

## Oxygen demand, chemical (COD), colorimetric, dichromate oxidation

Parameter and Code:

Oxygen demand, chemical, total, I-3561-85 (COD in mg/L): 00340

### 1. Application

This method may be used to analyze water-suspended sediment containing between 10 and 500 mg/L chemical oxygen demand (COD).

### 2. Summary of method

2.1 Organic and other oxidizable materials are oxidized by digestion with an acid-dichromate solution in the presence of silver sulfate catalyst. The COD concentration is determined spectrometrically by measuring the absorbance of the  $\text{Cr}^{+3}$  that is formed.

2.2 Additional information about the principles of the method may be found in Jirka and Carter (1975).

### 3. Interferences

3.1 Reducing substances such as ferrous iron and chloride interfere, because they are oxidized by dichromate in acid solution. Chlorides constitute the largest and most common interference, with 1 mg/L  $\text{Cl}^{-1}$  equivalent to 0.226 mg/L COD. To eliminate chloride interference as great as 2,000 mg/L, add mercuric sulfate to the acid-dichromate digestion solution.

3.2 Chromium(III) interferes. One milligram per liter is equivalent to 0.719 mg/L COD. Levels great enough to have significant effect on the accuracy are unlikely in natural water samples.

3.3 Ferric iron concentrations less than 5000 mg/L do not interfere.

### 4. Apparatus

4.1 *Ampules*, glass, 10-mL capacity.

4.2 *Centrifuge*, Sorvall SS-3 Automatic Superspeed or equivalent.

4.3 *Spectrometer* for use at 600 nm: Refer to the manufacturer's manual to optimize instrument.

### 5. Reagents

5.1 *Potassium acid phthalate standard solution I*, 1.0 mL = 10.0 mg COD: Dissolve 8.500 g potassium acid phthalate, which has been dried for 2 h at 110°C, in demineralized water and dilute to 1,000 mL.

5.2 *Potassium acid phthalate standard solution II*, 1.0 mL = 1.0 mg COD: Dilute 100 mL potassium acid phthalate standard solution I to 1,000 mL with demineralized water. This solution is used to prepare working standards at time of analysis.

5.3 *Potassium dichromate-mercuric sulfate digestion solution*: To approx 700 mL demineralized water, add 10.216 g  $\text{K}_2\text{Cr}_2\text{O}_7$  and 33.0 g  $\text{HgSO}_4$ . **CAUTION: Hazardous.** Slowly, and with constant stirring, add 167 mL concentrated  $\text{H}_2\text{SO}_4$  (sp gr 1.84). Mix until dissolved. After the solution cools, dilute to 1 L with demineralized water.

5.4 *Silver sulfate solution*: Dissolve 22 g  $\text{Ag}_2\text{SO}_4$  in a 9-pound bottle of concentrated  $\text{H}_2\text{SO}_4$  (sp gr 1.84).

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

## 6. Procedure

6.1 Heat the ampules at  $500^\circ\text{C}$  for 6 h, and cool.

6.2 Pipet 2.5 mL of a well-mixed sample into an ampule.

6.3 Prepare a blank and sufficient standards containing from 10 to 500 mg/L COD using potassium acid phthalate standard solution II. Pipet 2.5 mL of each into ampules.

6.4 Add 1.5 mL potassium dichromate-mercuric sulfate digestion solution to each ampule (NOTE 1).

NOTE 1. Protective eyeglasses and clothing are mandatory for this entire procedure, because sulfuric acid and potassium dichromate solutions at high temperatures are especially hazardous.

6.5 Add 3.5 mL silver sulfate solution to each ampule.

6.6 Heat-seal the ampules and shake vigorously.

6.7 Heat the ampules in an oven at  $150^\circ\text{C}$  for 2 h.

6.8 Cool the ampules to room temperature in a cold-water bath.

6.9 Centrifuge the solutions at 5,000 rpm for 15 min.

6.10 Set the spectrophotometer at 600 nm and adjust the absorbance to 0.000 with the digested blank.

6.11 Individually transfer each standard and sample to the sample cuvette, preferably using an automated flow-through cell, and read and record each absorbance value. Care must be taken not to disturb any precipitate when pouring the sample into the cuvette (NOTE 2).

NOTE 2. A Technicon AutoAnalyzer system, consisting of a sampler, proportioning pump, cartridge manifold, colorimeter, recorder, and printer, may be used in place of the spectrophotometer to measure the absorbance of the digested solution (Jirka and Carter, 1975). Steps 6.2 to 6.9 remain unchanged.

## 7. Calculations

Determine the milligrams per liter of COD in each sample from a plot of absorbances of standards.

## 8. Report

Report oxygen demand, chemical (COD), total (00340), concentrations as follows: less than 10 mg/L, as <10 mg/L; 10 mg/L and above, two significant figures.

## 9. Precision

For potassium acid phthalate standards, the precision for a single operator expressed in terms of the percent relative standard deviation is as follows:

Mean (mg/L)	Relative standard deviation (percent)
50	14
400	2

### Reference

Jirka, A. M., and Carter, M. J., 1975, Micro semiautomated analysis of surface and wastewaters for chemical oxygen demand: Analytical Chemistry, v. 47, no. 8, p. 1397-1402.