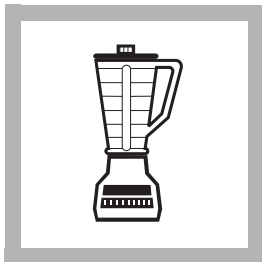
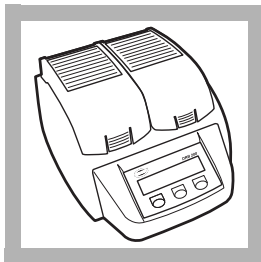


Reactor Digestion Method* USEPA approved for reporting wastewater analysis** Digestion



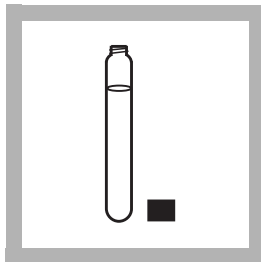
1. Homogenize 500 mL of sample for 2 minutes in a blender.

Note: For the 0-15,000 mg/L range, homogenize 100 mL of sample. Pour the blended sample into a 250-mL beaker. Stir with a magnetic stirrer while withdrawing a sample aliquot. This improves accuracy and reproducibility.



2. Turn on the DRB 200 Reactor. Preheat to 150 °C.

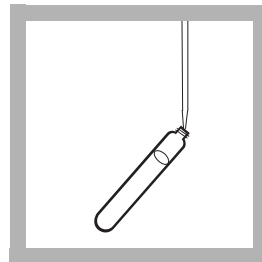
Note: See DRB 200 user manual for selecting pre-programmed temperature applications.



3. Remove the cap of a COD Digestion Reagent Vial for the appropriate range:

Sample Conc. Range (mg/L)	COD Digestion Reagent Vial Type
0 to 150	Low Range
0 to 1500	High Range
0 to 15,000	High Range Plus

Note: The reagent mixture is light-sensitive. Keep unused vials in the opaque shipping container, in a refrigerator if possible. The light striking the vials during the test will not affect results.



4. Hold the vial at a 45-degree angle. Pipet 2.00 mL (0.2 mL for the 0 to 15,000 mg/L range) of sample into the vial.
Note: For the 0-15,000 mg/L range, pipet only 0.20 mL of sample, not 2.00 mL of sample, using a TenSette Pipet. For greater accuracy analyze a minimum of three replicates and average the results.

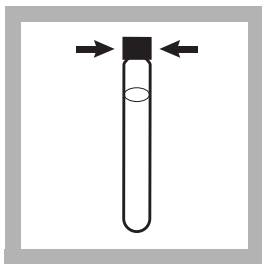
Note: Spilled reagent will affect test accuracy and is hazardous to skin and other materials. Do not run tests with vials which have been spilled. If spills occur, wash with running water.

Caution: Some of the chemicals and apparatus used in this procedure may be hazardous to the health and safety of the user if inappropriately or accidentally misused. Please read all warnings and the safety section of this manual. Wear appropriate eye protection and clothing. If contact occurs, flush the affected area with running water. Follow all instructions carefully.

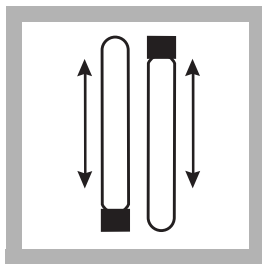
* Jirka, A.M.; Carter, M.J. *Analytical Chemistry*, 1975, 47(8). 1397.

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

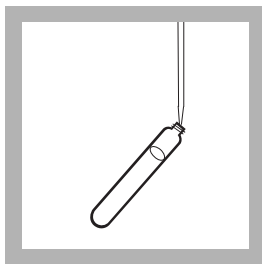
OXYGEN DEMAND, CHEMICAL, continued



5. Replace the vial cap tightly. Rinse the outside of the COD vial with deionized water and wipe the vial clean with a paper towel.

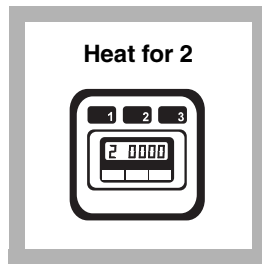


6. Hold the vial by the cap and over a sink. Invert gently several times to mix the contents. Place the vial in the preheated DRB 200 Reactor.
Note: The vial will become very hot during mixing.

