



Designation: D1252 – 06 (Reapproved 2020)

# Standard Test Methods for Chemical Oxygen Demand (Dichromate Oxygen Demand) of Water<sup>1</sup>

This standard is issued under the fixed designation D1252; 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.

*This standard has been approved for use by agencies of the U.S. Department of Defense.*

## 1. Scope

1.1 These test methods cover the determination of the quantity of oxygen that certain impurities in water will consume, based on the reduction of a dichromate solution under specified conditions. The following test methods are included:

Test Method A — Macro COD by Reflux Digestion and Titration  
Test Method B — Micro COD by Sealed Digestion and Spectrometry

1.2 These test methods are limited by the reagents employed to a maximum chemical oxygen demand (COD) of 800 mg/L. Samples with higher COD concentrations may be processed by appropriate dilution of the sample. Modified procedures in each test method (Section 15 for Test Method A, and Section 24 for Test Method B) may be used for waters of low COD content (<50 mg/L).

1.3 As a general rule, COD results are not accurate if the sample contains more than 1000 mg/L  $\text{Cl}^-$ . Consequently, these test methods should not be applied to samples such as seawaters and brines unless the samples are pretreated as described in Appendix X1.

1.4 This test method was used successfully on a standard made up in reagent water. It is the user's responsibility to ensure the validity of these test methods for waters of untested matrices.

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.* For specific hazard statements, see Section 8, 15.6, and 24.5.

<sup>1</sup> These test methods are under the jurisdiction of ASTM Committee D19 on Water and are the direct responsibility of Subcommittee D19.06 on Methods for Analysis for Organic Substances in Water.

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*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>

- 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
- D3223 Test Method for Total Mercury in Water
- D3370 Practices for Sampling Water from Flowing Process Streams
- D5847 Practice for Writing Quality Control Specifications for Standard Test Methods for Water Analysis
- D5905 Practice for the Preparation of Substitute Wastewater
- E60 Practice for Analysis of Metals, Ores, and Related Materials by Spectrophotometry
- E275 Practice for Describing and Measuring Performance of Ultraviolet and Visible Spectrophotometers

## 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*—The term “oxygen demand” (COD) in these test methods is defined in accordance with Terminology D1129 as follows:

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

<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.

#### 4. Summary of Test Methods

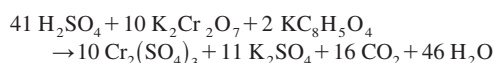
4.1 Most organic and oxidizable inorganic substances present in water are oxidized by a standard potassium dichromate solution in 50 % sulfuric acid (vol/vol). The dichromate consumed (Test Method A) or tri-valent chromium produced (Test Method B) is determined for calculation of the COD value.

4.2 The oxidation of many otherwise refractory organics is facilitated by the use of silver sulfate that acts as a catalyst in the reaction.

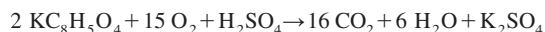
4.3 These test methods provide for combining the reagents and sample in a manner that minimizes the loss of volatile organic materials, if present.

4.4 The oxidation of up to 1000 mg/L of chloride ion is inhibited by the addition of mercuric sulfate to form stable and soluble mercuric sulfate complex. A technique to remove up to 40 000 mg/L chloride is shown in [Appendix X1](#) for Test Method B. The maximum chloride concentration that may be tolerated with the procedure for low COD, Test Method A ([15.10](#)), has not been established.

4.5 The chemical reaction involved in oxidation of materials by dichromate is illustrated by the following reaction with potassium acid phthalate ( $\text{KC}_8\text{H}_5\text{O}_4$ ):



Since 10 mol of potassium dichromate has the same oxidation power as 15 mol of oxygen, the equivalent reaction is:



Thus, 2 mol of potassium acid phthalate consumes 15 mol of oxygen. The theoretical COD of potassium acid phthalate is 1.175 g of oxygen per gram of potassium acid phthalate ([Table 1](#)).

#### 5. Significance and Use

5.1 These test methods are used to chemically determine the maximum quantity of oxygen that could be consumed by biological or natural chemical processes due to impurities in water. Typically this measurement is used to monitor and control oxygen-consuming pollutants, both inorganic and organic, in domestic and industrial wastewaters.

