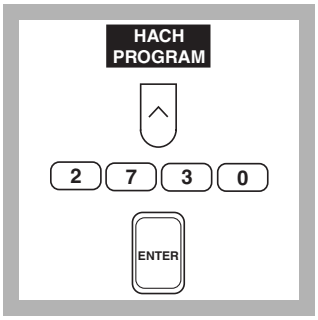
OXYGEN DEMAND, Chemical

Method 10067 **Manganese III Digestion Method* (with optional chloride removal)**

(20 to 1000 mg/L COD)

Scope and Application: *For water and wastewater.*

* U.S. Patent 5,556,787



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

Select the stored program number for Manganese III COD by pressing **2730** with the numeric keys.

Press: **ENTER**

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

2. The display will show:

HACH PROGRAM: 2730 COD, Mn III

The wavelength (λ), **510 nm**, is automatically selected.

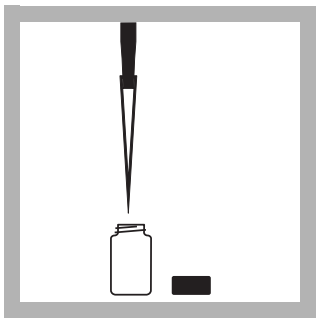
3. Turn on the COD Reactor and heat to 150 °C while preparing the sample and blank.

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

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

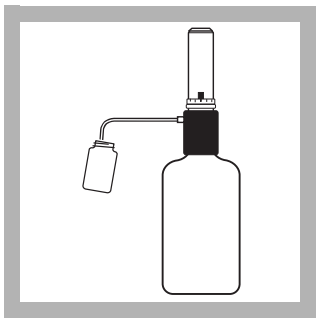
Note: *Continue mixing the sample while pipetting if suspended solids are present.*

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 accidently 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.



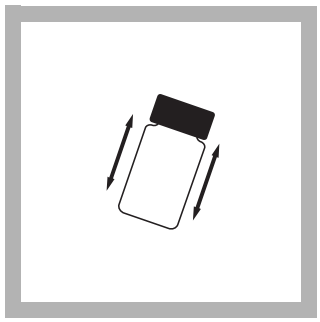
5. Using a TenSette Pipet or a pipet and safety bulb, pipet 9.0 mL of homogenized sample into an empty glass mixing cell. If the sample COD exceeds 1000 mg/L, dilute the sample as described in *Table 1*.

Note: *Continue mixing the sample while pipetting samples with suspended solids.*



6. 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.*



7. 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.*

8. Prepare a blank (see note) by repeating steps 6-8, using 9.0 mL of deionized water for the sample.

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).*

Note: *The reagent blank is stable and can be re-used. Verify reagent blank quality by measuring the absorbance of the reagent blank versus a clean COD vial filled with deionized water. The absorbance for the blank should be about 1.41-1.47.*

Table 1 Dilution Table

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 to 4500 mg/L COD

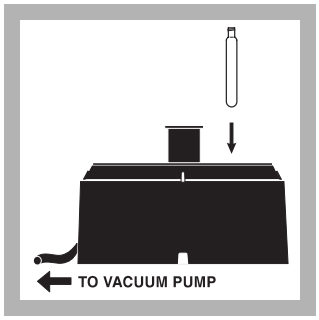
Sample Volume (2.0 mL) + Deionized water (7.0 mL) = Total Volume (9.0 mL)

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

Standard test range is 50 to 1000 mg/L COD.

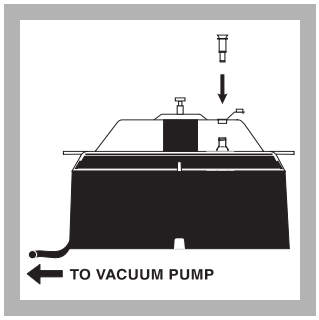
Example Test Range = 4.5 (50) to 4.5 (1000) = 225 to 4500 mg/L COD

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 performing the sample chloride removal procedure.

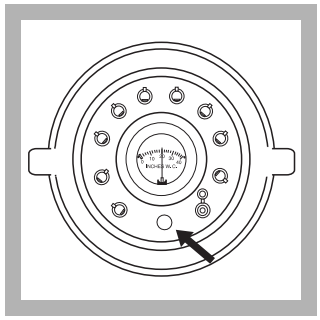


9. Label each Mn III COD vial and remove the cap. Place the vials in one of the numbered holes in the Vacuum Pretreatment Device (VPD)* base.

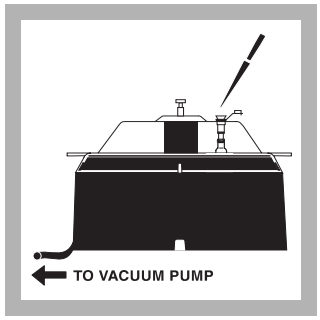
Note: *The VPD must be attached to a vacuum pump (not an aspirator-type vacuum) that can create a vacuum of 20–25 inches of mercury.*



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.



