



Designation: D1252 – 06 (Reapproved 2020)

Standard Test Methods for Chemical Oxygen Demand (Dichromate Oxygen Demand) of Water¹

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 (ϵ) 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 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.

¹ 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.

Current edition approved Jan. 1, 2020. Published January 2020. Originally approved in 1953. Last previous edition approved in 2012 as D1252 – 06 (2012) ^{ϵ 1}. DOI: 10.1520/D1252-06R20.

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:²

- 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.

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.

4. Summary of Test Methods

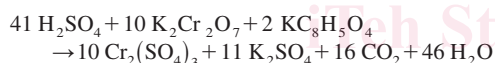
4.1 Most organic and oxidizable inorganic substances present in water are oxidized by a standard potassium dichromate solution in 50 % sulfuric acid (vol/vol). The dichromate consumed (Test Method A) or tri-valent chromium produced (Test Method B) is determined for calculation of the COD value.

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.

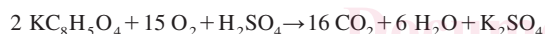
4.3 These test methods provide for combining the reagents and sample in a manner that minimizes the loss of volatile organic materials, if present.

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.³

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

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

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

Component	Reactivity, Percent of Theoretical				
	1 ^A	2 ^B	3 ^C	4 ^D	5 ^E
<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

^A Hamilton, C. E., unpublished data.

^B Moore, W. A., and Walker, W. W., *Analytical Chemistry*, Vol 28, 1956, p. 164.

^C Dobbs, R. A., and Williams, R. T., *ibid.*, Vol 35, 1963 p. 1064.

^D 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.

^E 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.⁴

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

⁴ *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 (H_2SO_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 (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

standard grade, previously dried at 103°C for 2 h, in water and dilute to 1 L in a volumetric flask.

14.7 *Potassium Dichromate Solution, Standard (0.025 N)*—Dilute 100.0 mL of 0.25 N potassium dichromate solution to 1 L. This solution is necessary only for determination of COD in the range of 10 to 50 mg/L.

14.8 *Sulfuric Acid-Silver Sulfate Solution*—Dissolve 15 g of powdered silver sulfate (Ag_2SO_4) in 300 mL of concentrated sulfuric acid (sp gr 1.84) and dilute to 1 L with concentrated sulfuric acid (sp gr 1.84).

15. Procedure

15.1 Homogenize the sample by blending if necessary. Place 50.0 mL of the sample in a reflux flask. If less than 50 mL of the sample is used, make up the difference in water, then add the sample aliquot and mix. Samples containing more than 800 mg/L COD are diluted and mixed precisely with water and 50.0 mL of the diluted sample are placed in a reflux flask.

NOTE 1—If the sample is diluted, it must consume at least 5 mL of dichromate. Dilute the sample if more than 20 mL of the titrant is needed to reach the endpoint.

15.2 Place 50 mL of water in a reflux flask for the blank determination.

15.3 Place the reflux flasks in an ice bath and add 1 g of powdered mercuric sulfate, 5.0 mL of concentrated sulfuric acid, and several glass beads or boiling stones. Mix well to complete dissolution.

15.4 With the flasks still in the ice bath, add slowly and with stirring, 25.0 mL of 0.25 N standard potassium dichromate solution.

15.5 With the flasks still in the ice bath, add 70 mL of sulfuric acid-silver sulfate solution slowly such that the solution temperature is maintained as low as possible, preferably below 40°C.

NOTE 2—If a particular waste is known to contain no volatile organic substances, the acid mixture may be added gradually, with less precaution, while the flask is immersed in the iced bath.

15.6 Attach the flasks to the condensers and start the flow of cold water. (**Warning**—Take care to ensure that the contents of the flask are well mixed; if not, superheating may result and the mixture may be expelled from the open end of the condenser.)

15.7 Apply heat to the flasks and reflux for 2 h. Place a small beaker or other cover over the open end of each condenser to prevent intrusion of foreign material.

