This test method was used successfully with reagent grade water spiked with pure compounds, freshwater sources for drinking water treatment plants and treated drinking water.

¹ This test method is under the jurisdiction of ASTM Committee [D19](#) on Water and is the direct responsibility of Subcommittee [D19.06](#) on Methods for Analysis for Organic Substances in Water.

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

1.6 This test method is applicable to oxidizable matter, <50 μm that can be introduced into the sensor.

NOTE 1—This test method can be performed (1) immediately in the field or laboratory on an unpreserved sample, and (2) in the laboratory on a properly preserved sample following the stated hold times.

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

1.8 *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 hazard statements, see Section 9.

1.9 *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

- [D1129 Terminology Relating to Water](#)
- [D1193 Specification for Reagent Water](#)
- [D1252 Test Methods for Chemical Oxygen Demand \(Dichromate Oxygen Demand\) of 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](#)
- [D5847 Practice for Writing Quality Control Specifications for Standard Test Methods for Water Analysis](#)

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. Terminology

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

3.1.1 *chemical oxygen demand, n*—the amount of oxygen required under specified test conditions for the oxidation of water borne organic and inorganic matter.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *theoretical oxygen demand, n*—the calculated amount of oxygen required to oxidize a compound to its final oxidation products based on stoichiometry.

4. Summary of Test Method

4.1 Photoelectrochemical oxygen demand is determined by photoelectrochemical oxidation. A sample is mixed with an electrolyte containing lithium nitrate (LiNO₃) and introduced into a sensor containing TiO₂ nanoparticles immobilized on a thin film. The TiO₂ is irradiated with a UV LED, oxidizing the sample and generating an electrical signal proportional to the chemical oxygen demand of the sample. A schematic of this working principle is provided in Fig. 1.

4.2 Photoelectrochemical oxygen demand recovery of known amounts of theoretical oxygen demand (as pure compound) in reagent grade water are shown in Table 1.

4.2.1 A slope of unity for a given compound in Table 1 demonstrates that photoelectrochemical oxygen demand was a complete predictor of theoretical oxygen demand over the theoretical oxygen demand range tested. Each range comprised five concentrations.

4.3 Photoelectrochemical oxygen demand recovery of known amounts of theoretical oxygen demand (as sorbitol) in reagent grade water, surface water, filtered drinking water and finished drinking water are shown in Fig. 2.

TABLE 1 Photoelectrochemical Oxygen Demand Recovery of Various Pure Compounds in Reagent Grade Water^A

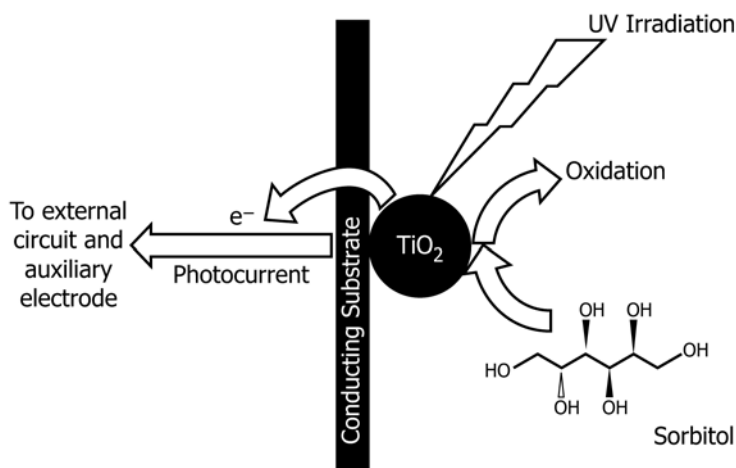
Pure Compound	Range of Theoretical Oxygen Demand Added—mg/L	Slope (mx+b)
Caffeine	1.2–24.2	0.69x – 0.36
Phenylalanine	0.9–17.8	1.14x – 1.18
Sodium Acetate	0.7–13.3	0.79x – 1.34
Sodium Formate	0.3–6.7	0.96x – 0.58
Sodium Oxalate	0.2–3.3	1.47x – 0.13
Tryptophan	0.9–18.8	1.01x – 0.62
Tyrosine	0.9–17.0	1.01x – 0.87

^A Adapted from Stoddart, A., K., and Gagnon, G. A., "Application of Photoelectrochemical Chemical Oxygen Demand to Drinking Water," *Journal of American Water Works Association*, Vol 106, No. 9, 2014, pp. 383–390.

