

# Chemical Oxygen Demand (COD Vials)

LR COD: 0 - 150 mg/L  
HR COD: 0 - 1500 mg/L  
HR+ COD: 0 - 15,000 mg/L

## SAFETY INFORMATION

COD reagent vials contain sulfuric acid, which causes severe burns. Read the SDS (available at [www.chemetrics.com](http://www.chemetrics.com)) before using. Wear appropriate personal protective equipment. Perform this test procedure under a hood.

## 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 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).

## OPTIONS FOR OBTAINING TEST RESULTS

- Use preprogrammed CHEMetrics or Hach<sup>1</sup> instrumentation for direct readout. Follow the Set-up and Measurement procedures in the instrument's operator's manual.
- 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.

**NOTE:** COD standard solutions 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.*

## 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. Secure the cap onto the COD vial. Do not over-tighten as this may compromise the closure integrity.
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. Make certain that the cap is secured tightly, then invert each vial several times. Place the vial in a rack to cool. Store the vials in the dark and allow at least 30 minutes for them to cool to room temperature. If COD vials are not cooled to room temperature, the accuracy of the test results may be compromised.  
**CAUTION:** Hot vials may shatter if dropped or cooled rapidly.
12. For instrument setup when using preprogrammed CHEMetrics or Hach instrumentation, refer to the instrument's operator's manual. For other brand spectrophotometers, use the following information:

		Calibration Equation
Range	Wavelength	
LR COD	420	$\text{ppm (mg/L)} = (-331)(\text{abs}) - 0.6$
HR COD	620	$\text{ppm (mg/L)} = (2301)(\text{abs}) - 3$
HR+ COD	620	$\text{ppm (mg/L)} = (23010)(\text{abs}) - 3$

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 to zero or set reagent blank.
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.  
**Note:** When using the HR+ COD Vials with the V-2000 Photometer or the A-7325 HR COD SAM, multiply the photometer output by 10 to obtain the actual test result. This is necessary for any direct read photometer that uses the same program for HR and HR+ COD vials.
15. If applicable, use the range specific calibration equation in Step 12 to convert absorbance values to test results in mg/L COD.

## SOURCES OF ERROR

Mercury containing LR COD and HR COD reagents are formulated to withstand interferences from up to 2000 ppm chloride. Mercury containing HR+ 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 LR COD and HR COD reagents are 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.

## REFERENCES

- APHA Standard Methods, 22nd ed., method 5220 D - 1997.
- 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).



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