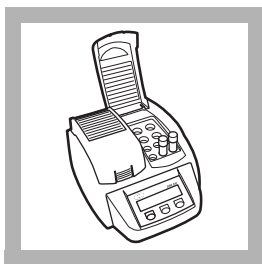


7. Prepare a blank by repeating Steps 3 to 6, substituting 2.00 mL (0.2 mL for the 0 to 15,000 mg/L range) deionized water for the sample.
Note: Be sure the pipet is clean.

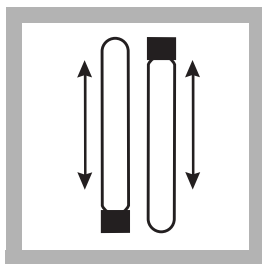
Note: One blank must be run with each set of samples. Run samples and blanks with vials from the same lot number (lot # is on the container label).



8. Heat the vials for 2 hours.
Note: Many samples are digested completely in less than two hours. If desired, measure the concentration (while still hot) at 15 minute intervals until the reading remains unchanged. Cool vials to room temperature for final measurement.



9. Turn the reactor off. Wait about 20 minutes for the vials to cool to 120 °C or less.



10. Invert each vial several times while still warm. Place the vials into a rack. Wait until the vials have cooled to room temperature.
Note: If a pure green color appears in the reacted sample, measure the COD and, if necessary, repeat the test with a diluted sample.

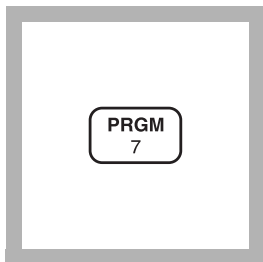


11. Use one of the following analytical techniques to measure the COD:

- Colorimetric method, 0-150 mg/L COD
- Colorimetric method, 0-1,500 mg/L COD
- Colorimetric method, 0-15,000 mg/L COD

OXYGEN DEMAND, CHEMICAL, continued

Colorimetric Determination, 0 to 150 mg/L COD

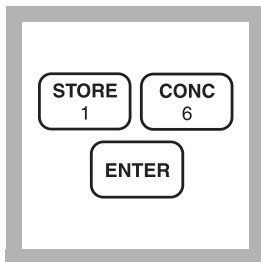


1. Enter the stored program number for chemical oxygen demand (COD), low range.

Press: **PRGM**

The display will show:

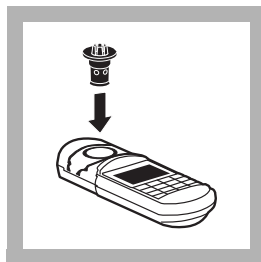
PRGM ?



2. Press: **16 ENTER**

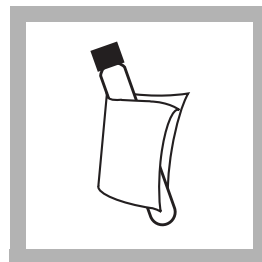
The display will show **mg/L, COD** and the **ZERO** icon.

Note: For alternate form (O_2), press the **CONC** key.

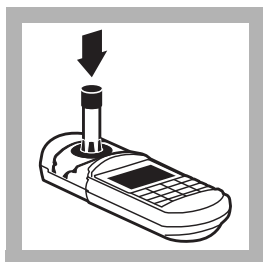


3. Insert the COD/TNT Adapter into the cell holder by rotating the adapter until it drops into place. Then push down to fully insert it.

Note: For increased performance, a diffuser band covers the light path holes on the adapter. Do not remove the diffuser band.



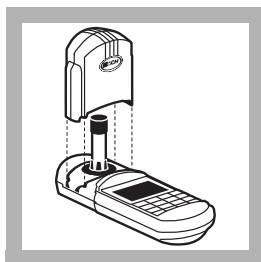
4. Clean the outside of the blank with a towel. *Note:* Wiping with a damp towel, followed by a dry one, will remove fingerprints or other marks.



5. Place the blank in the adapter.

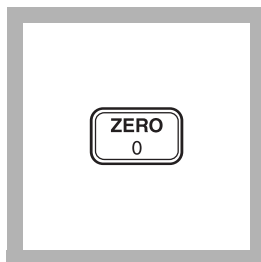
Push straight down on the top of the vial until it seats solidly into the adapter.

Note: Do not move the vial from side to side as this can cause errors.



6. Tightly cover the vial with the instrument cap.

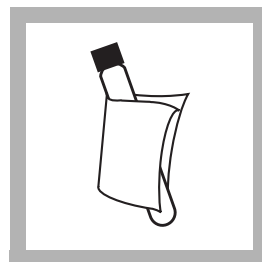
Note: The blank is stable when stored in the dark. See Blanks for Colorimetric Determination following these procedures.



