Oxygen Demand, Chemical
Manganese III Digestion Method (with optional chloride removal*)

Scope and Application: For COD in drinking water, industrial process waters, or wastewater.

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

Press: 432 READ/ENTER

The display will show:

Dial nm to 510

* U.S. Patent No. 5,667,754

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

Note: See Instrument Setup to enter this method into the DR/2000.

Note: For DR/3000s:
Press: MANUAL PROGRAM
Place the reagent blank in the instrument.
Press: ZERO
Enter: -754.8 CONC FACTOR
Press: 0 CONC
Place the sample in the instrument and read concentration directly.

Note: DR/2000s with software versions 3.0 and greater will display "P" and the program number.

Note: DR/2000 with software versions 3.0 and greater will not display "Dial to" message if the wavelength is already set correctly. The display will show the message in Step 3. Proceed with Step 4.

2. Rotate the wavelength dial until the display shows:

510 nm

Note: Approach wavelength settings from the higher to lower values.

3. Press: READ/ENTER

The display will show:

mg/l Mn III COD

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.

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

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. If the sample contains chloride†, go to step 7 and follow the chloride removal procedure.

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 and the chloride removal procedure is not necessary, 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.

6. Prepare a blank by substituting 0.50 mL of deionized water for the sample. Continue with Step 20 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 1.46–1.51 for the DR/2000 and 1.45–1.51 for the DR/3000.

Chloride Removal Procedure (steps 7–19)

7. 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.

8. 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.

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### Table 1 Dilution Table (Use With Chloride Removal Procedure only)

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

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

**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 x 20 to 4.5 x 1000 = 90–4500 mg/L COD

It is best to use 0.5 mL or more for diluting. If sample values exceed 18000 mg/L COD, use a separate sample dilution before the sample chloride removal procedure.
9. 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.

10. Using a clean pipet, prepare a blank by repeating Steps 7–9, using 9.0 mL of deionized water as 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 1.42–1.47 for the DR/2000 and 1.43–1.47 for the DR/3000.

**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).

11. If not already on, turn on the COD Reactor and heat to 150 °C. Place the shield in front of the reactor.

**Note:** Ensure safety devices are in place to protect the analyst from splattering should leakage occur. Spilled reagent will affect test accuracy and is hazardous. Do not run tests with vials which have been spilled.

12. Label each Mn III COD vial and remove the cap. Place the vials in 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.
13. 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.

14. 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.

15. Pipet 0.60 mL of acidified sample (prepared in Steps 7–9) into the CRC. Pipet 0.60 mL of acidified blank into another CRC. It should take about 30 to 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 the flow starts, then reduce the vacuum down to 20 inches of water. Proceed as usual.

16. Close the vacuum regulator valve completely to achieve full vacuum. After one minute under full vacuum, open the VPD vacuum regulator valve to release the vacuum.

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

17. Turn the pump off. Remove the VPD top and set it beside the base.

18. 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 forceps 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.

19. 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: 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.

20. Place the vials in the COD Reactor that was preheated to 150 °C. Digest for one hour.
21. 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.

22. Remove the vials from the water and wipe with a clean, dry paper towel. Invert the vials several times to mix.

23. Insert the COD Vial Adapter into the cell holder with the marker to the right.

24. Place the blank into the adapter. Place the cover on the adapter.

25. Press: **ZERO**

The display will show: **WAIT**

then:

0. mg/L Mn III COD

26. 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.

27. Place the sample into the adapter with the Hach logo facing the front of the instrument. Place the cover on the adapter.

28. Press: **READ/ENTER**

The display will show: **WAIT**

then the result in mg/L COD will be displayed.

**Note:** Adjust the result for any sample dilution in steps 5 or 7.

**Note:** In the constant-on mode, pressing READ/ENTER is not required. WAIT will not appear. When the display stabilizes, read the result.
Instrument Setup

**DR/2000s With Software Version 3.0 and greater**

1. Turn the instrument on. Press **SHIFT METHOD** to enter the configuration mode. The display will show: **MOMENTARY** or **CONSTANT ON**

2. Press the **UP ARROW** key twice to select **HACH UPDATE**. Press **READ/ENTER**. The display will show: **ENTER #**:  

3. Press: 

   ![Keys used](image)

   The display will show: **P 432 ENTER nm**

   **Note:** If you make an error, press **SHIFT CLEAR** and re-enter the number. When the number is correct, press **READ/ENTER**.