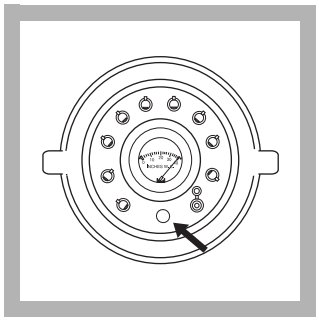
11. Turn the vacuum pump on and adjust the vacuum regulator valve on top of the VPD until the internal gauge reads 20 inches of water.



12. Pipet 0.60 mL of acidified sample (prepared in steps 6–8) into the CRC. Pipet 0.60 mL of acidified blank into another CRC. It should take 30–45 seconds to draw the liquid through the CRC into each vial.

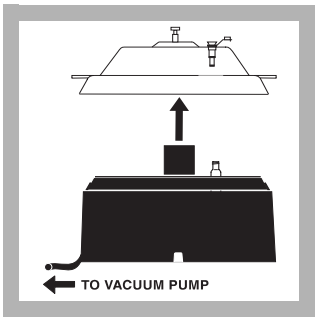
Note: *If the sample does not flow through the CRC, increase the vacuum until flow starts, then reduce the vacuum down to 20 inches of water. Proceed as usual.*

*Patent Pending
**U.S. Patents 5,667,754; 5,683,914

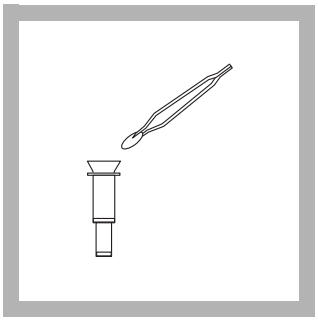


13. Close the vacuum regulator valve completely to achieve full vacuum. After 1 minute of full vacuum, slide the VPD back and forth several times to dislodge any drops clinging to the cartridge.

Note: *The maximum range of the VPD vacuum gauge is 40 inches of water; it will not indicate the full vacuum level obtained. Full vacuum is 20-25 inches of mercury; this can be measured at the vacuum pump with a gauge calibrated for inches of mercury.*



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

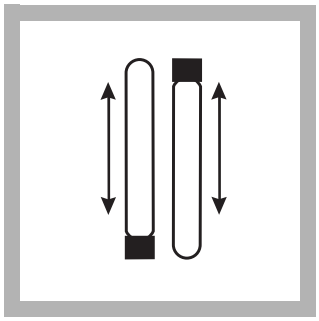


15. Use forceps to remove the filter from the top of each CRC. Place each filter in the corresponding Mn III COD Vial (use the numbers on the VPD as a guide).

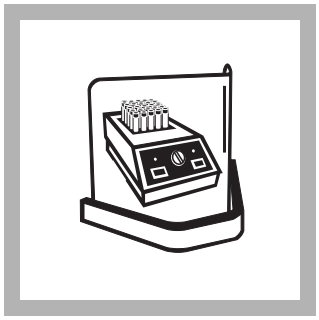
Note: *To avoid cross contamination, clean forcep tips between samples by wiping with a clean towel or rinsing with deionized water.*

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

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



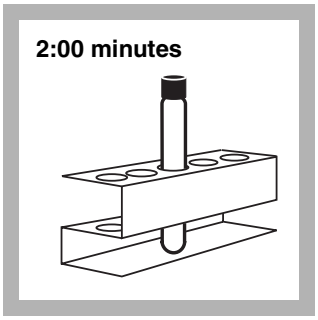
16. Remove the Mn III COD vial from the vacuum chamber and replace the original cap. Screw the cap on tightly. Invert several times to mix.



17. Place the vials in the COD 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.*

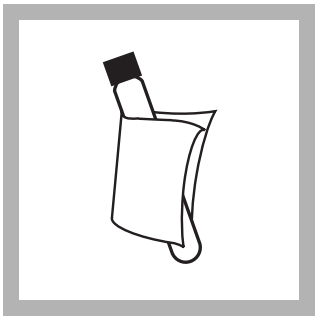
Note: *Samples can be digested up to 4 hours to oxidize more resistant organics. The prepared blank must be treated in the same manner.*



18. Place the vials in a cooling rack for two minutes. Then cool the vials to room temperature in a cool water bath or tap water (takes about three minutes).

Note: *If the solution develops a colorless upper layer and a purple lower layer, invert the vial several times and proceed. This will not affect test results.*

Note: *Use the Hach COD Lifter to transfer several vials at once.*

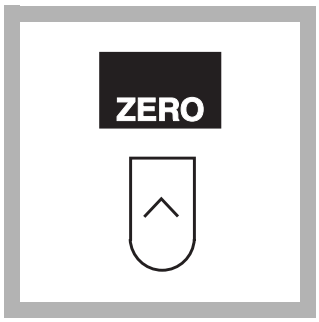


19. Remove the vials from the water and wipe with a clean, dry paper towel.

Invert the vials several times to mix.

