

STANDARD OPERATING PROCEDURE For SM 5220 B

The Determination of Chemical Oxygen Demand Open Reflux Method

SOP #: SM 5220 B

REVISION #: 0

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Page 1 of 10

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TABLE OF CONTENTS

	Page
LIST OF REVISIONS	3
LIST OF TABLES	4
1.0 SCOPE AND APPLICATION	5
2.0 SUMMARY OF METHOD	5
3.0 DEFINITIONS	5
4.0 INTERFERENCES	5
5.0 SAFETY	6
6.0 EQUIPMENT AND SUPPLIES	6
7.0 REAGENTS AND STANDARDS	6
8.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE	6
9.0 QUALITY CONTROL	7
10.0 CALIBRATION AND STANDARDIZATION	7
11.0 PROCEDURE	7
13.0 METHOD PERFORMANCE	8
14.0 POLLUTION PREVENTION	8
15.0 WASTE MANAGEMENT	8
16.0 REFERENCES	8
17.0 TABLES AND VALIDATION DATA	9



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Page: 3 of 10

LIST OF REVISIONS

Rev. #	Date	Description of Revision	Page #
0	September 2000	None	
0	September 2000	Replaced old DEP Logo with state seal + MassDEP (December 2006)	Title page & header



LIST OF TABLES

	Page
TABLE 1. VALIDATION DATA.....	9
TABLE 2. PRECISION OF CHEMICAL OXYGEN DEMAND (COD) IN REAGENT WATER BY STANDARD METHOD 5220 B	9
TABLE 3. METHOD DETECTION LIMIT (MDL) FOR CHEMICAL OXYGEN DEMAND ANALYSIS IN REAGENT WATER BY STANDARD METHOD 5220 B ...	10



1.0 SCOPE AND APPLICATION

- 1.1 The open reflux method is suitable for a wide range of wastes where a large sample size is preferred. The closed reflux methods are more economical in the use of metallic salt reagents, but require homogenization of samples containing suspended solids to obtain reproducible results.
- 1.2 Oxidation of most organic compounds is 95 to 100 % of the theoretical value. Pyridine and related compounds resist oxidation and volatile organic compounds are oxidized only to the extent that they remain in contact with the oxidant. (They escape to the vapor space). Straight chain aliphatic compounds are oxidized more effectively when silver sulfate (Ag_2SO_4) is added as a catalyst.
- 1.3 Ammonia, present in either the waste or liberated from nitrogen containing organic matter, is not oxidized in the absence of significant concentration of free chloride ions.

2.0 SUMMARY OF METHOD

- 2.1 The chemical oxygen demand (COD) is used as a measure of the oxygen equivalent of the organic matter content of a sample that is susceptible to oxidation by a strong chemical oxidant. For samples from a specific source, COD can be related empirically to BOD, organic carbon, or organic matter.
- 2.2 A boiling mixture of chromic and sulfuric acids oxidizes most types of organic matter. A sample is refluxed in strongly acid solution with a known excess of potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$). After digestion, the remaining unreduced $\text{K}_2\text{Cr}_2\text{O}_7$ is titrated with ferrous ammonium sulfate (FAS) to determine the amount of $\text{K}_2\text{Cr}_2\text{O}_7$ consumed and the oxidizable organic matter is calculated in terms of oxygen equivalent. The samples are normally refluxed for two hours.

3.0 DEFINITIONS

- 3.1 Oxygen equivalent- Potassium dichromate reacts with the organic matter in the sample. The oxygen equivalent is the weight of oxygen that would be needed to react with that same amount of organic matter.

4.0 INTERFERENCES

- 4.1 Nitrite exerts a COD of 1.1 mg O_2 /mg NO_2^- -N. Because the concentrations of NO_2^- in waters rarely exceed 1 or 2 mg NO_2^- -N/L, the interference is considered insignificant and usually is ignored. Sulfamic acid can be added to the potassium dichromate solution to eliminate this interference.
- 4.2 Reduced inorganic species such as ferrous iron, sulfide, manganous manganese, etc., are oxidized quantitatively under the test conditions.
- 4.3 The difficulties caused by the presence of the halides can be overcome largely, though not completely, by complexing with mercuric sulfate before the refluxing procedure. Although 1 g is specified for 50mL sample, a lesser amount may be used where sample



chloride concentration is known to be less than 2000 mg/L, as long as a 10:1 ratio of $\text{HgSO}_4:\text{Cl}$ is maintained. Do not use the test for samples containing more than 2000 mg/L.

5.0 SAFETY

- 5.1 Potassium dichromate is a carcinogen. Use facemask when preparing solutions from reagent.
- 5.2 All mercury salts (HgSO_4) should be treated with the utmost care.

6.0 EQUIPMENT AND SUPPLIES

- 6.1 Boiling flasks fitted with condensers.
- 6.2 Heating units.
- 6.3 Burets (5-mL vol.).
- 6.4 Analytical Balance - capable of reading to 0.1 mg.