4. Press: 

   ![Keys used](image)

   The display will show: **P 432 Decimal? 00.00**

5. Use the arrow keys to correctly position the decimal point. Press the **DOWN ARROW** key twice. The display will show:

   **DECIMAL? 0000.**

6. Press **READ/ENTER** to accept the decimal position.

   The display will show: **P 432 UNITS?**

7. Use the arrow keys to select the appropriate unit of measure. Press the **DOWN ARROW** key twice.

   The display will show: **P 432 mg/l**

8. Press **READ/ENTER** when the correct unit of measure is displayed.

   This display will show: **P 432 mg/l _**

9. Construct the display to read the correct method symbol. The symbol must be entered exactly as shown including single spaces preceding III and COD:

   **Mn III COD**

   The two ways to enter the display string for the method symbol are: 1) using ASCII codes and 2) scrolling to the characters. Each method is described below. Use the method that is most convenient for you.
Using ASCI Codes:

a. Enter each number code followed by 2 presses of the READ/ENTER key:

77 ENTER ENTER
110 ENTER ENTER
32 ENTER ENTER
73 ENTER ENTER
73 ENTER ENTER
73 ENTER ENTER
32 ENTER ENTER
67 ENTER ENTER
79 ENTER ENTER
68 ENTER ENTER

b. Complete method symbol entry by pressing READ/ENTER a third time after keying the final code.

Scrolling to the characters:

a. Select letters and numbers by scrolling to the correct character with the arrow keys.

b. To make a letter uppercase, press the SHIFT key.

c. The space is the character displayed after one press of the DOWN ARROW key.

d. Make sure to enter the display line EXACTLY as shown, including the spaces. Do not enter trailing spaces.

e. Accept each symbol by pressing READ/ENTER.

f. To end symbol entry, press READ/ENTER a second time after accepting the last character.

10. When the instrument is out of symbol entry mode, the display will read: P 432 TIMER

11. This method has no timers, so press READ/ENTER.

The display will show: #0 STANDARD

12. Press READ/ENTER to display the zero data pair.

The display will show: 0.000 Abs 0000. mg/l

13. Press READ/ENTER. The display will show: #1 STANDARD

14. Press READ/ENTER. The display will prompt for entry of the first concentration point:

#1 0000. mg/l
15. Enter concentration point #1 by pressing **1000** so that the display shows:
   
   # 1 1000. mg/l

16. Press **READ/ENTER**. The display will prompt for entry of the first absorbance point:

   # 1 0.000 Abs

17. Enter absorbance point #1. Before entering the number, press **SHIFT/8** to enter a minus sign, then press **1325**. The display will show:

   # 1 –1.325 Abs

18. Press **READ/ENTER**. The display will show the first data pair:

   -1.325 Abs 1000. mg/l

19. Press **READ/ENTER** to accept the first data pair. The display will show:

   #2 STANDARD

20. Press **SHIFT READ/ENTER** to complete data point entry. The display will show: #:

21. Enter the validation number **3953**. The display will show: #: 3953

22. Press **READ/ENTER**. The display will show: COMPLETED

   then: P 432 mg/l Mn III COD

If the display shows **INCORRECT #**, then prompts for the validation number, a mistake may have been made during data entry. Make sure the validation number is correct. If so, the error occurred during some other portion of the method entry. Press **METH** and respond to the **ABORT?** message by pressing **READ/ENTER**, then re-enter the method.

The instrument is now ready for use with method 432.

**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 I) for more information.
Method Performance (data is for Mn III COD without the chloride removal procedure)

**Precision**

<table>
<thead>
<tr>
<th>COD Standard</th>
<th>DR/2000 95% Confidence Limits</th>
<th>DR/3000 95% Confidence Level</th>
</tr>
</thead>
<tbody>
<tr>
<td>800 mg/L</td>
<td>±24 mg/L</td>
<td>±22 mg/L</td>
</tr>
</tbody>
</table>

**Estimated Detection Limit**

For DR/2000

<table>
<thead>
<tr>
<th>Program</th>
<th>DR/2000 EDL</th>
</tr>
</thead>
<tbody>
<tr>
<td>432</td>
<td>4 mg/L</td>
</tr>
</tbody>
</table>

For DR/3000, EDL: 4 mg/L

**Sensitivity**

For DR/2000

Program Number: 432

<table>
<thead>
<tr>
<th>Portion of Curve</th>
<th>ΔAbs</th>
<th>ΔConcentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Entire range</td>
<td>0.010</td>
<td>8 mg/L</td>
</tr>
</tbody>
</table>