15.8 Allow the flasks to cool and wash down the condensers with about 25 mL of water before removing flasks. If a round-bottom flask has been used, transfer the digestate to a 500-mL Erlenmeyer flask, washing out the reflux flask three or

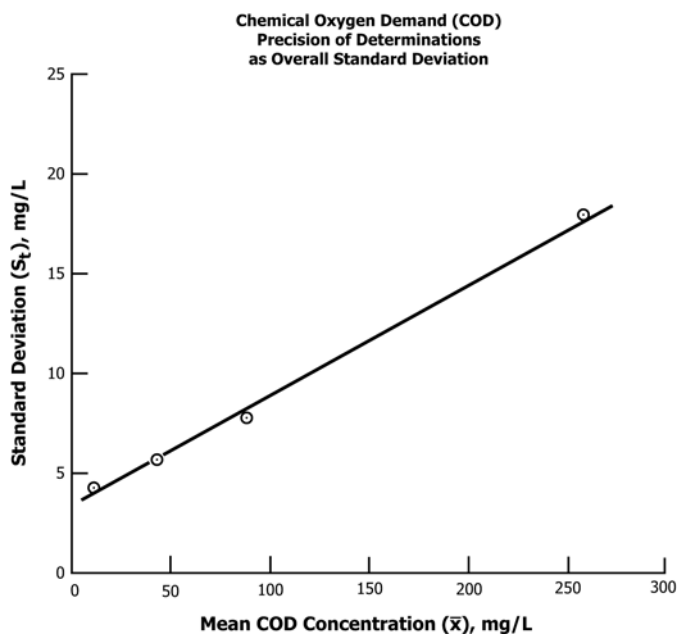


FIG. 1 Test Method A, Chemical Oxygen Demand (COD) Precision of Determination as Overall Standard Deviation

four times with water. Dilute the acid solution to about 300 mL with water and allow the solution to cool to about room temperature.

15.9 Add 8 to 10 drops of phenanthroline ferrous sulfate solution and titrate the excess dichromate with 0.25 N ferrous ammonium solution. The color change at the end point will be sharp, changing from a blue-green to a reddish hue. If the solution immediately turns a reddish-brown upon the addition of the indicator, repeat the analysis on a smaller sample aliquot.

NOTE 3—To avoid unnecessary pollution of the environment, dispose of mercury-containing waste solution properly. Refer to Test Method D3223, Appendix XI, for instructions.

15.10 For waters of low COD (10 to 50 mg/L), use 0.025 N potassium dichromate and ferrous ammonium sulfate solutions (14.2 and 14.7). If the COD is determined to be higher than 50 mg/L after using these reagents, reanalyze the sample, using the more concentrated reagents.

16. Calculation

16.1 Calculate the COD in the sample in milligrams per litre as follows:

$$\text{COD, mg/L} = ((A - B)N \times 8000)/S$$

where:

A = ferrous ammonium sulfate solutions required for titration of the blank, mL,

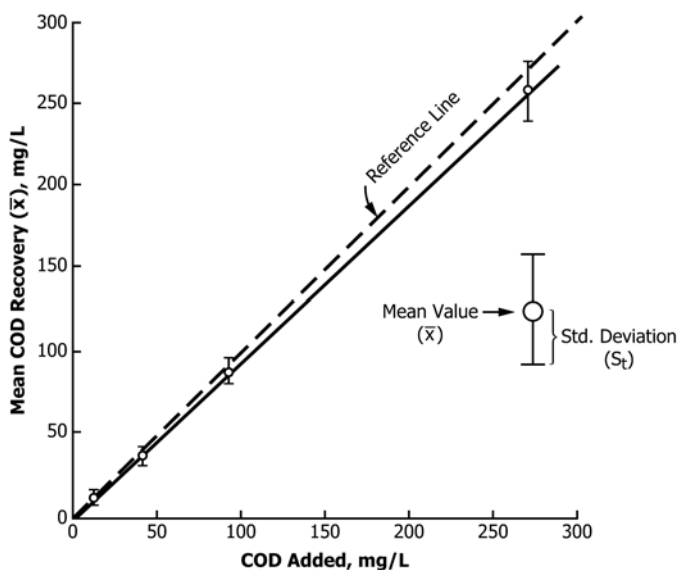


FIG. 2 Test Method A, Chemical Oxygen Demand (COD) Bias of Determinations

B = ferrous ammonium sulfate solution required for titration of the sample, mL,
 N = normality of the ferrous ammonium sulfate solution, and
 S = sample used for the test, mL.

17. Precision and Bias⁵

17.1 The overall precision of Test Method A within the range from 10 to 300 mg/L varies with the quantity being tested according to Fig. 1.

17.2 The data used in the calculation of precision are from EPA “Method Research Study 3” (1971) that involved two levels of COD, 12.3 mg/L (86 laboratories) and 270 mg/L (82 laboratories), and EPA “Water Pollution Laboratory Performance Evaluation, No. 8” (1982) that involved two levels of COD, 40.2 mg/L (65 laboratories) and 92 mg/L (67 laboratories).

