Designation: D 6697 – 01

An American National Standard

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

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:*

D 596 Practice for Reporting Results of Analysis of Water[3]

D 1129 Terminology Relating to Water[3]

D 1193 Specification for Reagent Water[3]

D 2777 Determination of Precision and Bias of Applicable Methods of Water[3]

D 5789 Writing Quality Control Specifications for Standard Test Methods for Organic Constituents[3]

D 5905 Practice for the Preparation of Substitute Wastewater[4]

E 60 Practice for Photometric and Spectrophotometric Methods for Chemical Analysis of Metals[5]

E 275 Practice for Describing and Measuring Performance of Ultraviolet, Visible and Near Infrared Spectrophotometers[6]

3. Terminology

3.1 *Definitions*:

3.1.1 For definitions of terms used in this test method refer to Definitions D 1129.

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

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[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] *Annual Book of ASTM Standards*, Vol 11.01.

[4] *Annual Book of ASTM Standards*, Vol 11.02.

[5] *Annual Book of ASTM Standards*, Vol 03.05.

[6] *Annual Book of ASTM Standards*, Vol 14.01.

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 E 60. Spectrophotometers shall conform to Practice E 275.

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.[7]

8.2 *Purity of Water*—Unless otherwise indicated, reference to water shall mean reagent water conforming to Specification D 1193, Type I or Type II.

8.3 *Chloride Removal Agent*—Sodium Bismuthate ($NaBiO_3$) in an inert medium, packaged in single-use cartridges.[8]

8.4 *Manganese III COD Reagent*—Premeasured COD Tubes of reagent and catalyst.[8] 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 D 3370.

10.2 Collect samples in glass or plastic bottles free of organic contamination. Fill containers completely and cap

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[7] "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."

[8] 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.

tightly. Analyze biologically active samples as soon as possible after collection. Homogenize samples to assure representative samples. Store samples up to 28 days by adjusting the pH to 2 or less with sulfuric acid (about 2mL per liter) and storing at 4°C.

11. Calibration and Standardization

11.1 Most instruments are precalibrated by the manufacturer and/or can be calibrated by the user by determining a correlation between COD concentration and absorbance. Check the manufacturer's instructions for details.

11.2 *Calibration Preparation*:

11.2.1 Prepare a series of quantitative dilutions of potassium hydrogen phthalate standard in reagent water. At least five concentrations over the range of 80-1000 mg/L are recommended.

11.2.2 Carry these standards (in triplicate) and a reagent water blank through the analysis procedure. If the chloride removal process is to be used for sample analysis, it should be used for preparation of the calibration standards as well.

11.2.3 Create a calibration graph, or program the colorimeter or spectrophotometer with the calibration data.

12. Procedure [9]

12.1 Review Precautions in Section 9 and the manufacturer's instructions before proceeding.

12.2 Homogenize 100-mL portions of samples containing suspended solids for at least 30 seconds in a blender or other homogenizer.

12.3 If the sample contains chloride (See 6.1), remove the chloride (see 12.3.1-12.3.8). If the sample does not contain chloride, proceed to 12.4.

12.3.1 Stir the sample while measuring 9.00 mL homogenized sample into a glass mixing vial. (For samples of over 1000 mg/L COD, measure a smaller aliquot of homogenized sample, and dilute to 9.00 mL with reagent water.

NOTE 1—The procedure is designed for a final volume of 9.00 mL at this point. See Section 13 for suggested dilutions and correction factors.) Take caution to assure a representative sample volume.

12.3.2 Add 1.00 mL concentrated sulfuric acid.

12.3.3 Cap tightly and mix well. **Warning—**The solution and vessel will become hot. Cool to room temperature before proceeding.

12.3.4 Prepare a reagent blank and any standards as in 12.3.1-12.3.3, using 9.00 mL reagent water or standard respectively as the sample. Carry the reagent blank and standards through the chloride removal process along with the sample.

12.3.5 Attach vacuum pretreatment device to vacuum pump. Close regulator valve completely on vacuum pretreatment device, turn on pump and adjust regulator valve on vacuum to 508-635 mm (20-25 inches) of mercury as read at the pump. Open the regulator valve on the vacuum pretreatment device until the internal gauge on the vacuum pretreatment device reads 508 (20 inches) of water.