20. Insert the COD Vial Adapter into the sample cell module by sliding it under the thumb screw and into the alignment grooves. Fasten with the thumb screw.

21. Place the blank into the sample cell compartment. Close the light shield.

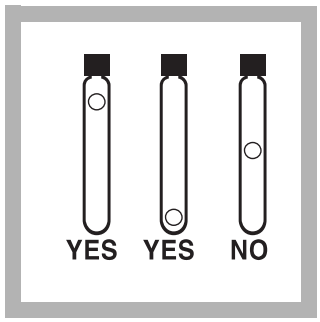


22. Press the soft key under ***ZERO.***

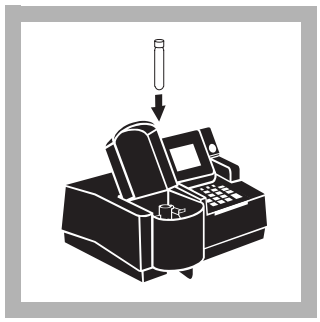
The display will show:

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.*



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 vial in the adapter. Close the light shield. Results in mg/L COD (or chosen units) will be displayed.

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

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

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.

Sample Collection, Preservation 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 Section *1.2.2 Correcting for Volume Additions*.

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 ±24 mg/L COD. An 800-mg/L COD Standard Solution can also be purchased directly from Hach (see *OPTIONAL APPARATUS*).

To adjust the calibration curve using the reading obtained with the 800-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*.

Method Performance

(Data is for Manganese III COD without the chloride removal procedure)

Precision
Standard: 500 mg/L COD

Program	95% Confidence Limits
2730	497–503 mg/L COD

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

Estimated Detection Limit (EDL)

Program	EDL
2730	4 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: 2730

Portion Of Curve	ΔAbs	ΔConcentration
Entire range	0.010	8 mg/L

See Section *1.5.3 Sensitivity Explained* for more information.

Calibration Standard Preparation

To perform a calibration using the manganese III method, prepare a 10,000-mg/L COD stock solution by diluting 0.8510 grams of dried (120 °C, overnight) KHP to 100 mL with deionized water using Class A glassware. Mix thoroughly.

Prepare calibration standards containing 100, 300, 500, 800 and 1000 mg/L COD as follows:

a. Into five different 100-mL volumetric flasks, pipet 1.00, 3.00, 5.00, 8.00 and 10.00 mL of the 10,000-mg/L COD stock solution using Class A glassware.

b. Dilute to the mark with deionized water. Stopper the flasks and invert each of them 10 times to mix.

c. Using the Manganese III COD 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.

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 four hours for samples that are difficult to oxidize.

Safety

Good safety habits and laboratory techniques should be used throughout the procedure. Consult the *Material Safety Data Sheets* for information specific to the reagents used. For additional information, refer to Section *1*.

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 COD	1	25/pkg	26234-25
Sulfuric Acid, concentrated, ACS	1 mL	2.5 L	979-09
Water, deionized	varies	4 L	272-56

REQUIRED APPARATUS

Blender, 120 VAC	1	each	26747-00
Blender Container, 50–250 mL	1	2/pkg	26748-00
Cap, with inert Teflon liner, for mixing bottle	varies	12/pkg	24018-12
COD Reactor, 115-230 VAC, 50-60 Hz	1	each	45600-00
or			
COD Reactor, 230 VAC, 50 Hz	1	each	45600-02
DR/4000 Test Tube Adapter	1	each	48189-00
Forceps, extra fine point	1	each	26696-00
Pipet, TenSette, 1.0 to 10.0 mL	1	each	19700-10
Pipet Tips, for 19700-10 TenSette Pipet	2	50/pkg	21997-96
Pipet, TenSette, 0.1 to 1.0 mL	1	each	19700-01
Pipet Tips, for 19700-01 TenSette	2	50/pkg	21856-96
Safety Shield	1	each	23810-00
Test Tube Rack, COD	1	each	18641-00
Vacuum Pretreatment Device (VPD)	1	each	49000-00
Vacuum Pump	1	each	14697-00
Vial, glass, for sample + acid	2	each	24277-00

OPTIONAL REAGENTS

COD Standard Solution, 800-mg/L COD	200 mL		26726-29
Potassium Acid Phthalate, ACS	500 g		315-34

OPTIONAL APPARATUS

Dispenser for sulfuric acid, 0.5-5.9 mL, digital	each		25631-37
Pipet Tips, for 19700-01 TenSette	1000/pkg		21856-28

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