5.2 The relationship of COD to other water quality parameters such as TOC and TOD is described in the literature.<sup>3</sup>

#### 6. Interference and Reactivity

6.1 Chloride ion is quantitatively oxidized by dichromate in acid solution. (1.0 mg/L of chloride is equivalent to 0.226 mg/L of COD.) As the COD test is not intended to measure this demand, concern for chloride oxidation is eliminated up to 1000 mg/L of chloride by complexing with mercuric sulfate.

6.1.1 Up to 40 000 mg/L chloride ion can be removed with a cation based ion exchange resin in the silver form as

**TABLE 1 Test Method A, Recovery of Theoretical COD for Various Organic Material**

Component	Reactivity, Percent of Theoretical				
	1 <sup>A</sup>	2 <sup>B</sup>	3 <sup>C</sup>	4 <sup>D</sup>	5 <sup>E</sup>
<i>Aliphatic Compounds</i>					
Acetone	98	...	96	94	...
Acetic acid	92	92	98	...	...
Acrolein	62	...	...	...	...
Butyric acid	89	93	...	...	...
Dextrose	95	...	...	...	...
Diethylene glycol	93	...	...	70	...
Ethyl acetate	95	...	...	85	...
Methyl ethyl ketone	98	...	...	90	...
<i>Aromatic Compounds</i>					
Acetophenone	89	...	...	...	...
Benzaldehyde	...	...	...	80	...
Benzene	60–98	...	41	...	...
Benzoic acid	98	...	...	100	...
Diethyl phthalate	83	...	...	...	...
Diphenyl	81	...	...	...	...
<i>o</i> -cresol	95	...	...	95	...
Toluene	83	...	...	45	...
Potassium acid phthalate	100	...	...	...	...
<i>Nitrogen Compounds</i>					
Acrylonitrile	48	...	...	44	...
Adenine	...	...	...	...	59
Aniline	80	...	...	74	...
Butyl amine	57	...	...	...	...
Pyridine	0	...	1	...	2
Quinoline	...	...	...	...	87
Trimethylamine	1	...	...	...	...
Tryptophane	...	...	...	...	87
Uric acid	...	...	...	...	61

<sup>A</sup> Hamilton, C. E., unpublished data.

<sup>B</sup> Moore, W. A., and Walker, W. W., *Analytical Chemistry*, Vol 28, 1956, p. 164.

<sup>C</sup> Dobbs, R. A., and Williams, R. T., *ibid.*, Vol 35, 1963 p. 1064.

<sup>D</sup> Buzzell, J. C., Young, R. H. F., and Ryckman, D. W., "Behaviors of Organic Chemicals in the Aquatic Environment; Part II, Dilute Systems," *Manufacturing Chemists Association*, April 1968, p. 34.

<sup>E</sup> Chudoba, J., and Dalesicky, J., *Water Research*, Vol 7, No. 5, 1973, p. 663.

described in [Appendix X1](#) when using Test Method B. Since this pretreatment was not evaluated during the interlaboratory study, the user of the test method is responsible to establish the precision and bias of each sample matrix.

6.2 Oxidizable inorganic ions, such as ferrous, nitrite, sulfite, and sulfides are oxidized and measured as well as organic constituents.

#### 7. Reagents

7.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. All reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.<sup>4</sup>

7.2 *Purity of Water*—Unless otherwise indicated, reference to water shall be understood to mean reagent water that meets

<sup>3</sup> *Handbook for Monitoring Industrial Wastewater*, U.S. Environmental Protection Agency, Aug. 1973, pp. 5-10 to 5-12.

<sup>4</sup> *ACS Reagent Chemicals, Specifications and Procedures for Reagents and Standard-Grade Reference Materials*, 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.

the purity specifications of Type I or Type II water, presented in Specification [D1193](#).

## 8. Hazards

8.1 Exercise extreme care when handling concentrated sulfuric acid, especially at the start of the refluxing step ([15.7](#)).

8.2 Silver sulfate is poisonous; avoid contact with the chemical and its solution.

8.3 Mercuric sulfate is very toxic; avoid contact with the chemical and its solution.

## 9. Sampling

9.1 Collect the sample in accordance with Practices [D3370](#).

9.2 Preserve samples by cooling to 4°C if analyzed within 24 h after sampling, or preserve for up to 28 days at 4°C and at pH < 2 by addition of concentrated sulfuric acid. The addition of 2 mL of concentrated sulfuric acid per litre at the time of collection will generally achieve this requirement. The actual holding time possible without significant change in the COD may be less than 28 days, especially when easily oxidizable substances are present. It is the responsibility of the users of the test method to ensure the maximum holding time for their samples.