12.3.6 Remove caps from reagent-filled COD tubes and place into the holes in the vacuum pretreatment device base. Replace the top of the vacuum pretreatment device and pipet 0.60-mL of the prepared sample into separate chloride removal agent cartridges that have been seated in the top of the vacuum pretreatment device. Treat the reagent blank and any standards in the same manner.

12.3.7 Draw the sample and blank through the chloride removal agent into reagent-filled COD Tubes, at a controlled vacuum of 508 mm (20 inches) of water, as read at the vacuum pretreatment device internal gauge. This must be complete within 45 seconds. Complete transfer of any remaining sample in the cartridge by closing the regulator valve on the vacuum pretreatment device completely; allow one minute for complete transfer . Do not reuse the chloride removal agent cartridge. The procedure has been designed to account for the small liquid volume retained by the chloride removal agent cartridge.

12.3.8 Transfer the filter (and any retained solids) from the chloride removal cartridge to the COD tube. Proceed to 12.5.

12.4 If the sample does not contain chloride (See 6.1), proceed as follows:

12.4.1 Pipet 0.50 mL sample into a reagent-filled COD tube. (For samples over 1000 mg/L COD, dilute a smaller aliquot of homogenized sample according to 13.2.1.)

12.4.2 Pipet 0.50 mL of reagent water and any standard into their respective COD tubes. Carry the reagent blank and standards through the procedure along with the sample. Proceed with 12.5.

12.5 Cap the screw-top tubes, mix well and place the sample, standard(s) and the reagent blank into the heating block preheated to 165°C. Heat at 165°C for two hours. Remove from block and cool to room temperature.

12.6 Fill an empty photometric cell with reagent water. Fill the photometric cell (if different from the reaction container) with the prepared sample for COD. Read the displayed sample results against the reagent water filled cell at 510 nm. The prepared reagent blank serves as a quality control only, and will not be used to zero the instrument. Invert the cell several times prior to reading and ensure that the filter disc and any undigested suspended solids are allowed to settle, so that they do not interfere with photometric readings.

13. Calculation

13.1 No calculations are required for direct reading instruments. COD concentrations are read directly from the instrument. See specific manufacturer instructions.

13.2 For instruments displaying percent transmittance or absorbance, use the curve created in 11.2, or a calibration table created for the curve, to convert the results into concentration values.

13.2.1 If the sample was diluted, apply the appropriate dilution factor to the result.

Suggested Dilution Table
(for use with chloride removal procedure only)

Sample (mL)	Reagent Water (mL)	Range (mg/L COD)	Multiplication Factor
6.0	3.0	30–1500	1.5
3.0	6.0	60–3000	3
1.0	8.0	180–9000	9

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[9] This procedure is covered by U.S. Patents No 5683914, 5667754 and 5556787. Interested parties are requested to submit information regarding identification of alternatives to ASTM Headquarters.

13.2.2 For other dilutions that are not listed in the table, or for samples that do not contain chloride, calculate the multiplication factor as follows:

$$(\text{sample volume} + \text{reagent water volume})/\text{sample volume} = \text{multiplication factor}$$

13.3 All COD calculations to be in concentration units of mg/L.

14. Report

14.1 Report the results of the test as mg/L COD. Include a description of the procedure and any variations in operation or other conditions.

14.2 Refer to Practice D 596. This reference provides guidelines for the reporting of results of water analyses to laboratory clients in a complete and systematic fashion.

15. Quality Assurance/Quality Control

15.1 Minimum quality control requirements are method blanks, initial demonstration of proficiency, verification of calibration and verification of control at representative analyte concentrations. Additional recommendations for precision, bias and interlaboratory traceability follows. For a general discussion of quality control and good laboratory practices, see Practice D 5789.

15.2 *Method Blank*—Reagent water blanks are carried through the procedure with each set or batch of samples, and are to be used as a quality control only. The value obtained for the reagent water blank should be lower than the MDL.

