

Oxygen demand, chemical (COD), titrimetric, dichromate oxidation

Parameters and Codes:

Oxygen demand, chemical, total, 0.025N dichromate, I-3562-85 (COD in mg/L): 00335
Oxygen demand, chemical, total, 0.25N dichromate, I-3560-85 (COD in mg/L): 00340
Oxygen demand, chemical, total-in-bottom-materials, dry wt, I-5560-85 (COD in mg/kg): 00339

1. Application

1.1 This method may be used to analyze natural water and industrial waste containing more than 50 mg/L chemical oxygen demand (COD) and less than 2,000 mg/L of chloride. Samples containing less than 50 mg/L COD need to be analyzed as directed in paragraph 6.10. COD values for samples containing more than 2,000 mg/L of chloride need to be corrected as indicated in paragraph 6.11.

1.2 This method may be used to analyze samples of bottom material containing more than 100 mg/kg chemical oxygen demand (COD). Samples containing less than 1,000 mg/kg COD need to be analyzed as directed in paragraph 6.10.

1.3 Bottom material may be analyzed by the procedure after it has been prepared as directed in method P-0810 or P-0811.

2. Summary of method

2.1 Organic and other oxidizable material is oxidized by refluxing with standard acid-dichromate solution in the presence of silver sulfate catalyst. The excess dichromate is titrated with standard ferrous ammonium sulfate, using orthophenanthroline ferrous complex as indicator.

2.2 For additional information, see American Society for Testing and Materials, (1984).

3. Interferences

Reducing substances such as ferrous iron, nitrites, and chlorides interfere, because they are oxidized. Chlorides constitute by far the greatest and most common interference, being quantitatively oxidized by dichromate in acid solution. One milligram of chloride per liter is

equivalent to 0.226 mg/L COD. To eliminate chloride interference, add mercuric sulfate to the sample to form a soluble mercuric chloride complex. Nitrite interference may be eliminated by incorporating in the standard dichromate solution 10 mg of sulfamic acid for each milligram of nitrite in the reflux flask.

4. Apparatus

4.1 *Reflux apparatus*, consisting of 500-mL Erlenmeyer flask and water-cooled condenser, with ground-glass joints and made of heat-resistant glass.

4.2 *Hotplate* or heating mantle.

5. Reagents

5.1 *Ferrous ammonium sulfate standard solution I*, approx 0.250N: Dissolve 98.0 g $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ in demineralized water. Add 20 mL concentrated H_2SO_4 (sp gr 1.84), cool, and dilute to 1 L with demineralized water. To standardize: Dilute 25.0 mL standard 0.2500N $\text{K}_2\text{Cr}_2\text{O}_7$ solution to 250 mL. Add 20 mL concentrated H_2SO_4 (sp gr 1.84) and cool. Titrate with the ferrous ammonium sulfate solution, using 8 to 10 drops ferroin indicator. Compute normality of the ferrous ammonium sulfate standard solution to four decimal places. The solution must be standardized daily or before use.

5.2 *Ferrous ammonium sulfate standard solution II*, 0.025N: Dilute 100 mL of ferrous ammonium sulfate standard solution I to 1,000 mL with demineralized water. The normality of this solution is dependent upon the standardized normality of solution I.

5.3 *Mercuric sulfate*, powdered HgSO_4 .

5.4 *Orthophenanthroline ferrous sulfate (ferroin) indicator solution*: Dissolve 1.48 g 1,10-(ortho)-phenanthroline monohydrate and 0.70 g $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ in 100 mL water. The prepared indicator is available commercially.

5.5 *Potassium dichromate standard solution I*, 0.2500N: Dissolve 12.2588 g $\text{K}_2\text{Cr}_2\text{O}_7$ primary standard, dried for 2 h at 110°C , in demineralized water and dilute to 1,000 mL.

5.6 *Potassium dichromate standard solution II*, 0.0250N: Dilute 100 mL of potassium dichromate standard solution I to 1,000 mL with demineralized water.

5.7 *Silver sulfate*, powder, Ag_2SO_4 .

5.8 *Sulfamic acid*, crystals.

5.9 *Sulfuric acid*, concentrated (sp gr 1.84).

6. Procedure

6.1 Follow instructions in paragraph 6.1.1 for natural waters and industrial wastes, and in paragraph 6.1.2 for bottom materials.

6.1.1 Pipet 50.0 mL of a well-mixed sample or of a smaller volume diluted to 50.0 mL into the reflux flask.

6.1.2 Weigh, to the nearest milligram, an amount of wet sample (1.0 g max) that will consume approx one-half of the 0.2500N $\text{K}_2\text{Cr}_2\text{O}_7$ solution added in paragraph 6.5. Transfer the sample to the reflux flask and add 50 mL demineralized water.

