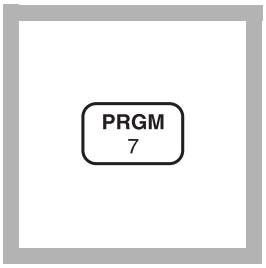
OXYGEN DEMAND, CHEMICAL (20 to 1,000 mg/L) For water and wastewater

Manganese III Digestion Method* (with chloride removal)



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

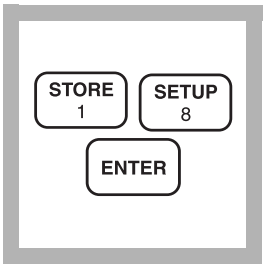
Press: **PRGM**

The display will show:

PRGM ?

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

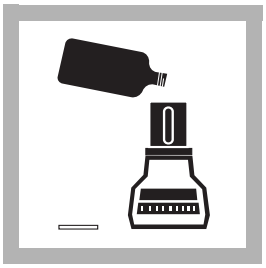
Note: *Preheat the COD Reactor to 150 °C for use later in the procedure.*



2. Press: **18 ENTER**

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

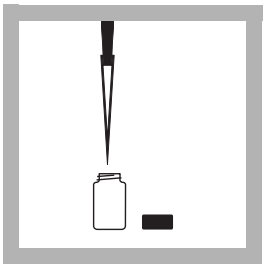
Note: *For alternate forms (O_2), press the* **CONC** *key.*



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.*



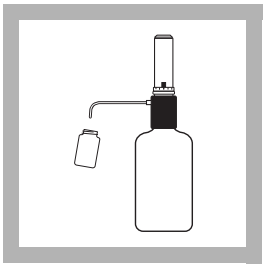
Chloride Removal Procedure

4. Using a TenSette Pipet or a pipet and safety bulb, pipet 9.0 mL of homogenized sample into an empty glass mixing cell. If the sample COD exceeds 1000 mg/L, dilute the sample as described in *Table 1*.

Note: *If suspended solids are present, continue mixing the sample while pipetting.*

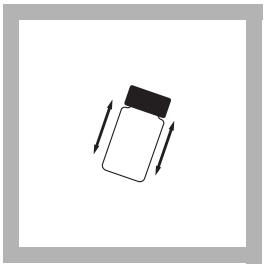
Caution: Some of the chemicals and apparatus used in this procedure may be hazardous to the health and safety of the user if inappropriately handled or accidentally misused. Please read all warnings and the safety section of this manual. Wear appropriate eye protection and appropriate clothing. If contact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

* U.S. Patent 5,556,787



5. Using an automatic dispenser or TenSette Pipet, add 1.0 mL of concentrated sulfuric acid to the mixing cell.

Note: *Mixing concentrated sulfuric acid and water is not additive. Adding 1.0 mL of concentrated sulfuric acid to 9.0 mL of sample does not result in a final volume of 10.0 mL. This factor is built into the calibration curve.*



6. Cap the cell tightly and invert it several times. The solution will become hot. Cool to room temperature before proceeding.

Note: *Acidified samples are stable for several months when refrigerated at 4 °C.*

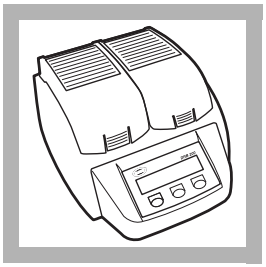
PREPARE BLANK

7. Prepare a blank (see note) by repeating Steps 4-6, substituting 9.0 mL of deionized water for the sample.

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, when using chloride removal, should be about 1.31-1.36.*

Note: *Use a clean pipet or rinse it thoroughly.*

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



8. If not already on, turn on the DRB 200 Reactor and heat to 150 °C.

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

Table 1 Dilution Table (for use with Chloride Removal Procedure Only)

Sample (mL)	Deionized Water (mL)	Range (mg/L COD)	Multiplication Factor
6.0	3.0	30-1500	1.5
3.0	6.0	60-3000	3
1.0	8.0	180-9000	9
0.5	8.5	360-18000	18

All dilutions require that the ratio of sample to sulfuric acid remain at 9:1. For other dilutions that are not listed in Table 1, simply add the sample volume + deionized water and divide by the sample volume to obtain the multiplication factor.