15.3 *Calibration Verification*—A calibration standard should be carried through the procedure at the beginning of each day, to verify that the most recent calibration is still valid.

15.3.1 Prepare a 300-mg/L potassium hydrogen phthalate standard, and perform the procedure (beginning at 12.3 or 12.4, as appropriate for expected use with normal sample matrices).

15.3.2 Observed response should be ±10 % of anticipated response or 300 ± 30 mg/L COD (Limits based upon interlaboratory study). If unacceptable results are obtained, recalibration is recommended.

15.4 *Initial Demonstration of Proficiency*—Each new analyst should perform the following procedure, to assure that he/she is capable of using the test method to generate meaningful data.

15.4.1 Prepare an 800-mg/L potassium hydrogen phthalate standard. Carry seven replicates of this standard through the procedure (beginning at 12.3 or 12.4, as appropriate for expected use with normal sample matrices).

15.4.2 The observed response should fall within the acceptable ranges given in Table 1. These criteria are derived from the interlaboratory precision and bias study. Refer to Practice D 5789 to develop limits for standards at other concentrations.

15.5 *Quality Control Samples*:

15.5.1 To ensure that the test method is in control, analyze a quality control sample at 800 mg/L or other selected concentration. Frequency should be determined by the analyst, but should be at least 5 % of the workload, or daily.

15.5.2 The value obtained should be within acceptable limits. Refer to Table 1. Again, these criteria were derived from the interlaboratory study. Analysts should recalibrate and/or reanalyze samples run since the last quality control sample, if unacceptable results are obtained.

15.6 *Duplicates*:

15.6.1 Analysis of duplicates at a frequency of 5 % of the sample workload or once per batch of sample is recommended to assess the precision of the method on matrix samples.

15.6.2 Calculate the standard deviation of the duplicate values and compare to the single operator precision found in the Precision and Bias statement. For further information regarding application of the F test, refer to Practice D 5789.

15.6.3 Analysts obtaining results outside acceptable limits should implement corrective action, including verifying adequacy of sample preparation techniques.

15.7 *Recovery Spikes*:

15.7.1 While analysis of spiked samples will not verify efficacy of digestion of certain organic compounds, nor make the analyst aware of the presence of interfering species, the procedure can provide an indication of whether reagents and equipment are operating as expected.

15.7.2 Analysis of spiked matrix samples at a frequency of 5 % of the sample workload or on at least one sample from each batch is recommended to ensure that the method is in control for each sample matrix. Add aliquots of potassium hydrogen phthalate standard to 100-mL portions of sample and carry these through the procedure. The concentration of the spike in addition to the background concentration must fall within the range of the method (80-1000 mg/L COD). Correct for any dilutions caused by the standard.

15.7.3 Calculate percent recovery. Results should be within acceptable limits. See Table 1, section 15.4.2 for these limits. Refer to D 5789 to develop limits for spikes at other concentrations. If results do not fall within these limits, one of the following must be employed: the matrix interference must be removed, all samples in the batch must be analyzed by a test method not affected by the matrix interference, or the results must be qualified with an indication that they do not fall within the performance criteria of the test method.

15.8 *Interlaboratory Traceability/Independent Reference Material*—To verify the quantitative value produced by the test method, analyze an independent reference material as a regular sample once per quarter. The concentration of the reference material should be in the range of 80 to 1000 mg/L COD and results should be within the control limits specified by the outside source.

TABLE 1 Criteria for Quality Control Requirements

Sample Concentration	QC Check & Recovery Spike	Proficiency Demonstration	
	Acceptance Range for QC Check & Recovery Spike	Max Acceptable Standard Deviation	Acceptance Range for Mean Recovery
800 mg/L COD	667 to 907 mg/L	36.5	686 to 892

16. Precision and Bias [10]

16.1 This test method was tested by 12 laboratories with each operator analyzing each sample on 1 day. These collaborative test data were obtained on three matrices: reagent water

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[10] Supporting data for the precision and bias statements have been filed at ASTM Headquarters. Request RR:D19 - 1170.