7. Press: **ZERO**

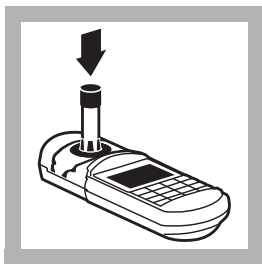
The cursor will move to the right, then the display will show:

0 mg/L COD



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

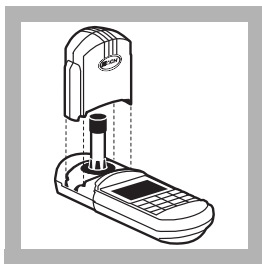
OXYGEN DEMAND, CHEMICAL, continued



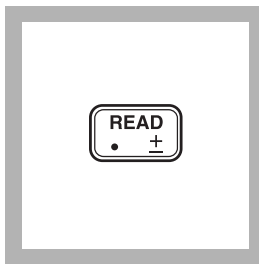
9. Place the sample vial in the adapter.

Push straight down on the top of the vial until it seats solidly into the adapter.

Note: Do not move the vial from side to side as this can cause errors.



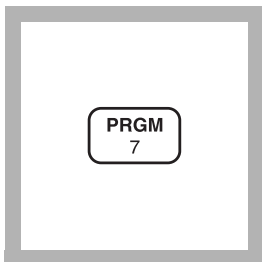
10. Tightly cover the vial with the instrument cap.



11. Press: **READ**

The cursor will move to the right, then the result in mg/L COD will be displayed.

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

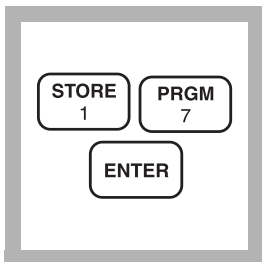


1. Enter the stored program number for chemical oxygen demand, high range.

Press: **PRGM**

The display will show:

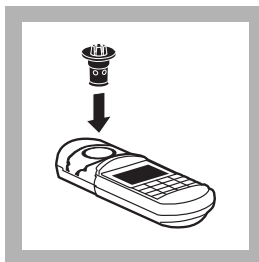
PRGM ?



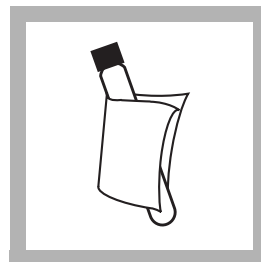
2. Press: **17 ENTER**

The display will show **mg/L, COD** and the **ZERO** icon.

*Note: For alternate form (O₂), press the **CONC** key.*



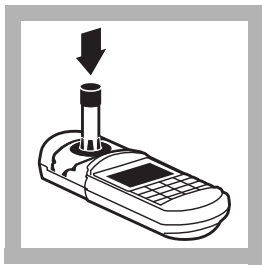
3. Insert the COD/TNT Adapter into the cell holder by rotating the adapter until it drops into place. Then push down to fully insert it.



4. 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.

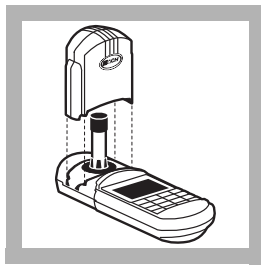
OXYGEN DEMAND, CHEMICAL, continued



5. Place the blank in the adapter.

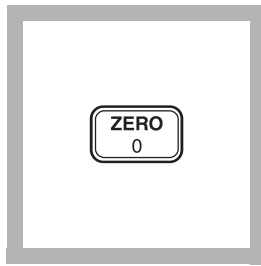
Push straight down on the top of the vial until it seats solidly into the adapter.

Note: Do not move the vial from side to side as this can cause errors.



6. Tightly cover the sample cell with the instrument cap.

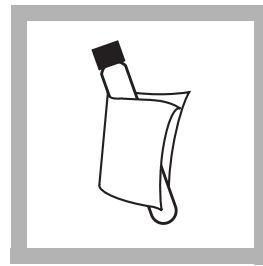
The blank is stable when stored in the dark. See Blanks for Colorimetric Determination following these procedures.



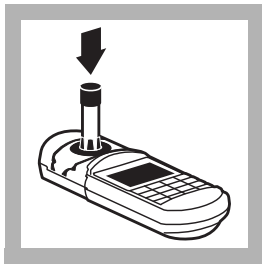
7. Press: **ZERO**

The cursor will move to the right, then the display will show:

0 mg/L COD



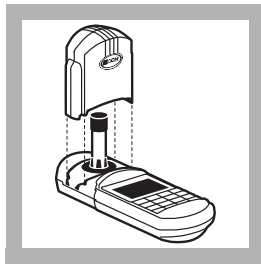
8. Clean the outside of the sample vial with a towel.



