Designation: D6697 – 01

Standard Test Method for Determination for Chemical Oxygen Demand (Manganese III[1] Oxygen Demand) of Water[2]

This standard is issued under the fixed designation D6697; 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 the colorimetric determination of the quantity of oxygen that certain impurities in water will consume, based on the reduction of a manganese III solution under specified conditions. This standard method does not use characteristic heavy metal reagents, thus eliminating environmental and disposal concerns apparent in other methods.

1.2 This test method determines chemical oxygen demand colorimetrically using manganese III to obtain a visible color intensity inversely proportional to the chemical oxygen demand of the sample. Analytical test kits conforming to these methods are available commercially in ranges from 80 to 1,000 mg/L (ppm) chemical oxygen demand. It is the user's responsibility to ensure the validity of these test methods for their specific samples and matrices.

1.3 *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 Sections 9 and 12.

2. Referenced Documents

2.1 *ASTM Standards:*[3]

D596 Guide for Reporting Results of Analysis of Water
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
D5789 Practice for Writing Quality Control Specifications for Standard Test Methods for Organic Constituents[4]
D5905 Practice for the Preparation of Substitute Wastewater
E60 Practice for Analysis of Metals, Ores, and Related Materials by Molecular Absorption Spectrometry
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 test method refer to Definitions D1129.

3.2 *Definitions of Terms Specific to This Standard:*

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.

3.2.2 *MSDS*, *n*—Material Safety Data Sheet; should be included with all reagents.

4. Summary of Test Method

4.1 This test method consists of oxidation of sample organic matter by manganese III, a strong, chemical oxidant, and subsequent measure of the organic matter oxygen equivalent. Manganese III changes quantitatively from purple towards colorless when it reacts with organic matter. The reaction mechanism of the method is illustrated by the following equation, using potassium hydrogen phthalate as an example:

$$KC_8H_5O_4 + 7.5\ O_2 \rightarrow 8\ CO_2 + 2\ H_2O + KOH$$

4.1.1 Manganese III typically oxidizes about 80 % of the organic compounds. Studies have shown that the reactions are reproducible, and test results can be correlated empirically to biochemical oxygen demand (BOD) values and hexavalent chromium COD tests. None of the above oxygen demand tests provide 100 % oxidation of all organic compounds.

4.2 Calibration is based on the oxidation of potassium acid phthalate (KHP), which is adequate for most applications. This calibration may be developed by the user, or the manufacturer may provide a curve that it has developed for its instruments. A different response may be seen in analyzing various wastewaters. Special waste streams or classes will require a separate calibration to obtain a direct mg/L COD reading or to generate a correction factor for the precalibrated KHP response. The

[1] Trivalent Manganese.

[2] 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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[3] 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] Withdrawn. The last approved version of this historical standard is referenced on www.astm.org.

sample digestion time can be extended for up to four hours for samples that are difficult to oxidize.

4.3 For samples containing chloride, pretreatment to remove chloride interference is necessary. Chloride removal is accomplished by introducing the sample to the chloride removal agent before sample reaction with the manganese III oxidant.

4.4 The sample, with or without chloride-removal pretreatment, is introduced carefully into a screw-top tube that contains the manganese III reagent.

4.5 The sealed tube is heated in a heating block at 165 ± 2 °C for two hours. After digestion, the COD concentration is determined spectrophotometrically at the absorbance maximum of 510 nm.

5. Significance and Use

5.1 This and other COD test methods are used to chemically determine the quantity of oxygen that certain impurities in water will consume. Typically this measurement is used to monitor and control oxygen-consuming pollutants, both inorganic and organic, in domestic and industrial wastewater applications.

5.2 For samples from a specific source, COD can be related empirically to BOD, organic carbon, or organic matter. The COD value is useful for monitoring and process control after this correlation has been established.