5. Significance and Use

5.1 This test method describes a rapid method to determine the maximum quantity of oxygen that may be consumed by impurities in water. As outlined in Test Methods D1252, chemical oxygen demand is typically used to monitor and control oxygen-consuming pollutants, both organic and inorganic, in domestic and industrial wastewaters. This photoelectrochemical oxygen demand test method is specific for measuring organics and inorganics in freshwater sources for drinking water treatment plants and treated drinking water matrices. This photoelectrochemical oxygen demand test method is not intended for domestic and industrial wastewaters to replace Test Methods D1252.

5.2 This test method does not require the use of the hazardous reagents, such as mercuric sulfate, potassium dichromate and silver sulfate, that are associated with chemical oxygen demand. It can also provide a result more rapidly than chemical oxygen demand as samples do not require reflux.



Adapted from Zhao, H., Jiang, D., Zhang, S., Catterall, K., and John, R., "Development of a Direct Photoelectrochemical Method for Determination of Chemical Oxygen Demand," *Analytical Chemistry*, Vol 76, No. 1, 2004, pp. 155–160.

FIG. 1 Working Principle of Photoelectrochemical Oxygen Demand Determination

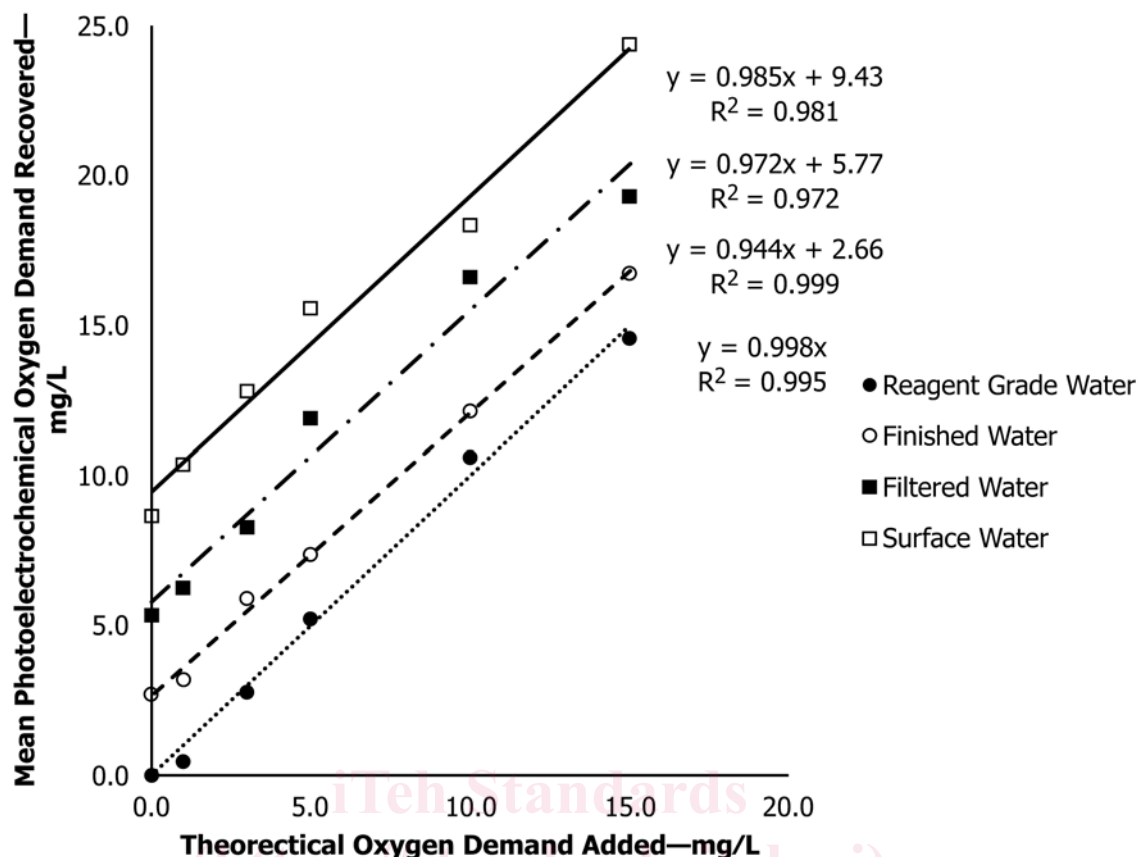


FIG. 2 Demonstration of Photoelectrochemical Oxygen Demand Recovery from Reagent Grade Water, Surface Water, Filtered Drinking Water and Finished Drinking Water

6. Interferences

