



Designation: D6238 – 98 (Reapproved 2017)

## Standard Test Method for Total Oxygen Demand in Water<sup>1</sup>

This standard is issued under the fixed designation D6238; 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 ( $\epsilon$ ) indicates an editorial change since the last revision or reapproval.

### 1. Scope

1.1 This test method covers the determination of total oxygen demand in the range from 100 to 100 000 mg/L, in water and wastewater including brackish waters and brines (see 6.5). Larger concentrations, or samples with high suspended solids, or both, may be determined by suitable dilution of the sample.

1.1.1 Since the analysis is based on the change in oxygen reading of the carrier gas compared to that when a sample is introduced (see 4.1), the measurement range is a function of the amount of oxygen in the carrier gas. The higher the desired concentration range, the more oxygen required in the carrier gas. Under recommended conditions, the carrier gas concentration should be between two to four times the maximum desired oxygen demand.

1.1.2 The lower measurement range is limited by the stability of the baseline oxygen detector output. This signal is a function of the permeation system temperature, carrier gas flow rate, oxygen detector temperature, and reference sensor voltage. Combined, these variables limit the minimum recommended range to 2 to 100 mg/L.

1.1.3 The upper measurement range is limited by the maximum oxygen concentration in the carrier gas (100 %). With the recommended conditions of carrier gas concentration being two to four times the maximum oxygen demand, this limits the maximum possible oxygen demand to between 250 000 to 500 000 mg/L. However, as a practical application to water analysis, this test method will consider a maximum range of 100 000 mg/L.

1.2 This test method is applicable to all oxygen-demanding substances under the conditions of the test contained in the sample that can be injected into the reaction zone. The injector opening limits the maximum size of particles that can be injected. If oxygen-demanding substances that are water-insoluble liquids or solids are present, a preliminary treatment may be desired. These pretreatment methods are described in Annex A2.

<sup>1</sup> 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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1.3 This test method is particularly useful for measuring oxygen demand in certain industrial effluents and process streams. Its application for monitoring secondary sewage effluents is not established. Its use for the monitoring of natural waters is greatly limited by the interferences defined in Section 6.

1.4 In addition to laboratory analysis, this test method is applicable to on-stream monitoring. Sample conditioning techniques for solids pretreatment applications are noted in Annex A2.

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

1.6 *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.*

1.7 *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>

D888 Test Methods for Dissolved Oxygen in Water

D1129 Terminology Relating to Water

D1192 Guide for Equipment for Sampling Water and Steam in Closed Conduits (Withdrawn 2003)<sup>3</sup>

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

D3856 Guide for Management Systems in Laboratories Engaged in Analysis of Water

<sup>2</sup> 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.

<sup>3</sup> The last approved version of this historical standard is referenced on www.astm.org.

[D5789 Practice for Writing Quality Control Specifications for Standard Test Methods for Organic Constituents \(Withdrawn 2002\)](#)<sup>3</sup>

[D5847 Practice for Writing Quality Control Specifications for Standard Test Methods for Water Analysis](#)

### 3. Terminology

#### 3.1 Definitions:

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

#### 3.2 Definitions of Terms Specific to This Standard:

3.2.1 *total oxygen demand (TOD), n*—the amount of oxygen required to convert the elements in compounds to their most stable oxidized forms.

### 4. Summary of Test Method

4.1 The total oxygen demand (TOD) measurement is achieved by continuous analysis of the concentration of oxygen in a combustion process gas effluent. The decrease in oxygen resulting from introduction of the sample into the combustion zone is a measure of oxygen demand.

4.2 The oxidizable components in a liquid sample introduced into a carrier gas stream containing a fixed amount of oxygen flowing through a 900°C combustion tube are converted to their stable oxides. The momentary reduction in the oxygen concentration in the carrier gas is detected by an oxygen sensor and indicated on a digital display or recorded.

4.3 The TOD for the sample is obtained by comparing the peak height to a calibration curve of peak heights for TOD standard solutions. The TOD for the standard solution is based on experimentally observed reactions in which carbon is converted to carbon dioxide, hydrogen to water, combined nitrogen including ammonia to nitric oxide, and elemental or organic sulfur to sulfur dioxide. Sample injection is achieved by means of an automatic valve, that provides unattended multiple sampling in the laboratory or on-stream monitoring.

