OXYGEN DEMAND, Chemical

✔ **Method 8000**

Reactor Digestion Method*

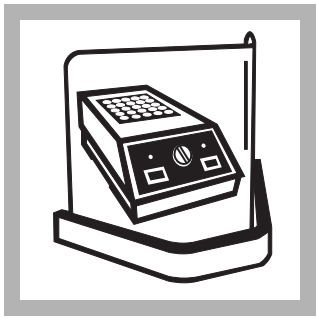
(0 to 1500 and 0 to 15,000 mg/L COD)

Scope and Application: *For water, wastewater and seawater; digestion required; 0–1500 mg/L range is USEPA Approved** for wastewater analyses. The detection limit is 3 mg/L or 30 mg/L COD for the 0–1500 mg/L and the 0–15,000 mg/L range, respectively.*

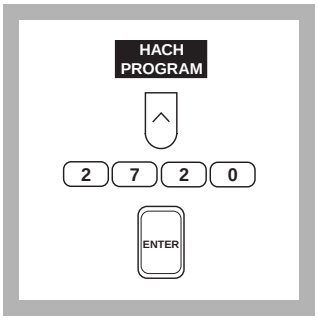
* Jirka, A.M.; Carter, M.J., *Analytical Chemistry,* 1975, 47(8), 1397

** *Federal Register,* April 21, 1980, *45*(78), 26811-26812. The 0–15,000 mg/L range is NOT USEPA approved.

Colorimetric Measurement, 0 to 1,500 and 0 to 15,000 mg/L COD



1. Perform the digestion for this method as described in "Oxygen Demand, Chemical, Digestion Procedure" which precedes the COD colorimetric procedures.



2. Press the soft key under ***HACH PROGRAM***.

Select the stored program number for high range and high range plus COD by pressing **2720** with the numeric keys.

Press: **ENTER**

Note: *If samples cannot be analyzed immediately, see Sample Collection, Preservation and Storage following these steps.*

3. The display will show:

HACH PROGRAM:
2720
COD, HR, HR PLUS

The wavelength (λ), **620 nm**, is automatically selected.

4. Insert the Test 'N Tube Adapter into the sample cell module by sliding it under the thumb screw and into the alignment grooves. Fasten with the thumb screw.

Note: *The Test Tube Adapter is NOT designed to allow readings on hot vials (150 °C).*

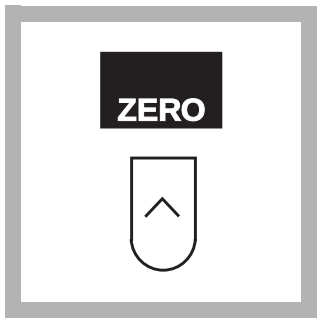
5. Clean the outside of the blank with a towel.

Note: *Wiping with a damp towel, followed by a dry one, will remove fingerprints or other marks.*

6. Place the blank into the adapter with the Hach logo facing the front of the instrument. Close the light shield.

Note: *Preparation of the blank is described in the digestion procedure.*

Note: *The blank is stable when stored in the dark; see Blanks for Colorimetric Measurement following these procedures.*



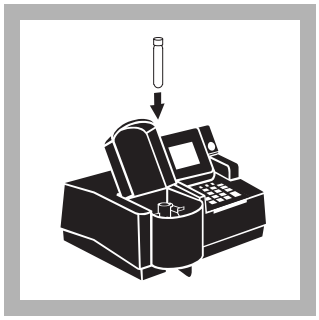
7. Press the soft key under ***ZERO.***

The display will show:

0 mg/L COD

Note: *For alternate concentration units press the soft key under* ***OPTIONS****. Then press the soft key under* ***UNITS*** *to scroll through the available options. Press* **ENTER** *to return to the read screen.*

8. Clean the outside of the sample vial with a towel.



9. Place the sample vial into the adapter with the Hach logo facing the front of the instrument. Close the light shield. Results in mg/L COD (or chosen units) will be displayed.

Note: *When High Range Plus COD Digestion Reagent Vials are used, multiply the displayed value by ten.*

Note: *For most accurate results with samples near 1,500 or 15,000 mg/L COD, repeat the analysis with a diluted sample.*

Note: *Results may be expressed as mg/L COD or mg/L O_2. Press the soft keys under* ***OPTIONS*** *and then press* ***FORM:*** *to scroll through the available choices.*

Interferences

Chloride
Chloride is the primary interference when determining COD concentration. Each COD vial contains mercuric sulfate that will eliminate chloride interference up to the level specified in column 2. Samples with higher chloride concentrations should be diluted. Dilute the sample enough to reduce the chloride concentration to the level given in column 3.

Table 1 Interfering Substances and Suggested Treatments

Vial Type Used	Maximum Cl^- concentration in sample (mg/L)	Suggested Cl^- concentration of diluted sample (mg/L)	Maximum Cl^- concentration in sample with 0.5 g $HgSO_4$ Added (mg/L)
Ultra Low Range	2000	1000	NA
Low Range	2000	1000	8000
High Range	2000	1000	4000
Ultra High Range	20,000	10,000	40,000

If sample dilution will cause the COD concentration to be too low for accurate measurement, add 0.50 g of mercuric sulfate ($HgSO_4$) to each COD vial before the sample is added. The additional mercuric sulfate will raise the maximum chloride concentration allowable to the level given in column 4.