6. Interferences

6.1 Chloride is the most common interference; up to 1000 mg/L chloride can be removed by sample pretreatment (See 12.3). If chloride is known to be absent, the pretreatment can be omitted. Determine if chloride will affect test results by analyzing routine samples with and without the chloride removal and compare results. A separate sample portion may be tested for chloride concentration. Chloride will contribute to the manganese III COD value at a rate of approximately 0.31 mg/L COD per mg/L chloride present in the sample. Most wastewater samples will require chloride removal.

6.2 Ammonia causes a positive interfere with the test in the presence of chloride.

6.3 Volatile materials will be lost if the sample is mixed before the tube is sealed. Volatile materials will also be lost during sample homogenization.

7. Apparatus

7.1 *Spectrophotometer or Filter Photometer*, suitable for measurements at 510-nm using the tubes in 7.3 as absorption cells. COD tube contents also may be transferred to spectrophotometer cells for measurement in 12.6. Filter photometers and photometric practices shall conform to Practice E60. Spectrophotometers shall conform to Practice E275.

7.2 *Heating Block*, capable of maintaining a temperature of 165 ± 2°C throughout. If possible, block temperature should be monitored during testing with a calibrated thermometer.

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

7.4 *Apparatus for Blending or Homogenizing Samples*, A laboratory blender is recommended, although a household blender may be used. Other laboratory homogenizers may provide acceptable performance.

7.5 *Vacuum Pretreatment Device*, consisting of vacuum chamber connected to a pump assembly that draws sample through the chloride removal agent. An internal gauge on the vacuum chamber must be utilized to indicate a vacuum level of 508-mm (20 inches) of water. The pump must be capable of generating and displaying a vacuum of 508-635 mm (20-25 inches) of mercury.

7.6 *Mixing Vials*, borosilicate, 20-30mL capacity, with TFE-fluorocarbon-lined screw closures.

8. Reagents

8.1 *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.[5]

8.2 *Purity of Water*—Unless otherwise indicated, reference to water shall mean reagent water conforming to Specification D1193, Type I or Type II.

8.3 *Chloride Removal Agent*—Sodium Bismuthate ($NaBiO_3$) in an inert medium, packaged in single-use cartridges.[6]

8.4 *Manganese III COD Reagent*—Premeasured COD Tubes of reagent and catalyst.[6] Reagent is stabilized by complexation in sulfuric acid solution where there are several possible manganese III complexes. The predominant species in 11N H_2SO_4 are $Mn_2(SO_4)_3$ and two hydrated species, $[Mn(H_2O)_5HSO_4]^{2+}$ and $[Mn(H_2O)_5(HSO_4)_2]^{+}$.

8.5 *Potassium Acid Phthalate Solution, Standard (1 mL = 1 mg COD)*—Dissolve 0.851 g of dried (120°C, overnight) potassium acid phthalate ($KC_8H_5O_4$), primary standard, in water and dilute to 1L.

8.6 *Sulfuric Acid*—(H_2SO_4)concentrated, reagent grade (sp gr 1.84)

9. Precautions

9.1 Exercise extreme care when handling concentrated sulfuric acid.

9.2 The steps listed under the Procedure section are general, procedural summations. In all matters, it is important to refer to the selected manufacturer and the specific test instructions for necessary details contributing to proper and accurate testing results.

9.3 Use appropriate safety precautions and equipment for heating and handling hot tubes. See manufacturer's instructions and Material Safety Data Sheet (MSDS) for hazards.

10. Sampling

10.1 Collect the sample in accordance with Practices D3370.

[5] "Reagent Chemicals, American Chemical Society Specifications," Am. Chemical Soc., Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see "Reagent Chemicals and Standards," by Joseph Rosin, D. Van Nostrand Co., Inc., New York, NY, and the "United States Pharmacopeia."

[6] The sole source of supply of the reagent known to the committee at this time is Hach Company, P.O. Box 389, Loveland, CO 80539 USA. The Manganese III COD Reagent is available commercially as OxyVer® COD Reagent.