Example:

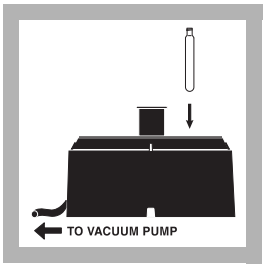
Dilute the sample to a range of 90-4500 mg/L COD

Sample Volume (2.0 mL) + Deionized water (7.0 mL) = Total Volume (9.0 mL)

$$\text{Multiplication Factor} = \frac{\text{Total Volume}}{\text{Sample Volume}} = \frac{9.0\text{ mL}}{2.0\text{ mL}} = 4.5$$

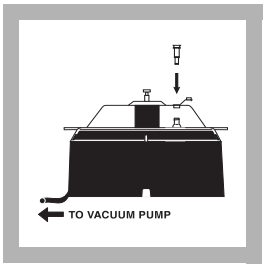
Standard test range is 20-1000 mg/L COD. Example Test Range = 4.5 (20) to 4.5 (1000) = 90-4500 mg/L COD

It is best to use 0.5 mL or more of sample for diluting. If sample values exceed 18,000 mg/L COD, use a separate sample dilution before the sample chloride removal procedure.

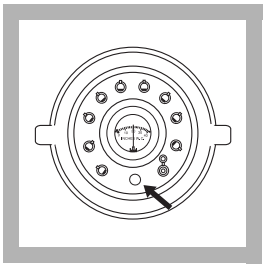


9. Label each Mn III COD vial and remove the cap. Place the vial in one of the numbered holes in the Vacuum Pretreatment Device (VPD)* base.

Note: *The VPD must be attached to a vacuum pump (not an aspirator-type vacuum) that can create a vacuum of 20 to 25 inches of mercury.*

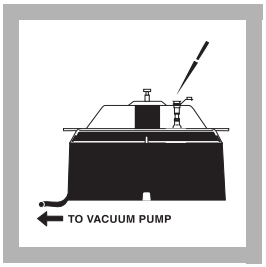


10. Place the VPD top on the base. Insert a fresh Chloride Removal Cartridge (CRC)** directly above each Mn III COD Reagent Vial. Plug any open holes in the VPD top using the stoppers provided.



11. Turn the vacuum pump on and adjust the vacuum regulator valve on top of the VPD until the internal gauge reads 20 inches of water.

Note: *The optimum setting allows the sample to flow through the CRC in about 30 to 45 seconds.*

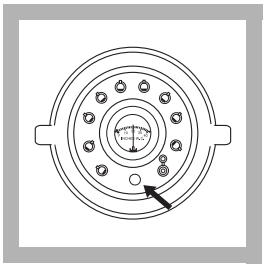


12. Pipet 0.60 mL of acidified sample (made in Steps 4-6) into the CRC. Pipet 0.60 mL of acidified blank into another CRC.

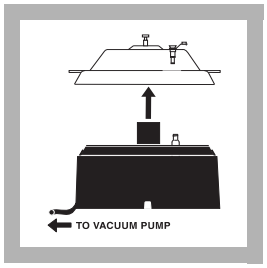
Note: *If the sample does not flow through the CRC, increase the vacuum until flow starts, then reduce the vacuum to 20 inches of water. Proceed as usual.*

* Patent Pending.

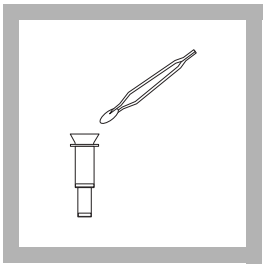
** U.S. patents 5,667,754 and 5,683,914.



13. Close the vacuum regulator valve completely to achieve full vacuum. After one minute under full vacuum, slide the VPD back and forth several times to dislodge any drops clinging to the cartridge.