4.4 For monitoring applications, pretreatment of the sample may be required. However, no single instruction can be written since pretreatment steps will be a function of the specific characteristics of the sample stream.

### 5. Significance and Use

5.1 The measurement of oxygen demand parameters is critical to the control of process wastewaters. Biochemical oxygen demand (BOD) and chemical oxygen demand (COD) analyzers have long time cycles and in the case of COD analyzers use corrosive reagents with the inherent problem of disposal. Total oxygen demand analysis is faster, approximately 3 min, and uses no liquid reagents in its analysis.

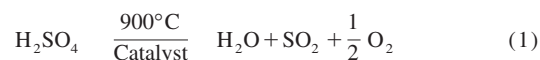
5.2 TOD can be correlated to both COD and BOD, providing effective on-line control.

5.3 TOD offers several features which make it a more attractive measurement than carbon monitoring using total carbon (TC) or total organic carbon (TOC) analyzers. TOD is unaffected by the presence of inorganic carbon. TOD analysis will also indicate noncarbonaceous materials that consume or contribute oxygen. For example, the oxygen demand of ammonia, sulfite and sulfides will be reflected in the TOD measurement. Also, since the actual measurement is oxygen consumption, TOD reflects the oxidation state of the chemical compound (that is, urea and formic acid have the same number of carbon atoms, yet urea has five times the oxygen demand of formic acid).

### 6. Interferences

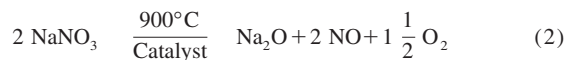
6.1 The dissolved oxygen concentrations will contribute a maximum error of 8 ppm. This error is only significant on ranges below 0 to 100 ppm when samples have no dissolved oxygen (DO) content. When operating in this range and samples contain low DO concentrations then compensation may be necessary. Measure the DO in both solutions in accordance with Test Methods [D888](#). Adjust the TOD result as follows: If DO of the sample is less than in the standard, subtract DO variation. If DO of the sample is greater than in the standard, add DO variation to the TOD result.

6.2 Sulfuric acid will normally decompose under sample combustion conditions as follows:



The oxygen release will result in a reduction in the TOD reading. However, alkali metal sulfates (that is, sodium and potassium salts) do not decompose under the combustion conditions. If sulfates are present in the samples, adjust to pH 11 with NaOH prior to analysis.

6.3 Nitrate salts decompose under sample combustion conditions as follows:



The resulting generation of oxygen reduces the oxygen demand.

6.4 Heavy metal ions have been reported to accumulate in the system resulting in a significant loss of sensitivity. The history of the combustion column appears to be a major factor contributing to interferences of this nature. Similarly, high concentrations of dissolved inorganic salts will tend to build up and coat the catalyst as indicated by a loss of sensitivity. To correct the problem, replace the combustion tube and refractory packing material and clean the catalyst in accordance with the manufacturer's recommendations. The effects of these problems can be minimized by dilution of the sample.