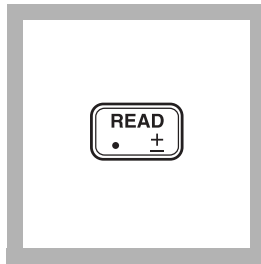
9. Place the sample in the adapter.

Push straight down on the top of the vial until it seats solidly into the adapter.

Note: Do not move the vial from side to side as this can cause errors.



10. Tightly cover the sample cell with the instrument cap.



11. Press: **READ**

The cursor will move to the right, then the result in mg/L COD will be displayed.

Note: When using High Range Plus COD Digestion Reagent Vials, multiply the reading by 10.

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

Sampling 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 *Correction for Volume Additions* (Section 1) for more information.

Accuracy Check

Standard Solution Method

Check the accuracy of the 0 to 150 mg/L range with a 100 mg/L standard. Prepare by dissolving 85 mg of dried (120 °C, overnight) potassium acid phthalate (KHP) in 1 liter of deionized water. Use 2.0 mL as the sample volume. The expected result will be 100 mg/L COD. As an alternative, dilute 10 mL of 1000-mg/L COD Standard Solution to 100 mL to make a 100-mg/L standard.

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. Alternatively, prepare a 500 mg/L standard by dissolving 425 mg of dried (120 °C, overnight) KHP. Dilute to 1 liter with deionized water. Use 2.0 mL of one of these solutions as the sample volume.

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.

Method Performance

Precision

Program #16: In a single laboratory, using a standard solution of 100 mg/L COD and two representative lots of reagent with the instrument, a single operator obtained a standard deviation of ± 2 mg/L COD.

Program #17: In a single laboratory, using a standard solution of 1000 mg/L COD and two representative lots of reagent with the instrument, a single operator obtained a standard deviation of ± 16 mg/L COD. For more information on Hach's precision statement, see *Section 1*.

OXYGEN DEMAND, CHEMICAL, continued

Estimated Detection Limit (EDL)

The EDL for program 16 is 4 mg/L COD. The EDL for program 17 is 30 mg/L COD. For more information on derivation and use of Hach's estimated detection limit, see *Section 1*.

Alternate reagents

Mercury-free COD2 Reagents can provide a mercury-free testing option for non-reporting purposes. For process control applications, COD2 reagents will eliminate mercury waste and save on disposal costs. These reagents are fully compatible with test procedures and calibration curves programmed into the DR/2400 spectrophotometer. Determine chloride and ammonia for accurate results.

Note: Mercury-free COD2 reagents are not approved for USEPA reporting. Request a copy of the COD Reagent Vial Information Brochure, Lit. No. 1356, for more information about specific applications.

Interferences

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 1 in *Table 1*. Samples with higher chloride concentrations should be diluted. Dilute the sample enough to reduce the chloride concentration to the level given in column 2.

If sample dilution will cause the COD concentration to be too low for accurate determination, 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 3.

Table 1

	Column 1	Column 2	Column 3
Vial Type Used	Maximum Cl^- concentration in sample (mg/L)	Maximum Cl^- concentration of diluted samples (mg/L)	Maximum Cl^- concentration in sample when 0.50 HgSO_4 added (mg/L)
Low Range	2000	1000	8000
High Range	2000	1000	4000
High Range Plus	20,000	10,000	40,000

Blanks for Colorimetric Determination

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 the appropriate wavelength (420 or 610 nm). Zero the instrument in the absorbance mode, using a vial containing 5 mL of deionized water and measure the absorbance of the blank. Record the value. Prepare a new blank when the absorbance has changed by about 0.01 absorbance units.

Summary of Method

The mg/L COD results are defined as the mg of O₂ consumed per liter of sample under 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 (Cr₂O₇²⁻) to green chromic ion (Cr³⁺). When the 0-150 mg/L colorimetric method is used, the amount of Cr⁶⁺ remaining is determined. When the 0-1,500 mg/L or 0-15,000 mg/L colorimetric method is used, the amount of Cr³⁺ produced is determined. The COD reagent also contains silver and mercury ions. Silver is a catalyst, and mercury is used to complex the chloride interference.

Pollution Prevention and Waste Management

Final samples will contain mercury (D009), silver (D011), and chromium (D007) at concentration levels regulated by the Federal RCRA. Please see *Section 3* for further information on proper disposal of these materials.