Bromide
Bromide interference will not be controlled by mercuric sulfate.

Sample Collection, Preservation and Storage

Collect samples in glass bottles. Use plastic bottles only if they are known to be free of organic contamination. Test biologically active samples as soon as possible. Homogenize samples containing solids to assure representative samples. Samples treated with sulfuric acid to a pH of less than 2 (about 2 mL per liter) and refrigerated at 4 °C can be stored up to 28 days. Correct results for volume additions; see Section *1.2.2 Correcting for Volume Additions*.

Accuracy Check

Standard Solution Method
0–1500 mg/L range: Check the accuracy of the 0 to 1,500 mg/L range by using either a 300-mg/L or 1000-mg/L COD Standard Solution. Use 2 mL of one of these solutions as the sample volume; the expected result will be 300 or 1000 mg/L COD respectively.

Or, prepare a 500-mg/L standard by dissolving 425 mg of dried (120 °C, overnight) KHP in 1000 mL of deionized water.

0–15,000 mg/L range: Check the accuracy of the 0 to 15,000 mg/L range by using a 10,000-mg/L COD standard solution. Prepare the 10,000-mg/L solution by dissolving 8.500 g of dried (120 °C, overnight) KHP in 1 liter of deionized water. Use 0.2 mL of this solution as the sample volume; the expected result will be 10,000 mg/L COD (display x 10).

To adjust the calibration curve using the reading obtained with 1000-mg/L COD Standard Solution, press the soft keys under ***METHOD OPTIONS, (MORE)*** then ***STD:OFF***. Press **ENTER** to accept the value and return to the read screen. The instrument will only allow adjustment if the entered concentration is within 10% of the measured concentration. See Section *1.5.5 Adjusting the Standard Curve* for more information.

Method Performance

Precision

0–1500 mg/L range
Standard: 1000 mg/L COD

Program	95% Confidence Limits
2720	998-1002 mg/L COD

0–15,000 mg/L range
Standard: 10,000 mg/L COD

Program	95% Confidence Limits
2720	9980-10,020 mg/L COD

For more information on determining precision data and method detection limits, refer to Section *1.5*.

Estimated Detection Limit

Program	EDL
2720 (0-1500 mg/L)	3 mg/L COD
2720 (0-15,000 mg/L)	30 mg/L COD

For more information on derivation and use of Hach's estimated detection limit, see Section *1.5.2*. To determine a method detection limit (MDL) as defined by the 40 CFR part 136, appendix B, see Section *1.5.1*.

Sensitivity
Program Number: 2720

Portion of Curve	ΔAbs	ΔConcentration
Entire Range	0.010	23.5 mg/L

See Section *1.5.3 Sensitivity Explained* for more information.

Blanks for Colorimetric Measurement

The blank may be used repeatedly for measurements using the same lot of vials. Store it in the dark. Monitor decomposition by measuring the absorbance at 620 nm. Zero the instrument in the absorbance mode using a culture tube (see *OPTIONAL EQUIPMENT AND SUPPLIES*) containing 5 mL of deionized water. Measure the absorbance of the blank and record the value. Prepare a blank when the absorbance has changed by about 0.01 absorbance units.

Calibration Standard Preparation

High Range:
To perform a high range (0–1500 mg/L) calibration using the reactor digestion method, prepare a 10,000-mg/L COD stock solution by diluting 0.85 g of dried (120 °C, overnight) KHP to 100-mL with deionized water using Class A glassware. Mix thoroughly.

Prepare calibration standards containing 200, 600, 1000, 1400 and 1600 mg/L COD as follows:

a. Into five different 100-mL volumetric flasks, pipet 2.0, 6.0, 10.0, 14.0, and 16.0 mL of the 10,000-mg/L COD stock solution using Class A glassware.

b. Dilute to the mark with deionized water. Stopper and invert 10 times to mix.

c. Using the COD Reactor Digestion Method and the calibration procedure described in the *User-Entered Programs* section of the *DR/4000 Spectrophotometer Instrument Manual*, generate a calibration curve from the standards prepared above.

High Range Plus:
To perform a super high range (0–15,000 mg/L) calibration using the reactor digestion method, prepare a 50,000-mg/L COD stock solution by diluting 8.5 g of dried (120 °C, overnight) KHP to 200-mL with deionized water using class A glassware. Mix thoroughly.

Prepare calibration standards containing 2000, 6000, 10000, and 14000 mg/L COD as follows:

a. Into four different 100-mL volumetric flasks, pipet 4.0, 12.0, 20.0 and 28.0 mL of the 50,000-mg/L COD stock solution using Class A glassware.

b. Dilute to the mark with deionized water. Mix thoroughly.

c. Using the COD Reactor Digestion Method (with High Range Plus COD vials) and the calibration procedure described in the *User-Entered Programs* section of the *DR/4000 Spectrophotometer Instrument Manual*, generate a calibration curve from the standards prepared above.

