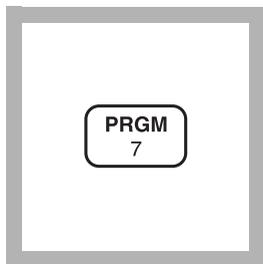


OXYGEN DEMAND, CHEMICAL (20 to 1,000 mg/L) For water and wastewater**Manganese III Digestion Method* (without chloride removal)**

1. Enter the stored program number for Manganese III COD.

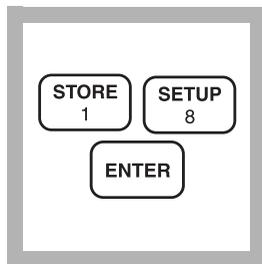
Press: **PRGM**

The display will show:

PRGM ?

Note: If samples cannot be analyzed immediately, see Sampling and Storage following these steps.

Note: Preheat the COD Reactor to 150 °C for use later in the procedure.



2. Press: **18 ENTER**

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

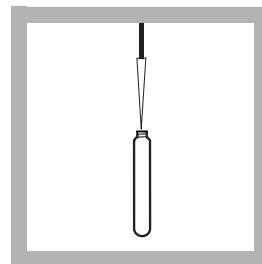
*Note: For alternate forms (O₂), press the **CONC** key.*



3. Homogenize 100 mL of sample for 30 seconds in a blender.

Note: Blending promotes even distribution of solids and improves accuracy and reproducibility.

Note: Continue mixing the sample while pipetting if suspended solids are present.



4. If chloride is not present in significant amounts[†], pipet 0.50 mL of homogenized sample into a Mn III COD vial. Cap and invert several times to mix.

Note: If the sample COD value is not between 20-1000 mg/L dilute the sample with deionized water to obtain a range of 20-1000 mg/L COD. Multiply the final result by the dilution factor.

[†] To determine if chloride will interfere, run the sample with and without the chloride removal procedure and compare the results.

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

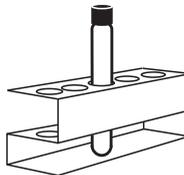
* U.S. Patent 5,556,787

OXYGEN DEMAND, CHEMICAL, continued

PREPARE BLANK



2:00 minutes



5. Prepare a blank (see note) by substituting 0.50 mL of deionized water for the sample. Continue with step 9 of this procedure.

Note: The reagent blank is stable and can be reused. Verify reagent blank quality by measuring the absorbance of the blank vs. a clean COD vial filled with deionized water. The absorbance range should be about 1.36-1.43.

6. Place the vials in the DRB 200 Reactor that is preheated to 150 °C. Digest for 1 hour.

Note: Boiling sample in the vials during digestion indicates the vial is not properly sealed; test results will be invalid.

Note: Samples can be digested up to 4 hours to oxidize more resistant organics. The prepared blank must be treated in the same manner.

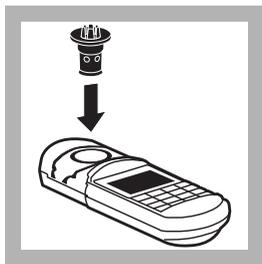
Note: See DRB 200 user manual for selecting pre-programmed temperature applications.

7. Remove the vials and place them in a cooling rack for two minutes to air cool. Then cool the vials to room temperature in a cool water bath or running tap water. This usually takes about three minutes.

Note: Occasionally a vial will develop a colorless upper layer and a purple lower layer. Invert the vial several times to mix and proceed. This will not affect test results.

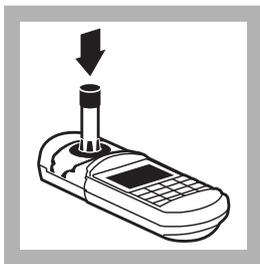
8. Remove the vials from the water and wipe with a clean, dry paper towel.

Invert the vials several times to mix.



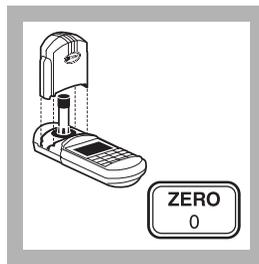
9. Insert the COD/TNT Adapter into the cell holder by rotating the adapter until it drops into place. Then push down to fully insert it.

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



10. Place the blank in the sample cell 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.



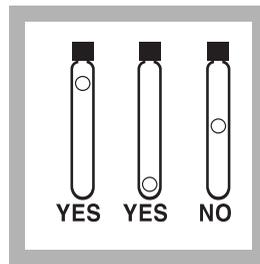
11. Tightly cover the sample cell with the instrument cap.

Note: Clean the COD vial with a towel to remove fingerprints or other marks.

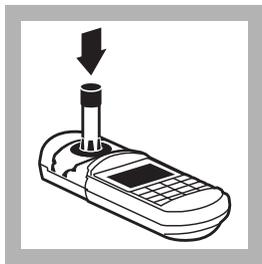
Press: **ZERO**

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

0 mg/L COD

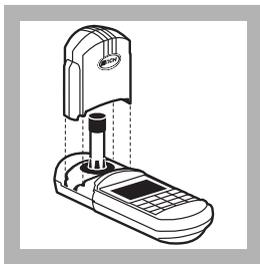


12. If the chloride removal was done, make sure the filter disc is not suspended in the middle of the vial; it can interfere with the instrument reading. Move it with gentle swirling or by lightly tapping the vial on the table top.



