



Water Analysis Systems

# COD

vials for the  
determination of  
chemical oxygen demand

## Test Procedure

Range 0 - 40 mg/L (ULR COD)  
Range 0 - 150 mg/L (LR COD)  
Range 0 - 1,500 mg/L (HR COD)  
Range 0 - 15,000 mg/L (HR+ COD)

### SAFETY INFORMATION

COD reagent vials contain sulfuric acid, which causes severe burns. Read the MSDS (available at [www.chemetrics.com](http://www.chemetrics.com)) before using. During any handling, wear laboratory grade safety glasses with top and side shields. Also wear gloves and protective clothing. Avoid contact with reagent. It is recommended that this test procedure be performed under a chemical fume hood.

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## TEST METHOD

Chemical oxygen demand is a measure of the oxidizable organic matter content of a wastewater sample. The sample is reacted with an acidic solution of potassium dichromate in the presence of a catalyst (silver) and digested for 2 hours at a temperature of 150°C. Oxidizable organic compounds reduce the dichromate ion ( $\text{Cr}_2\text{O}_7^{2-}$ ) to the chromic ion ( $\text{Cr}^{3+}$ ). In the ULR and LR COD kits, the decrease in dichromate ion is measured colorimetrically. In the HR and HR+ COD kits, the amount of chromic ion produced is measured. The test results are expressed as the number of milligrams of oxygen consumed per liter of sample (mg/Liter COD).

## REFERENCES

- APHA Standard Methods, 21st ed., method 5220 D (2005).  
ASTM D 1252-.06, Chemical Oxygen Demand (Dichromate Oxygen Demand) of Water, Test Method B.  
EPA Methods for Analysis of Waters and Wastes, method 410.4 (1983).  
A. M. Jirka and M. J. Carter, "Micro Semi-Automated Analysis of Surface and Wastewaters for Chemical Oxygen Demand," Analytical Chemistry, Vol. 47, p. 1397 (1975).  
J. A. Winter, "Method Research Study 3, Demand Analysis, An Evaluation of Analytical Methods for Water and Wastewater," USEPA, (1971).

## SOURCES OF ERROR

The ULR COD, LR COD and HR COD mercury containing COD reagents are formulated to withstand interferences from up to 2000 ppm chloride. The HR+ COD mercury containing COD reagent can be used on samples containing up to 20,000 ppm chloride without interference. Samples with higher chloride concentrations require dilution. Also, samples that contain high levels of chloride (>1000 ppm) and low levels of COD (<30% of the product range) will give false positive test results. In this case, sample dilution is recommended.

Mercury free reagents (LR COD and HR COD) are also available for samples containing less than 100 ppm chloride (less than 1000 ppm for the mercury free HR+ COD kit).

Choosing the correct range COD Kit is important. If the COD concentration in the sample is significantly above the range of the test kit being used, false low test results may be obtained.

The COD reagent is light sensitive. Store vials in the dark and at room temperature when not in use.

Good technique and elimination of contamination are necessary for accurate results. Wash all glassware with 20% Sulfuric Acid.

For COD testing, LED based photometers do not produce accuracy, precision and sensitivity equivalent to that attainable with spectrophotometers. For NPDES reporting purposes for COD, a spectrophotometer is the preferred method of measurement.

## CALIBRATION & ACCURACY CHECK

- To obtain test results in mg/Liter COD:
  - Use preprogrammed CHEMetrics or Hach<sup>1</sup> instrumentation for direct readout.
  - Use the supplied calibration equation (Step 12 of Test Procedure) for other brand spectrophotometers.
  - Generate a standard curve specific to the instrument being used by preparing a series of five standard solutions (one of which is a blank) which covers the expected range of the test.
- COD standard solutions (see Reorder Information) are used to check the accuracy of the test or to generate an instrument specific calibration curve.

*1. Hach Company does not warrant the accuracy of the calibrations it supplies when they are applied to reagents other than its own.*

## USE OF THE CHEMetrics V-2000 PHOTOMETER

- Install the 16 mm adapter into the V-2000 photo-meter. Turn the photometer on by pressing the **power** key.
- Insert the 16 mm ZEROING VIAL (supplied with the instrument) into the V-2000, cover the vial with the light shield, and press the **zero** key. "Wait" is displayed, then the result is displayed as "0.000".
- Press the **prgm** key, enter the appropriate program number (see below), then press the **yes** key. The instrument will display the appropriate method name and program number.