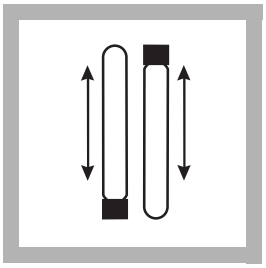
14. Open the VPD regulator valve to release the vacuum. Turn the pump off. Remove the VPD top and set it beside the base.



15. Use forceps to remove the filter from the top of each CRC. Place each filter in the corresponding Mn III COD Vial (use the numbers on the VPD as a guide).

Note: *If the sample does not contain suspended solids, it is not necessary to transfer the filter to the digestion vial.*

Note: *To avoid cross contamination, clean forceps tips between samples by wiping with a clean towel or rinsing with deionized water.*



16. Remove the Mn III COD vial from the vacuum chamber and replace the original cap. Screw the cap on tightly. Invert several times to mix.

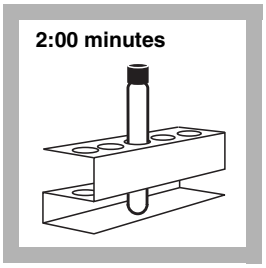
Note: *Dispose of the used Chloride Removal Cartridge. Do not reuse it.*

17. 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.*

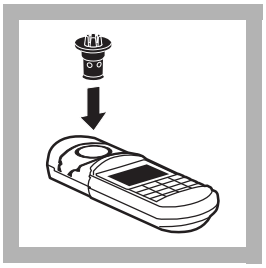


18. Remove the vials and place them in a cooling rack for two minutes to air cool. Then cool the vials to room temperature in a cool water bath or running tap water. This usually takes about three minutes.

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.*

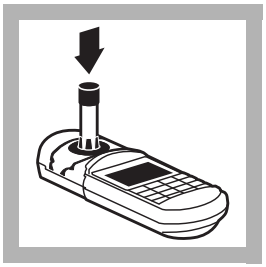
19. Remove the vials from the water and wipe with a clean, dry paper towel.

Invert the vials several times to mix.



20. 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.

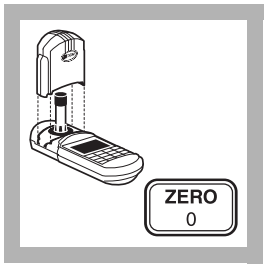
Note: *For increased performance, a diffuser band covers the light path holes on the adapter. Do not remove the diffuser band.*



21. 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.*



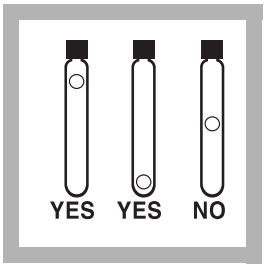
22. Tightly cover the sample cell with the instrument cap.

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

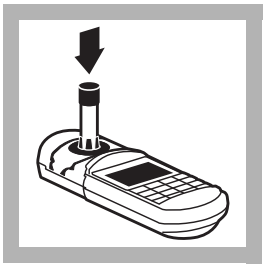
Press: **ZERO**

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

0 mg/L COD



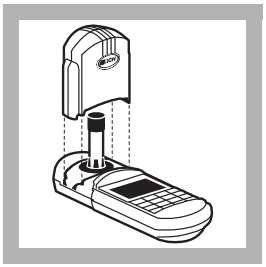
23. If the chloride removal was done, make sure the filter disc is not suspended in the middle of the vial; it can interfere with the instrument reading. Move it with gentle swirling or by lightly tapping the vial on the table top.



24. Place the sample in the adapter.

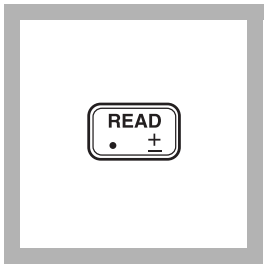
Push straight down on the top of the vial until it seats solidly into the adapter.

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



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

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



26. 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.*

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.

REQUIRED REAGENTS

Description	Quantity Required Per Test	Unit	Cat. No.
Chloride Removal Cartridges (CRC)	1	25/pkg	26618-25
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
Vacuum Pretreatment Device (VPD)	1	each	49000-00
Vacuum Pump, 115 V	1	each	14697-00
Vacuum Pump, 230V	1	each	14697-02

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.