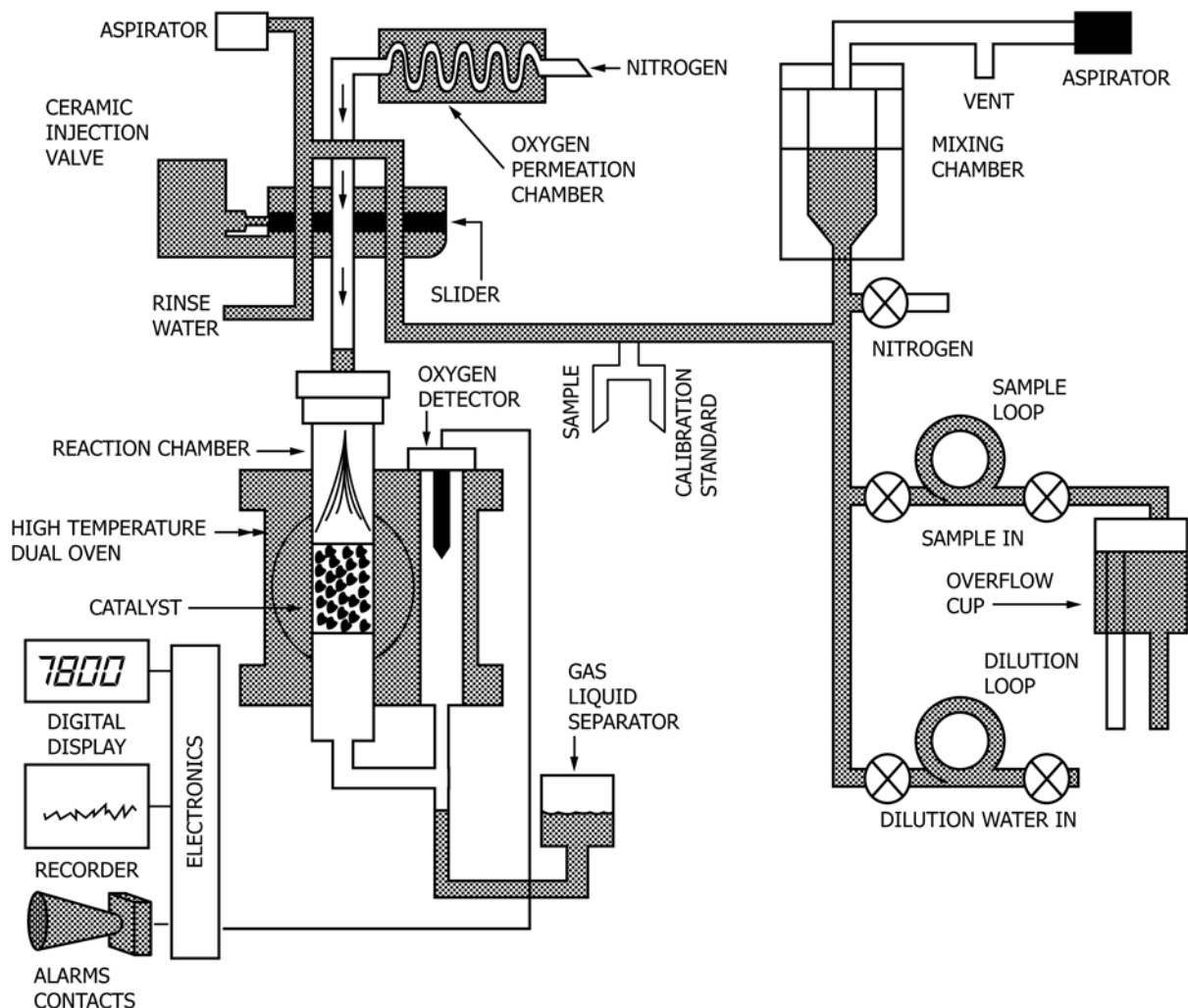


FIG. 1 Flow Diagram for TOD Analyzer

6.5 Some brackish waters and natural brines may exhibit base line drift. In such cases, continue to inject samples until a stable response is observed.

## 7. Apparatus

7.1 *Total Oxygen Demand Instrument*—(See Fig. 1), including a pure nitrogen source, an oxygen permeation system, sample injection valve, catalyst-combustion zone, gas flow controls, oxygen sensor and display or recorder, as detailed in Annex A2.<sup>4</sup>

7.2 *Homogenizing Apparatus*—A high speed blender, or a mechanical or ultrasonic homogenizer is satisfactory for homogenizing immiscible liquid samples and suspended solids (see Annex A1).

<sup>4</sup> The sole source of supply of the apparatus known to the committee at this time is Ionics, Inc., P.O. Box 9131, 65 Grove Street, Watertown, MA 02272. If you are aware of alternative suppliers, please provide this information to ASTM Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee that you may attend.

## 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, where such specifications are available.<sup>5</sup> 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*—Unless otherwise indicated, references to water shall be understood to mean reagent water conforming to Specification D1193, Type II except that distillation is not necessary.

<sup>5</sup> *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. Pharmaceutical Convention, Inc. (USPC), Rockville, MD.