6.1 Chloride is a known interfering agent. Results shown in Fig. 3 indicate that sorbitol recovery (target concentrations of 2, 3, 5, 10, 15 and 20 mg/L) was biased high at increasing chloride concentrations.

6.2 Similar to Test Methods D1252, some compounds are resistant to oxidation, while others are more easily oxidized. Photoelectrochemical oxidation demand has shown that all organic materials do not oxidize uniformly.³

6.3 Analysis of samples at pH ≥ 9 may bias results low. Results shown in Table 2 indicate that sorbitol recovery (target concentration of 5 mg/L) was biased low at pH 9.

6.4 This test method is applicable to oxidizable matter that can be introduced into the sensor. For large particles, the

internal ports, valves and tubing may limit the maximum size of particles that can be introduced into the sensor.

7. Apparatus

7.1 *Photoelectrochemical Oxygen Demand Analyzer*,⁴—An analyzer consisting of a reagent and sample introduction mechanism, an electrode block, UV LED, a sensor and a detector.

7.1.1 *Electrode Block*—A block housing the reference and auxiliary electrodes.

7.1.2 *UV LED*—A light source for illuminating the working electrode.

7.1.3 *Sensor*—A microcell containing a TiO₂ nanoparticle working electrode.

³ Stoddart, A. K., and Gagnon, G. A., "Application of Photoelectrochemical Chemical Oxygen Demand to Drinking Water," *Journal of American Water Works Association*, Vol 106, No. 9, 2014, pp. 383–390.

⁴ The sole source of supply of the photoelectrochemical oxygen demand analyzer known to the committee at this time is Mantech, Inc., Guelph, Ontario, Canada. 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.