TABLE 2 Final Statistical Summary for COD in Substitute Wastewater Samples

Sample Number	1–3	1–7	1–5	1–9	1–1	1–6	1–2	1–10	1–4	1–8
True Conc, mg/L COD	25	25	64	75	136	167	363	405	741	794
# of Retained Values	10	9	10	10	9	10	10	10	9	10
Mean Recovery (XBAR), mg/L COD	21	26	64	79	107	142	329	384	713	767
Recovery, %	84.80 %	104.44 %	100.31 %	104.93 %	78.92 %	84.85 %	90.72 %	94.69 %	96.21 %	96.61 %
Overall Standard Deviation (S_t)	13.7	9.7	14.1	14.0	8.9	18.7	34.2	62.7	22.5	42.3
Overall Relative Standard Deviation, %	64.82 %	37.10 %	21.93 %	17.85 %	8.29 %	13.22 %	10.38 %	16.35 %	3.15 %	5.52 %
Number of Retained Pairs	9		10		9		10		9	
Single Operator Standard Deviation (S_o)	4.10		8.72		14.08		30.59		19.70	
Analyst Relative Deviation, %	17.33 %		12.20 %		11.31 %		8.58 %		2.66 %	

TABLE 3 Final Statistical Summary for COD in KHP-Spiked Reagent Water

Sample Number	2–7	2–2	2–3	2–1	2–10	2–8	2–4	2–6	2–5	2–9
True Conc, mg/L COD	20	25	75	85	140	160	375	425	750	850
# of Retained Values	9	9	9	9	9	9	9	9	9	9
Mean Recovery (XBAR), mg/L COD	32	40	84	92	142	160	383	404	751	829
Recovery, %	160.00 %	158.22 %	112.44 %	107.71 %	101.43 %	100.14 %	102.16 %	95.11 %	100.19 %	97.50 %
Overall Standard Deviation (S_t)	16.1	21.4	13.0	18.7	18.8	10.1	25.6	34.2	30.1	46.0
Overall Relative Standard Deviation, %	49.63 %	54.18 %	15.37 %	20.43 %	13.26 %	6.33 %	6.69 %	8.47 %	4.01 %	5.55 %
Number of Retained Pairs	9		9		9		9		9	
Single Operator Standard Deviation (S_o)	8.53		7.46		9.57		9.34		23.98	
Analyst Relative Deviation, %	24.00 %		8.48 %		6.33 %		2.37 %		3.04 %	

TABLE 4 Final Statistical Summary for COD in KHP & Chloride Spiked Reagent Water

Sample Number	3–5	3–7	3–1	3–9	3–3	3–8	3–4	3–10	3–2	3–6
True Conc, mg/L COD	25	30	80	80	145	155	380	420	775	825
# of Retained Values	9	9	9	8	9	9	9	8	9	9
Mean Recovery (XBAR), mg/L COD	37	53	102	106	177	186	400	453	809	842
Recovery, %	148.00 %	177.78 %	127.36 %	132.81 %	122.15 %	120.22 %	105.32 %	107.80 %	104.36 %	102.03 %
Overall Standard Deviation (S_t)	20.4	22.4	23.4	22.5	25.6	23.9	25.1	26.3	39.8	36.2
Overall Relative Standard Deviation, %	55.17 %	41.99 %	23.01 %	21.15 %	14.46 %	12.82 %	6.27 %	5.82 %	4.93 %	4.30 %
Number of Retained Pairs	9		8		9		8		9	
Single Operator Standard Deviation (S_o)	11.29		16.73		10.55		8.07		24.06	
Analyst Relative Deviation, %	25.00 %		16.07 %		5.81 %		1.89 %		2.92 %	

spiked with potassium hydrogen phthalate , reagent water spiked with potassium hydrogen phthalate and chloride and ASTM Substitute Wastewater (See Practice D 5905). Ten samples were prepared in each matrix, and sent to the laboratories for analysis.

16.2 Results of this collaborative study may not be typical of results for matrices other than those studied.

16.3 Precision and Bias were determined in accordance to Specification D 2777. Final statistics for each of the three matrices can be found in Tables 2-4.

17. Keywords

17.1 COD; interference; KHP; manganese III; organics; oxidation