6.2 Add slowly, over a period of 2 to 3 min, 1 g HgSO_4 ; allow to stand 5 min, swirling frequently.

6.3 Add 1 g Ag_2SO_4 and a few glass beads that have been ignited at 600°C for 1 h.

6.4 Cool in ice water and add 75 mL concentrated H_2SO_4 (sp gr 1.84) slowly enough, with mixing, to prevent appreciable solution heating.

6.5 Add 25.0 mL 0.2500N $\text{K}_2\text{Cr}_2\text{O}_7$ solution and mix thoroughly by swirling (NOTE 1).

NOTE 1. If contents are not well mixed, superheating may result, and the contents of the flask may be expelled from the open end of the condenser.

6.6 Attach flask to condenser, start water flow, and reflux for 2 h.

6.7 Allow flask to cool and wash condenser with 25 mL demineralized water.

6.8 Dilute to 300 mL with demineralized water, cool to room temperature, and titrate the excess dichromate with ferrous ammonium

sulfate standard solution I, using 8 to 10 drops ferroin indicator solution. The end point is a sharp change from blue green to reddish brown.

6.9 A demineralized-water blank is carried through all steps of the procedure with each group of samples.

6.10 Samples containing less than 50 mg/L COD or 1,000 mg/kg COD should be reanalyzed, using 0.025N solutions of potassium dichromate and ferrous ammonium sulfate. A sample size should be selected so that no more than half the dichromate is reduced.

6.11 To determine COD on samples containing more than 2,000 mg/L of chloride, the following treatment should be used (Burns and Marshall, 1965). Add 10 mg HgSO_4 for each milligram of chloride ion in the sample aliquot. Prepare a series of chloride solutions containing from 2,000 to 20,000 mg/L with the concentration interval not exceeding 4,000 mg/L, and add 10 mg HgSO_4 to each solution for each milligram of chloride ion present. Determine the COD of the sample and chloride solution, starting with paragraph 6.2. Plot the COD values obtained versus milligrams per liter chloride. From this curve, COD values may be obtained for any desired chloride concentration. This value is subtracted as a correction factor to obtain the COD value of a sample.

7. Calculations

7.1 For natural waters and industrial wastes not requiring chloride correction:

$$\text{COD (mg/L)} = \frac{(A-B)N \times 8,000}{\text{mL sample}}$$

7.2 For natural waters and industrial wastes requiring chloride correction:

$$\text{COD (mg/L)} = \left[\frac{(A-B)N \times 8,000}{\text{mL sample}} - C \right] \times 1.20$$

where

COD = chemical oxygen demand from dichromate,

A = amount of ferrous ammonium sulfate for blank, milliliters,

B = amount of ferrous ammonium sulfate for sample, milliliters,

N = normality ferrous ammonium sulfate,

C = chloride-correction value from graph of chloride concentration versus COD,

and

1.20 = empirical compensation factor.

7.3 Compute the dry weight of the bottom-material samples as follows:

$$\text{Sample, dry weight (g)} = W \frac{(100-M)}{100}$$

where

W = wet weight of the sample, grams,

and

M = percentage moisture.

7.4 Determine the chemical oxygen demand in each bottom-material sample as follows (NOTE 2):

NOTE 2. Most bottom-material samples contain low concentrations of chloride; therefore, a chloride correction is not necessary.

$$\text{COD (mg/kg)} = \frac{(A-B)N \times 8,000}{\text{sample, dry weight (g)}}$$

where

COD = chemical oxygen demand from dichromate,

A = amount of ferrous ammonium sulfate for blank, milliliters,

B = amount of ferrous ammonium sulfate for sample, milliliters,

and

N = normality ferrous ammonium sulfate.

8. Report

8.1 Report COD, total, 0.025*N* dichromate (00335), as follows: less than 50 mg/L, whole numbers.

8.2 Report COD, total, 0.25*N* dichromate (00340), as follows: 50 mg/L and above, two significant figures.

8.3 Report COD, total-in-bottom-material, dry-weight (00339), as follows: less than 10,000 mg/kg, to the nearest 100 mg/kg; 10,000 mg/kg and above, two significant figures.

9. Precision

Precision data are not available for this method.

References

- American Society for Testing and Materials, 1984, Annual book of ASTM standards, section 11, water: Philadelphia, v. 11.01, p. 62-8.
- Burns, E. R., and Marshall, C., 1965, Correction for chloride interference in the chemical oxygen demand test: Water Pollution Control Federation Journal, v. 37, p. 1716-21.