## TEST METHOD A MACRO COD BY REFLUX DIGESTION AND TITRATION

### 10. Scope

10.1 The amount of dichromate consumed in Test Method A is determined by titration rather than the spectrophotometric procedure used in Test Method B. This test method is appropriate where larger sample volumes would provide better precision and better representativeness of where equipment or space limitations exist.

10.2 The precision of this test method in standard solutions containing low-volatility organic compounds has been examined in the range of approximately 10 to 300 mg/L.

### 11. Summary of Test Method

11.1 The sample and standardized dichromate solution, in a 50 % by volume sulfuric solution, is refluxed for a 2-h digestion period.

11.2 Excess dichromate after the digestion period is titrated with a standard ferrous ammonium sulfate solution using ortho-phenanthroline ferrous complex as an internal indicator.

### 12. Interferences

12.1 The test method does not uniformly oxidize all organic materials. Some compounds, for example, are quite resistant to oxidation, while others, such as carbohydrates, are easily oxidized. A guide to the behavior of various types of organic materials is provided in [Table 1](#).

12.2 Volatile organics that are difficult to oxidize may be partially lost before oxidation is achieved. Care in maintaining

a low-solution temperature (about 40°C) and permitting oxidation to proceed at the lower temperature for a period of time before reflux is initiated will result in higher recoveries of theoretical COD of volatile organics.

## 13. Apparatus

13.1 *Reflux Apparatus*—The apparatus consists of a 500-mL Erlenmeyer or a 300-mL round-bottom flask, made of heat-resistant glass connected to a 300-mm (12-in.) Allihn condenser by means of a ground-glass joint. Any equivalent reflux apparatus may be substituted, provided that a ground-glass connection is used between the flask and the condenser, and provided that the flask is made of heat-resistant glass.

13.2 *Sample Heating Apparatus*—A heating mantle or hot plate capable of delivering sufficient controlled heat to maintain a steady reflux rate in the reflux apparatus is satisfactory.

13.3 *Apparatus for Blending or Homogenizing Samples*—A household blender is satisfactory.

## 14. Reagents

14.1 *Ferrous Ammonium Sulfate Solution (0.25 N)*—Dissolve 98.0 g of ferrous ammonium sulfate solution ( $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ ) in water. Add 20 mL of sulfuric acid ( $\text{H}_2\text{SO}_4$ , sp gr 1.84), cool and dilute to 1 L. Standardize this solution daily before use. To standardize, dilute 25.0 mL of 0.25 N potassium dichromate solution ( $\text{K}_2\text{Cr}_2\text{O}_7$ ) to about 250 mL. Add 20 mL of sulfuric acid (sp gr 1.84) and allow the solution to cool. Titrate with the ferrous ammonium sulfate solution to be standardized, using the phenanthroline ferrous sulfate indicator as directed in [15.10](#). Calculate the normality as follows:

$$N = (A \times B) / C$$

where:

*N* = normality of the ferrous ammonium sulfate solution,  
*A* = potassium dichromate solution, mL,  
*B* = normality of the potassium dichromate solution, and  
*C* = ferrous ammonium sulfate solution, mL.

14.2 *Ferrous Ammonium Sulfate Solution (0.025 N)*—Dilute 100 mL of 0.25 N ferrous ammonium sulfate solution to 1 L. Standardize against 0.025 N potassium dichromate solution as in [14.1](#). This solution is required only if COD is determined in the range of 10 to 50 mg/L.

14.3 *Mercuric Sulfate*—Powdered mercuric sulfate ( $\text{HgSO}_4$ ).

14.4 *Phenanthroline Ferrous Sulfate Indicator Solution*—Dissolve 1.48 g of 1,10-(ortho)-phenanthroline monohydrate, together with 0.70 g of ferrous sulfate ( $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ), in 100 mL of water. This indicator may be purchased already prepared.

14.5 *Potassium Acid Phthalate Solution, Standard (1 mL = 1 mg COD)*—Dissolve 0.851 g of potassium acid phthalate ( $\text{KC}_8\text{H}_5\text{O}_4$ ), primary standard, in water and dilute to 1 L.

14.6 *Potassium Dichromate Solution, Standard (0.25 N)*—Dissolve 12.259 g of potassium dichromate ( $\text{K}_2\text{Cr}_2\text{O}_7$ ) primary