17.3 The test data were obtained on reagent grade water and these precision and bias values may not be applicable to more complex water matrices. It is the user’s responsibility to ensure the validity of this test method to waters of untested matrices.

17.4 The precision obtained by the interlaboratory study is overall, S_p . Since very carefully standardized samples in very pure water were used rather than natural samples collected by usual sampling procedures, the estimates do not include the increase in precision statistics and the potential change in bias that may be attributed to the sample collection activities.

17.5 The trend of the approximately 5 % negative bias is shown in Fig. 2.

⁵ Supporting data were taken from “Method Research Study 3” (1971) and “Water Pollution Laboratory Performance No. 8” (1982), Environmental Protection Agency, National Environmental Research Center, Analytical Quality Control Laboratory, Cincinnati, OH. Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D19-1044. Contact ASTM Customer Service at service@astm.org.

TABLE 2 Test Method A, Recovery and Precision Data

Prepared COD, mg/L	Recovered COD, mg/L	Bias, mg/L	% Bias	Statistically Significant
12.30	12.34	+0.04	+0.33	no
40.2	37.9	-2.3	-5.7	yes
92.0	88.6	-3.4	-3.7	yes
270	257	-13	-4.8	yes

17.6 Prepared Standards—Recoveries of known amounts of COD in the series of prepared standards (previously described) were as shown in Table 2.

**TEST METHOD B
MICRO COD BY SEALED DIGESTION AND
SPECTROMETRY**

18. Scope

18.1 This test method is essentially equivalent to Test Method A, but it utilizes micro volumes of the same reagents contained in a sealable ampule or a screw-top culture tube and a spectrophotometer or filter photometer to measure absorbance or transmittance at selected wavelengths. This test method is applicable where only small sample volumes are available and where large numbers of samples need to be analyzed. This test method requires less space per analysis and uses less of the reagents, minimizing costs and volume of wastes discharged.

18.2 This test method was tested on Type II reagent water. It is the user’s responsibility to ensure the validity of this test method for waters of untested matrices.

19. Summary of Test Method

19.1 The dichromate reagent and silver catalyst used in this test method are similar to those used in Test Method A, but the volumes employed are 1/20 th of those in Test Method A.

19.2 A sample aliquot is introduced carefully into an ampule or screw-top tube so that the sample is layered on top of previously introduced reagents and remains there until the ampule or tube is sealed. This technique limits evolution of heat of solution until the container is sealed, minimizing the loss of volatile organics.

19.3 After sealing, the ampule or tube is heated in an oven, sand bath, or heated block at 150 ± 2°C for 2 h. The COD concentration is determined spectrophotometrically after digestion. In the low COD range (5 to approximately 50 mg/L), the loss of hexavalent chromium is measured at 420 nm, while for the high range (50 to approximately 800 mg/L), the increase in trivalent chromium is measured at 600 nm. The ampule or tube serves as the absorption cell.

20. Interferences

20.1 Interferences identified in Section 6 are also applicable to the micro procedure.

20.2 Volatile materials will be lost if the sample is mixed with the reagents before the ampule or tube is sealed. Volatile materials will also be lost during sample homogenization.

20.3 Potentially, the loss of volatile organics in the micro procedure will be less than that which may occur in Test Method A. Thus, results between the two methods may differ if volatile materials are involved.

20.4 Spectrophotometric interferences may exist due to turbidity of precipitated salts that are too colloidal to settle in a reasonable period of time. Centrifugation may be used to speed separation of the salts. This test method does not address a titration procedure for the micro-volume, but if the digested samples do not clear or spectrophotometric interference is suspected, the COD result can be determined by titration.⁶

20.5 The ampule or tube must have window areas that are free of scratches or smudges. If a suitable window area is not available, do not consider transfer of the sample. The sample and the blank may be titrated and the results used to calculate a COD value (see 24.10).

21. Apparatus

21.1 *Spectrophotometer or Filter Photometer*, suitable for measurements at 600 nm and 420 nm using the ampules or tubes in 21.3 or 21.3.1 as absorption cells. Filter photometers and photometric practices shall conform to Practice E60. Spectrophotometers shall conform to Practice E275. For some spectrophotometers, poor sensitivity at 420 nm has been observed. A suggested minimum sensitivity for the spectrophotometer readout is 0.002 absorbance units per milligram per litre of COD for the low range procedure.

21.2 *Heating Oven*, sand bath, or block heater capable of maintaining a temperature of $150 \pm 2^\circ\text{C}$ throughout. If an oven is used and screw-top tubes are employed, ascertain that the caps can withstand the oven temperature and solution pressure. The heating device must be equipped with a high temperature shut-off set at 175 to 185°C.