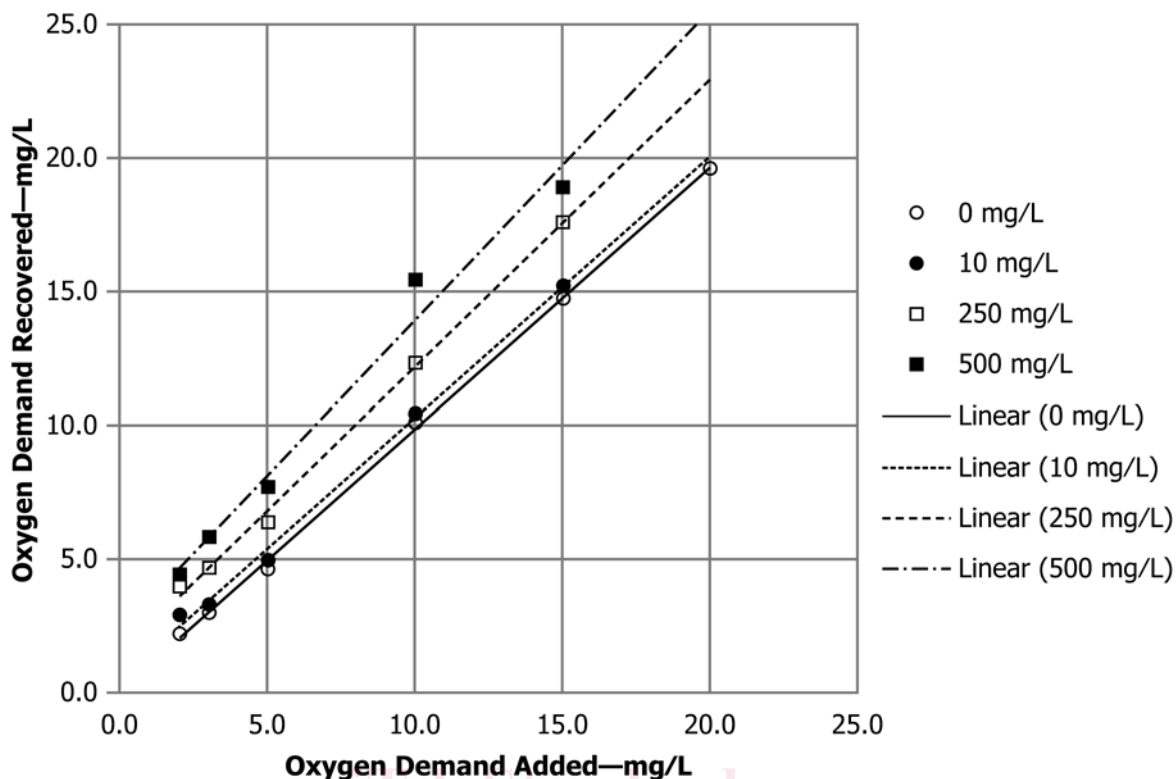


FIG. 3 Demonstration of Chloride Interference

TABLE 2 Photoelectrochemical Oxygen Demand Recovery of Sorbitol at Varying pH

pH	Photoelectrochemical Oxygen Demand Recovery—mg/L
5.85 ^A	4.5 ± 0.1
5.81 ^A	4.8 ± 0.1
5.01 ^B	4.6 ± 0.1
7.02 ^B	4.4 ± 0.1
7.44 ^B	4.8 ± 0.2
8.02 ^B	4.5 ± 0.2
8.61 ^B	4.5 ± 0.1
9.00 ^B	3.7 ± 0.1

^A Unadjusted pH.

^B pH adjusted with sulfuric acid or sodium hydroxide, or both.

7.1.4 *Detector*—a potentiostat capable of detecting the photocurrent generated.

8. Reagents and Materials

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.⁵ 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.

⁵ *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.

8.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent grade water conforming to Specification D1193, Type I.

8.3 Reagents:

8.3.1 *Calibrant*, 20 mg/L.

8.3.1.1 *Discussion*—Reagent is prepared from sorbitol (<2% by weight) and water. Weigh 20 mg of sorbitol. Dissolve the sorbitol in 1 L of water. 1 mg/L of calibrant is equivalent to 1 mg/L of theoretical oxygen demand.

8.3.2 *Electrolyte*, (<25 mg/L range), (proprietary).⁶

8.3.2.1 *Discussion*—reagent is prepared from lithium nitrate (<20% by weight), water and sorbitol. Electrolyte is used to dilute the sample for photocatalytic oxidation and to prepare electrolyte blank solution (8.3.3). The sorbitol in the electrolyte provides a baseline photocurrent.

8.3.3 *Electrolyte Blank Solution*, mix three parts water and one part electrolyte (8.3.2).

8.3.3.1 *Discussion*—Electrolyte blank solution is used to determine the photocurrent generated from the oxidation of water. The photocurrent generated from the oxidation of water is subtracted from the total photocurrent generated during the oxidation of the sample to determine the photocurrent generated due to the oxidation of the organic compounds in the sample.

⁶ The sole source of supply of the calibrant and proprietary electrolyte known to the committee at this time is Mantech, Inc., Guelph, Ontario, Canada. 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.