REQUIRED REAGENTS

Description	Qty/Test	Unit	Cat. No.
Select the appropriate COD Digestion Reagent Vial:			
Low Range, 0 to 150 mg/L COD.....	1 to 2 vials	25/pkg.....	21258-25
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 L.....	272-56

REQUIRED APPARATUS

Blender, Osterizer, 120 V, 14 speed.....	1	each.....	26160-00
Blender, Osterizer, 240 V, 14 speed.....	1	each.....	26160-02
DRB 200 Reactor, 110 V, 15 x 16 mm tubes			LTV082.53.40001

OXYGEN DEMAND, CHEMICAL, continued

REQUIRED APPARATUS (continued)

Description	Qty/Test	Unit	Cat. No.
DRB 200 Reactor, 220 V, 15 x 16 mm tubes		LTV082.52.40001	
COD/TNT Adapter.....	1.....	each	48464-00
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, 2.00 mL	1.....	each	14515-36
Pipet Filler, safety bulb	1.....	each	14651-00
Test Tube Rack.....	1 to 2 racks	each	18641-00

ALTERNATE REAGENTS*

COD2, LR, 0 to 150 mg/L COD	1-2 vials	25/pkg	25650-25
COD2, HR, 0 to 1500 mg/L COD.....	1-2 vials	25/pkg	25651-25
COD2, HR, 0 to 1500 mg/L COD.....	1-2 vials	150/pkg	25651-15
COD2, HR, 0 to 15,000 mg/L COD.....	1-2 vials	25/pkg	28343-25

OPTIONAL REAGENTS

Description	Unit	Cat. No.
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
Mercuric Sulfate.....	28.3 grams	1915-20
Oxygen Demand Standard (BOD, COD, TOC), 10-mL Ampules.....	16/pkg	28335-10
Potassium Acid Phthalate, ACS.....	500 g	315-34
Potassium Dichromate Standard Solution, 0.25 N.....	1000 mL*	1809-53
Sulfuric Acid, ACS	500 mL**	979-49
Wastewater Effluent Standard, Inorganic (NH ₃ -N, NO ₃ -N, PO ₄ , COD, SO ₄ , TOC)	500 mL	28332-49
Wastewater Influent Standard, Inorganic (NH ₃ -N, NO ₃ -N, PO ₄ , COD, SO ₄ , TOC)	500 mL	28331-49

OPTIONAL APPARATUS

Balance, analytical, 115 V.....	each	28014-01
Balance, analytical, 230 V.....	each	28014-02
Beaker, 250 mL	each	500-46H
Cylinder, graduated, 5 mL.....	each	508-37
DRB 200 Reactor, 110 V, 21 x 16 mm and 4 x 20 mm.....	LTV082.53.42001	
DRB 200 Reactor, 220 V, 21 x 16 mm and 4 x 20 mm.....	LTV082.52.42001	
DRB 200 Reactor, 110 V, 9 x 16 mm and 2 x 20 mm.....	LTV082.53.30001	

* Mercury-free COD2 reagents are not approved for USEPA reporting. Request a copy of the COD Reagent Vial Information Brochure, Lit. No. 1356, for more information about specific applications.

** Contact Hach for larger sizes.

OXYGEN DEMAND, CHEMICAL, continued

OPTIONAL APPARATUS (continued)

Description	Unit	Cat. No.
DRB 200 Reactor, 220 V, 9 x 16 mm and 2 x 20 mm	LTV082.52.30001	
Electromagnetic Stirrer, 120 V, with electrode stand.....	each.....	45300-01
Electromagnetic Stirrer, 230 V, with electrode stand.....	each.....	45300-02
Flask, volumetric, Class A, 1000 mL	each.....	14574-53
Flask, volumetric, Class A, 100 mL	each.....	14574-42
pH Paper, 1 to 11 pH units.....	5 rolls/pkg.....	391-33
Pipet, serological, 5 mL	each.....	532-37
Pipet Tips, for 19700-01 TenSette Pipet	1000/pkg.....	21856-28
Pipet, volumetric, Class A, 10 mL.....	each.....	14515-38
Spoon, measuring, 0.5 g.....	each.....	907-00
Stir Bar, 22.2 x 4.76 mm (7/8" x 3/16").....	each.....	45315-00
Stir Bar Retriever	each.....	15232-00
Timer.....	each.....	26304-00

For Technical Assistance, Price and Ordering

In the U.S.A.—Call 800-227-4224

Outside the U.S.A.—Contact the Hach office or distributor serving you.