21.3 *Culture Tubes*, borosilicate glass, 16 by 100 mm, with TFE-fluorocarbon-lined screw caps. Protect the caps and culture tubes from dust contamination.

21.3.1 *Ampules*, borosilicate glass, 10 mL, may be substituted for the culture tubes in 21.3. These ampules are rotated and uniformly sealed with a glass blowing torch after addition of sample and reagent solutions. The nominal path length of these ampules shall be 15 to 20 mm.

21.4 *Apparatus for Blending or Homogenizing Samples*—A tissue homogenizer is recommended. However, a household blender may be used, but a suitable reduction in particle size may not be obtained.

NOTE 4—A partial round robin, using cellulose filter paper as the organic material, demonstrated serious difficulties in achieving a representative subsample. The use of a blender followed by a tissue homogenizer was required.

22. Reagents

22.1 *Silver Sulfate Catalyst Solution*—Dissolve 22 g of silver sulfate (Ag_2SO_4) in a 4.09 kg (9 lb) bottle of concentrated sulfuric acid (H_2SO_4).

⁶ Messenger, A. L., "Comparison of Sealed Digestion Chamber and Standard Method COD Tests," *Journal Water Pollution Control Federation*, Vol 53, No. 2, February 1981, pp. 232–236.

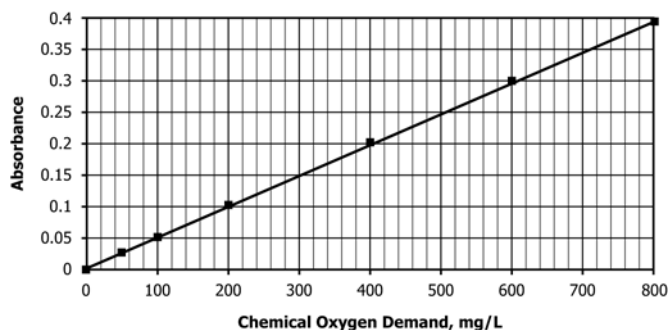


FIG. 3 Typical COD Calibration Curve for Spectrophotometric COD Method, Ampule Technique (Test Method B)

22.2 *Potassium Acid Phthalate Solution, Standard* (1 mL = 1 mg/L)—See 14.5.

22.3 *Potassium Dichromate Digestion Solution:*

22.3.1 *High Range*—Add 10.216 g of potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) dried at 103°C for 2 h, 167 mL of concentrated sulfuric acid (H_2SO_4) (sp gr 1.84) and 33.3 g of mercuric sulfate (HgSO_4) to about 750 mL of water, mix, and let cool. Dilute the solution to 1 L with water and mix thoroughly.

22.3.2 *Low Range*—Add 1.022 g of potassium dichromate, ($\text{K}_2\text{Cr}_2\text{O}_7$) (dried at 103°C for 2 h), 167 mL of concentrated sulfuric acid (H_2SO_4) (sp gr 1.84) and 33.3 g of mercuric sulfate (HgSO_4) to about 750 mL of water, mix, and cool. Dilute the solution to 1 L with water and mix thoroughly.

22.4 *Ferrous Ammonium Sulfate Solution (0.10 N)*—Dilute 400 mL of 0.25 N ferrous ammonium sulfate solution (see 14.1) to 1 L. Standardize against 0.25 N potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) as in 14.1.

22.5 *Ferrous Ammonium Sulfate Solution (0.01 N)*—Dilute 40 mL of 0.25 N ferrous ammonium sulfate solution (see 14.1) to 1 L. Standardize against 0.025 N potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) as in 14.1.

22.6 *Phenanthroline Ferrous Sulfate Indicator Solution*—See 14.4. If desired, the indicator may be diluted 1:5 for use in this test method.

23. Calibration

23.1 *High Range*—Dilute the following volumes of COD standard solution (see 22.2) to 50 mL with water. The high range procedure may be used for COD determination as low as 25 mg/L at the discretion of the analyst.

Potassium Acid Phthalate Standard Solution, mL	COD, mg/L
2.5	50
5	100
10	200
20	400
30	600
40	800

NOTE 5—A typical COD calibration curve for spectrophotometric COD method, ampule technique (Test Method B) is shown in Fig. 3.

23.2 *Low Range*—Dilute the following volumes of potassium acid phthalate standard solution to 200 mL with water. At the discretion of the analyst, the upper limit may be extended to approximately 150 mg/L.