Range/Method Name	Program Number
0-150 ppm (COD LR)	48
0-1500 ppm (COD HR)	49
0-15000 ppm (COD HR+)	49

- Follow Steps 1 through 11 of the **COD Test Procedure** on pages 4 and 5 of this booklet.
- Press the **setup** key and use the % or & keys until "BLANK" is displayed, then press the **yes** key.
- "SET BLNK?" will be displayed, press the **yes** key.
- "SAMPLE?" will be displayed. Insert a clean, dry, newly generated reagent blank vial into the V-2000, cover the vial with the light shield, then press the **yes** key. The instrument will read the blank, display an absorbance value momentarily, and then display the next setup function.
- Press **meas** key. The instrument display will return to the appropriate method name and program number. Insert a clean, dry, newly generated COD test vial into the V-2000, cover the vial with the light shield, then press the **meas** key again. The instrument will read the vial and display the test result.

**NOTE:** When running the COD HR+ method, the instrument readout must be multiplied by 10.

## SAMPLE COLLECTION

Collect samples in glass bottles. When it is necessary to preserve samples for storage, acidify to  $\text{pH} \leq 2$  with concentrated sulfuric acid. Store preserved samples at 4°C for no longer than 28 days after collection.

## TEST PROCEDURE

1. Homogenize 500 mL of sample for 2 minutes in a blender.

**Note:** Blending ensures an even distribution of any solids that may be present in the sample, thus improving the accuracy and reproducibility of the test.

2. Preheat the digester block to 150°C.
3. Remove the cap from a COD vial.
4. Pipet 2.00 mL (0.20 mL for HR+ COD) of sample into the vial. The contents of the vial will become hot.
5. Replace the cap onto the COD vial, securing it tightly.
6. Immediately invert the vial 10 times to mix well.  
**Caution:** When mixing, hold the vial by the cap only. The contents of the vial will become very hot.
7. Wipe the vial with a damp towel and place it in the preheated digester block.
8. Prepare the reagent blank by repeating Steps 3 through 7, using deionized water rather than sample in Step 4.

**Note:** At least one reagent blank must be run with each set of samples and with each new lot number of COD vials. Use a blank vial from the same lot as the test COD vials.

9. Allow the vials to heat in the digester block at 150°C for 2 hours.
10. Turn the digester block off and allow the vials to remain in the unit to cool for 15 to 20 minutes.
11. **Use caution**, the glass vials are still **very** hot. Carefully remove each vial from the digester block, making certain that the cap is secured tightly. Invert each vial several times, and then place it in a rack to cool to room temperature. Allow at least 30 minutes for the vials to cool. Store the vials in the dark during this cool down time.
12. If applicable, follow instrument specific procedures for selecting wavelength and zeroing the spectrophotometer.

Range, mg/L	Wavelength	Calibration Equation
0 - 40	350	ppm (mg/L) = -52.2 (abs) +0.3
0 - 150	420	ppm (mg/L) = -337.1 (abs)
0 - 1,500	620	ppm (mg/L) = 2301 (abs) -3
0 - 15,000	620	ppm (mg/L) = 23010 (abs) -3

13. Wipe the exterior of the reagent blank vial until it is clean and dry. Place the reagent blank vial into the instrument sample compartment. This reagent blank is used to zero the instrument.
14. Wipe the exterior of a test COD vial until it is clean and dry. Place the vial into the instrument sample compartment to obtain test results.
15. If applicable, use the range specific calibration equation in Step 12 to convert absorbance values to test results in mg/L COD.

## REORDER INFORMATION

(Jan. 13, Rev. 26)

### **Mercury Containing Reagent COD Kits:**

0 - 40 mg/L (ULR COD), contains 25 vials . . . . K-7340S

0 - 150 mg/L (LR COD), contains 25 vials . . . . K-7350S

0 - 150 mg/L (LR COD), contains 150 vials . . . . K-7355

0 - 1,500 mg/L (HR COD), contains 25 vials . . K-7360S

0 - 1,500 mg/L (HR COD), contains 150 vials . . K-7365

0 - 15,000 mg/L (HR+ COD), contains 25 vials K-7370S

0 - 15,000 mg/L (HR+ COD), contains 98 vials . K-7375

### **Mercury Free Reagent COD Kits:**

0 - 150 mg/L (LR COD), contains 25 vials . . . . K-7351S

0 - 150 mg/L (LR COD), contains 150 vials . . . . K-7356

0 - 1,500 mg/L (HR COD), contains 25 vials . . K-7361S

0 - 1,500 mg/L (HR COD), contains 150 vials . . K-7366

0 - 15,000 mg/L (HR+ COD), contains 25 vials K-7371S

0 - 15,000 mg/L (HR+ COD), contains 98 vials . K-7376

### **COD Standards:**

1,000 mg/L . . . . . A-7301

10,000 mg/L . . . . . A-7310

**Digester Block**, 120 V/240 V, holds 12 vials . A-0111

**COD Vial Rack**, stainless steel, holds 40 vials A-0107

## **CHEMetrics, Inc.**

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