7.0 REAGENTS AND STANDARDS

- 7.1 Standard potassium dichromate solution [(0.0417M) = (0.25N)]. Dissolve 12.259 g $\text{K}_2\text{Cr}_2\text{O}_7$ previously dried at 103°C for 2 hours, and 0.12 g sulfamic acid in reagent water and dilute to 1.0 L.
- 7.2 Ferroin indicator soln - dissolve 1.485 g 1,10 phenanthroline mono-hydrate and 695 mg $\text{FeSO}_4\cdot 7(\text{H}_2\text{O})$ in reagent water and dilute to 100 mL.
- 7.3 Standard ferrous ammonium sulfate (FAS) titrant (~ 0.25M) - dissolve 98 g $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2\cdot 6\text{H}_2\text{O}$ in reagent water. Add 20mL conc. H_2SO_4 , cool and dilute to 1.0 L
- 7.4 Mercuric Sulfate, HgSO_4 , crystals or powder.
- 7.5 Silver sulfate, Ag_2SO_4 , crystals or powder.
- 7.6 Potassium hydrogen phthalate (KHP) standard - Lightly crush and then dry KHP ($\text{HOOC}\text{C}_6\text{H}_4\text{COOH}$) to constant weight at 120°C . Dissolve 425 mg in reagent water and dilute to 1.0L. KHP has a theoretical COD of 1.176-mg O_2/mg and this solution has a theoretical COD of 500ug O_2/mL . This solution is stable when refrigerated for up to 3 months in the absence of visible biological growth.

8.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

- 8.1 Preferably collect samples in glass bottle.
- 8.2 Preserve samples by acidification to $\text{pH} < 2$ using conc. H_2SO_4 .
- 8.3 Samples may be stored for 28 days if acidified and kept at 4°C .



9.0 QUALITY CONTROL

- 9.1 A KHP standard must be analyzed with every batch.
- 9.2 Duplicates must be analyzed with every batch.
- 9.3 The FAS solution must be standardized each day.

10.0 CALIBRATION AND STANDARDIZATION

- 10.1 Standardize FAS: Dilute 10.0-mL standard $K_2Cr_2O_7$ to about 100 mL. Add 30-mL conc. H_2SO_4 and cool. Titrate with FAS using 2 to 3 drops ferroin indicator.

$$\text{Molarity FAS} = \frac{(\text{Vol. } K_2Cr_2O_7 \text{ Soln}) \times 0.25}{\text{Vol. FAS Titrant}}$$

11.0 PROCEDURE

- 11.1 Place 20 mL of sample with wide tip pipette in a 125 mL boiling flask.
- 11.2 Add 10.0 mL of 0.25N potassium dichromate solution to flask.
- 11.3 Add a pinch of $HgSO_4$ and a pinch of Ag_2SO_4 .
- 11.4 Attach flask to condenser and turn on cooling water.
- 11.5 Add 30-mL conc. H_2SO_4 through top of condenser while gently swirling flask. Mix thoroughly before applying heat. Cover open end of condenser with small beaker.
- 11.6 Reflux for two hours.
- 11.7 Cool and wash down condenser with reagent water. Disconnect reflux condenser and dilute mixture to about twice its volume with reagent water.
- 11.8 Cool to room temperature and titrate excess $K_2Cr_2O_7$ with FAS using 2 to 3 drops ferroin indicator. Use same amount of ferroin for all samples.



12.0 DATA ANALYSIS AND CALCULATIONS

$$COD \text{ as } mg \text{ } O_2 / L = \frac{(A - B) \times M \times 8000}{mL \text{ Sample}}$$

A = mL FAS used for blank

B = mL FAS used for sample

M = molarity of FAS

13.0 METHOD PERFORMANCE

13.1 SM (6 Laboratories) - At an average COD of 195 mg O_2 /L in the absence of chloride, the standard deviation was +/- 11 mg O_2 /L.

13.2 LFB (Theoretical Value = 500) - Average Recovery = 484 or 97%. Standard Deviation = 14.2.

13.3 MDL = 17 mg/L (7/8/98)

13.4 Relative Percent Difference for Duplicates - Average RPD = 6.16 Standard Deviation for RPD = 5.76.

14.0 POLLUTION PREVENTION

14.1 The quantity of chemicals purchased should be based on expected usage during its shelf life.

14.2 Actual reagent preparation volumes should reflect anticipated usage during its shelf life.

15.0 WASTE MANAGEMENT

15.1 The U.S. Environmental Protection Agency requires that laboratory waste management practices be consistent with all applicable rules and regulations.

16.0 REFERENCES

16.1 Standard Methods for the Examination of Water and Wastewater, 19th Edition, 1995, American Public Health Association.



17.0 TABLES AND VALIDATION DATA

Table 1. Validation Data

Sample #	Value	Reported Value	True Value	Acceptance
WP #39		175	192	139 - 232
WP #38		73.6	81.0	59.4 - 95.7

TABLE 2. Precision of Chemical Oxygen Demand (COD) in Reagent Water by Standard Method 5220 B

Date	Based on Sample Numbers	No. of Samples (n)	Precision (RPD) ^b					
			Mean	SD ^a	Warning Limits (± 2 SD)		Control Limits (± 3 SD)	
					Upper (UWL)	Lower (LWL)	Upper (UCL)	Lower (LCL)
^a SD = Standard deviation								
^b RPD = Relative percent difference								



TABLE 3. Method Detection Limit (MDL) for Chemical Oxygen Demand Analysis in Reagent Water by Standard Method 5220 B

Date of Study	No. of Samples Spiked (n)	Spiked Concentration (mg/L)	Accuracy (Mean % Recovery ^a)	Precision (SD ^b in mg/L)	MDL (mg/L)
<p>^a Recovery of spiked concentration</p> <p>^b SD = standard deviation of mean concentration measured</p> <p>^c Method Detection Level (MDL) is 0.02 mg/L F. WES' Reporting Detection Level (RDL) is 0.10 mg/L F.</p>					