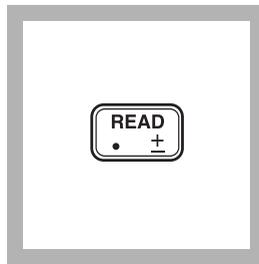
13. Place the sample in the adapter. Push straight down on the top of the vial until it seats solidly into the adapter.

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



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

Note: Clean the COD vial with a towel to remove fingerprints or other marks.



15. Press: **READ**

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

Note: Standard Adjust may be performed using a prepared standard (see Standard Adjust in Section 1).

Note: Adjust the result for any sample dilution in Steps 4 or 6.

Sampling and Storage

Collect samples in clean 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 concentrated sulfuric acid to a pH of less than 2 (about 2 mL per liter) and refrigerated at 4 °C may be stored up to 28 days. Correct results for volume additions; see *Correcting for Volume Additions (Section 1)* for more information.

Accuracy Check

Standard Solution Method

Prepare an 800 mg/L COD standard solution by adding 0.6808 g of dried (103 °C, overnight) potassium acid phthalate (KHP) to 1 liter of deionized water. Use 0.50 mL of this solution (0.60 mL for the chloride removal procedure) as the sample volume. The result should be 800 ±26 mg/L COD.

An 800 mg/L COD solution can also be purchased directly from Hach (see *Optional Reagents*).

Method Performance (for Manganic III COD without the chloride removal procedure)

Precision

In a single laboratory, using a standard solution of 800 mg/L COD and two representative lots of reagent with the instrument, a single operator obtained a standard deviation of ±23 mg/L COD.

Estimated Detection Limit (EDL)

The EDL for program 18 is 14 mg/L COD. For more information on derivation and use of Hach's estimated detection limit, see *Section 1*.

Interferences

Inorganic materials may also be oxidized by trivalent manganese and constitute a positive interference when present in significant amounts. Chloride is the most common interference and is removed by sample pretreatment with the Chloride Removal Cartridge. If chloride is known to be absent or present in insignificant levels, the pretreatment can be omitted. A simple way to determine if chloride will affect test results is to run

routine samples with and without the chloride removal, then compare results. Other inorganic interferences (i.e., nitrite, ferrous iron, sulfide) are not usually present in significant amounts. If necessary, these interferences can be corrected for after determining their concentrations with separate methods and adjusting the final COD test results accordingly.

Ammonia nitrogen is known to interfere in the presence of chloride; it does not interfere if chloride is absent.

Summary of Method

Chemical oxygen demand (COD) is defined as "... a measure of the oxygen equivalent of the organic matter content of a sample that is susceptible to oxidation by a strong chemical oxidant" (APHA Standard Methods, 19th ed., 1995). Trivalent manganese is a strong, non-carcinogenic chemical oxidant that changes quantitatively from purple to colorless when it reacts with organic matter. It typically oxidizes about 80% of the organic compounds. Studies have shown that the reactions are highly reproducible and test results correlate closely to Biochemical Oxygen Demand (BOD) values and hexavalent chromium COD tests. None of the oxygen demand tests provide 100% oxidation of all organic compounds.

A calibration is provided which is based on the oxidation of Potassium Acid Phthalate (KHP). A different response may be seen in analyzing various wastewaters. The KHP calibration is adequate for most applications. The highest degree of accuracy is obtained when test results are correlated to a standard reference method such as BOD or one of the chromium COD methods. Special waste streams or classes will require a separate calibration to obtain a direct mg/L COD reading or to generate a correction factor for the precalibrated KHP response. The sample digestion time can be extended up to 4 hours for samples which are difficult to oxidize.

OXYGEN DEMAND, CHEMICAL, continued

REQUIRED REAGENTS

Description	Quantity Required		
	Per Test	Unit	Cat. No.
Manganese III COD Reagent Vials, 20-1000 mg/L	1	25/pkg.....	26234-25
Sulfuric Acid, concentrated	1 mL.....	4 Kg.....	979-09
Water, deionized.....	varies	4 L.....	272-56

REQUIRED APPARATUS

Adapter, COD/TNT	1	each.....	48464-00
Blender, Osterizer, 120 Vac, 14-speed	1	each.....	26747-00
Blender Container, 118 mL.....	1	2/pkg.....	26748-00
Cap, with inert Teflon liner, for mixing bottle.....	varies	12/pkg.....	24018-12
DRB 200 Reactor, 110 V, 15 x 16 mm tubes		LTV082.53.40001	
DRB 200 Reactor, 220 V, 15 x 16 mm tubes		LTV082.52.40001	
Forceps, extra fine point	1	each.....	26696-00
Mixing Bottle, glass, for sample + acid	1	each.....	24276-06
Pipet, TenSette, 1.0 to 10.0 mL.....	1	each.....	19700-10
Pipet Tips, for 19700-10 TenSette	2	250/pkg.....	21997-25
Pipet, TenSette, 0.1 to 1.0 mL.....	1	each.....	19700-01
Pipet Tips, for 19700-01 TenSette	2	1000/pkg.....	21856-28
Test Tube Rack, stainless steel.....	1	each.....	18641-00

OPTIONAL REAGENTS

COD Standard Solution, 800 mg/L COD	200 mL.....	26726-29	
Oxygen Demand Standard (BOD, COD, TOC), 10-mL Ampules	16/pkg.....	28335-10	
Potassium Acid Phthalate	500 g.....	315-34	
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

Dispenser for sulfuric acid.....	each.....	25631-37	
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	
DRB 200 Reactor, 220 V, 9 x 16 mm and 2 x 20 mm		LTV082.52.30001	

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.