For DR/3000

<table>
<thead>
<tr>
<th>Portion of Curve</th>
<th>ΔAbs</th>
<th>ΔConcentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Entire Range</td>
<td>0.010</td>
<td>8 mg/L</td>
</tr>
</tbody>
</table>

**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).

**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 four hours for samples that are difficult to oxidize.

### REQUIRED REAGENTS

<table>
<thead>
<tr>
<th>Description</th>
<th>Quantity Required Per Test</th>
<th>Unit</th>
<th>Cat. No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chloride Removal Cartridges (CRC)</td>
<td>1</td>
<td>25/pkg</td>
<td>26618-25</td>
</tr>
<tr>
<td>Manganese III COD Reagent Vials, 20-1000 mg/L COD</td>
<td>1</td>
<td>25/pkg</td>
<td>26234-25</td>
</tr>
<tr>
<td>Sulfuric Acid, concentrated, ACS</td>
<td>1 mL</td>
<td>4 Kg.</td>
<td>979-09</td>
</tr>
<tr>
<td>Water, deionized</td>
<td>varies</td>
<td>4 L</td>
<td>272-56</td>
</tr>
</tbody>
</table>

### REQUIRED APPARATUS

<table>
<thead>
<tr>
<th>Description</th>
<th>Quantity Required Per Test</th>
<th>Unit</th>
<th>Cat. No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Adapter, COD, DR/2000 and DR/3000.</td>
<td>1</td>
<td>each</td>
<td>44799-00</td>
</tr>
<tr>
<td>Blender, 120 Vac</td>
<td>1</td>
<td>each</td>
<td>26747-00</td>
</tr>
<tr>
<td>Blender Container, 50-250 mL</td>
<td>1</td>
<td>each</td>
<td>26748-00</td>
</tr>
<tr>
<td>Cap, with inert Teflon liner, for mixing bottle</td>
<td>varies</td>
<td>12/pkg</td>
<td>24018-12</td>
</tr>
<tr>
<td>COD Reactor, 120/240 V, North American fuses and plug</td>
<td>1</td>
<td>each</td>
<td>45600-00</td>
</tr>
<tr>
<td>COD Reactor, 120/240 V, European power cord and fuses</td>
<td>1</td>
<td>each</td>
<td>45600-02</td>
</tr>
<tr>
<td>Forceps, extra fine point</td>
<td>1</td>
<td>each</td>
<td>26696-00</td>
</tr>
<tr>
<td>Mixing Bottle, glass, for sample + acid</td>
<td>1</td>
<td>each</td>
<td>24277-00</td>
</tr>
<tr>
<td>Pipet, TenSette, 1.0 to 10.0 mL</td>
<td>1</td>
<td>each</td>
<td>19700-10</td>
</tr>
<tr>
<td>Pipet Tips, for 19700-10 TenSette</td>
<td>2</td>
<td>50/pkg</td>
<td>21997-96</td>
</tr>
<tr>
<td>Pipet Tips, for 19700-10 TenSette</td>
<td>2</td>
<td>250/pkg</td>
<td>21997-25</td>
</tr>
<tr>
<td>Pipet, TenSette, 0.1 to 1.0 mL</td>
<td>1</td>
<td>each</td>
<td>19700-01</td>
</tr>
<tr>
<td>Pipet Tips, for 19700-01 TenSette</td>
<td>2</td>
<td>50/pkg</td>
<td>21856-96</td>
</tr>
<tr>
<td>Pipet Tips, for 19700-01 TenSette</td>
<td>2</td>
<td>1000/pkg</td>
<td>21856-28</td>
</tr>
<tr>
<td>Safety Shield</td>
<td>1</td>
<td>each</td>
<td>23810-00</td>
</tr>
<tr>
<td>Test Tube Rack, stainless steel</td>
<td>1</td>
<td>each</td>
<td>18641-00</td>
</tr>
<tr>
<td>Vacuum Pretreatment Device (VPD)</td>
<td>1</td>
<td>each</td>
<td>49000-00</td>
</tr>
<tr>
<td>Vacuum Pump, 115 V</td>
<td>1</td>
<td>each</td>
<td>14697-00</td>
</tr>
<tr>
<td>OR</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Vacuum Pump, 230 V</td>
<td>1</td>
<td>each</td>
<td>14697-02</td>
</tr>
</tbody>
</table>
OXYGEN DEMAND, CHEMICAL, continued

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 .................................................................................. each .......... 25631-37