Alternatively, use the High Range procedure and multiply the results by 10.

Alternate Reagents—COD2 Reagent Vials

For non-reporting purposes, COD2 Reagent can provide a mercury-free testing option, eliminating mercury waste and saving on disposal costs.

COD2 Reagent Vials use the same COD procedures and the same COD calibration curves programmed into the DR/4000.

COD2 Reagent is not acceptable for USEPA reporting purposes. Request Literature Code 1356 for applications where COD 2 Reagent Vials may be suitable.

Summary of Method

The mg/L COD results are defined as the mg of O_2 consumed per liter of sample under the conditions of this procedure. In this procedure, the sample is heated for two hours with a strong oxidizing agent, potassium dichromate. Oxidizable organic compounds react, reducing the dichromate ion ($Cr_2O_7^{2-}$) to green chromic ion (Cr^{3+}). When the 0-150 mg/L colorimetric or titrimetric method is used, the amount of Cr^{6+} remaining is determined. When the 0–1,500 mg/L or 0–15,000 mg/L colorimetric method is used, the amount of Cr^{3+} produced is determined. The COD reagent also contains silver and mercury ions. Silver is a catalyst, and mercury is used to complex chloride interferences.

Safety

Good safety habits and laboratory techniques should be used throughout the procedure. Consult the *Material Safety Data Sheet* for information specific to the reagents used. For additional information, refer to *SECTION 1 WASTE MANAGEMENT AND SAFETY*.

Pollution Prevention and Waste Management

Final samples will contain mercury (D009), silver (D011), and chromium (D007) at concentration levels regulated as hazardous waste by the Federal RCRA. Please see *SECTION 1 WASTE MANAGEMENT AND SAFETY* for further information on proper disposal of these materials.

REQUIRED REAGENTS AND STANDARDS

Description	Quantity Required per test	Unit	Cat. No.
Select the appropriate COD Digestion Reagent Vial:			
High Range, 0 to 1,500 mg/L COD	1 to 2 vials	25/pkg	21259-25
High Range Plus, 0 to 15,000 mg/L COD	1 to 2 vials	25/pkg	24159-25
Water, deionized	varies	4 liters	272-56

REQUIRED EQUIPMENT AND SUPPILES

COD Reactor, 115/230 VAC, North American plug	1	each	45600-00
COD Reactor, 230 VAC, 50 Hz, European plug	1	each	45600-02
DR/4000 Test Tube Adapter	1	each	48189-00
Pipet, TenSette, 0.1 to 1.0 mL	1	each	19700-01
Pipet Tips, for 19700-01 TenSette Pipet	1	50/pkg*	21856-96
Pipet, volumetric, Class A, 2 mL	1	each	14515-36
Pipet Filler, safety bulb	1	each	14651-00
Test Tube Rack	1 to 2 racks	each	18641-00

OPTIONAL REAGENTS AND STANDARDS

COD Digestion Reagent Vials, 0 to 150 mg/L COD	150/pkg	21258-15
COD Digestion Reagent Vials, 0 to 1,500 mg/L COD	150/pkg	21259-15
COD Standard Solution, 300-mg/L	200 mL	12186-29
COD Standard Solution, 1000-mg/L	200 mL	22539-29
COD2 Reagent Vials, High Range, 0–1500 mg/L	25/pkg	25651-25
COD2 Reagent Vials, High Range, 0–1500 mg/L	150/pkg	25651-15
COD2 Reagent Vials, Ultra High Range, 0–15,000 mg/L	25/pkg	28343-25
Mercuric Sulfate, ACS	28 g*	1915-20
Potassium Acid Phthalate, ACS	500 g	315-34
Sulfuric Acid, ACS, concentrated	500 mL*	979-49

OPTIONAL EQUIPMENT AND SUPPLIES

Description	Unit	Cat. No.
Beaker, 250-mL	each	500-46H
Culture Tube, 16 x 100 mm	6/pkg	22758-06
Culture Tube Cap (for 22758-06)	6/pkg	22411-06
Cylinder, graduated, 5-mL	each	508-37
Flask, volumetric, Class A, 100-mL	each	14574-42
Flask, volumetric, Class A, 250-mL	each	14574-46
Flask, volumetric, Class A, 1000-mL	each	14574-53
pH -Paper, pH 1.0 to 11.0	5 rolls/pkg	391-33
Pipet, serological, 5-mL	each	532-37
Pipet, volumetric, Class A, 2.00-mL	each	14515-04
Pipet, volumetric, Class A, 6.00-mL	each	14515-06
Pipet, volumetric, Class A, 8.00-mL	each	14515-08
Pipet, volumetric, Class A, 10.00-mL	each	14515-38
Pipet, volumetric, Class A, 20.00-mL	each	14515-20
Safety shield, for COD reactor	each	50030-00
Spoon, measuring, 0.5-g	each	907-00

RELATED LITERATURE—Ask for your copy by literature code number.

Title	Literature Code No.
COD Disposal Information Brochure	4144
COD2 Reagent Vials Information Brochure	1356

* Contact Hach for larger sizes.

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