Oxygen, Demand Chemical

DOC316.53.01102

Manganese III Reactor Digestion Method without chloride removal **Method 10067**

30 to 1000 mg/L COD Mn **Test 'N Tube™ Vials**

Scope and application: For water and wastewater.

Test preparation

Instrument-specific information

Table 1 shows all of the instruments that have the program for this test. The table also shows the adapter and light shield requirements for the applicable instruments that can use Test 'N Tube vials.

To use the table, select an instrument, then read across to find the applicable information for this test.

Table 1 Instrument-specific information for Test 'N Tube vials

Instrument	Adapters	Light shield
DR6000, DR5000	—	—
DR3900	—	LZV849
DR3800, DR2800, DR2700	—	LZV646
DR1900	9609900 (D[1])	—
DR900	4846400	Cover supplied with the instrument

Before starting

Install the instrument cap on the DR900 cell holder before ZERO or READ is pushed.
DR3900, DR3800, DR2800 and DR2700: Install the light shield in Cell Compartment #2 before this test is started.
Chloride interferes with the test. To determine if the sample contains chloride, use Quantab® Titrator Strips for low range chloride.
If the test result is over-range, dilute a fresh sample with a known volume of deionized water and do the test again. Multiply the result by the dilution factor.
Use the same lot of vials (samples and blank) for all tests.
The reagent blank vial can be used for multiple tests. Fill a clean COD vial with deionized water and use this vial to zero the instrument, then measure the absorbance of the reagent blank vial. The absorbance value should be approximately 1.41–1.47. Prepare a new reagent blank vial if the absorbance is outside of this range.
If the sample boils during the digestion, the vial is not properly sealed. Test results will be invalid.
Spilled reagent have an effect on the test accuracy and is hazardous. Do not run tests with spilled vials.
Review the Safety Data Sheets (MSDS/SDS) for the chemicals that are used. Use the recommended personal protective equipment.
Dispose of reacted solutions according to local, state and federal regulations. Refer to the Safety Data Sheets for disposal information for unused reagents. Refer to the environmental, health and safety staff for your facility and/or local regulatory agencies for further disposal information.

[1] The D adapter is not available with all instrument versions.

Items to collect

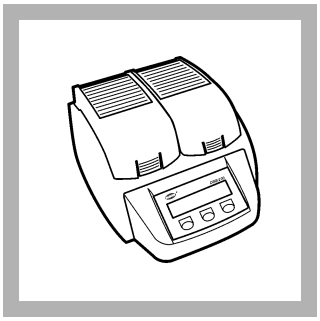
Description	Quantity
Manganese III COD Reagent Vials, 20–1000 mg/L COD	1–2
Blender, 2-speed	1
DRB200 reactor	1
Pipet, TenSette®, 0.1–1.0 mL	1
Pipet tips, for TenSette® Pipet, 0.1–1.0 mL	2
Test tube rack	1
Water, deionized	0.5 mL

Refer to Consumables and replacement items on page 5 for order information.

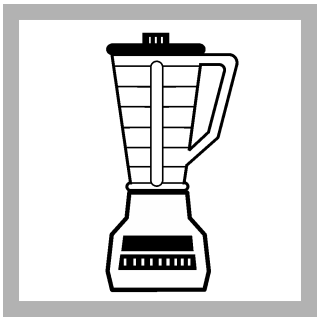
Sample collection and storage

- 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 that contain solids to get a representative sample.
- To preserve samples for later analysis, adjust the sample pH to less than 2 with concentrated sulfuric acid (approximately 2 mL per liter). No acid addition is necessary if the sample is tested immediately.
- Keep the preserved samples at 2–6 °C (36–43 °F) for a maximum of 28 days.
- Correct the test result for the dilution caused by the volume additions.

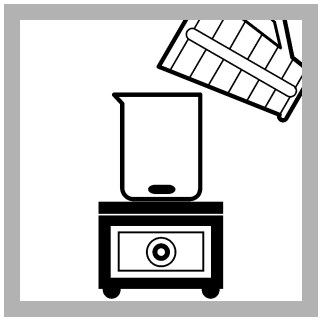
Test procedure



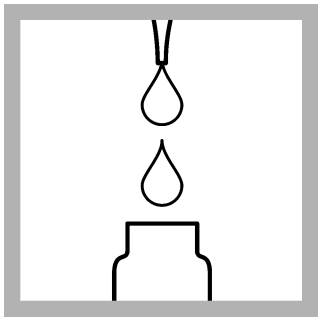
1. Set the DRB200 reactor power to on. Set the temperature to 150 °C.



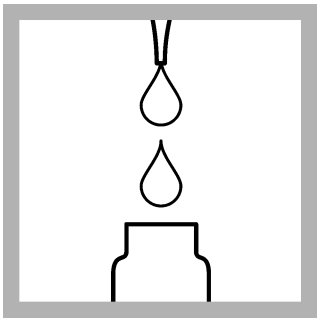
2. Measure 100 mL of sample in a blender. Blend for 30 seconds or until homogenized.
If the sample does not have suspended solids, ignore this step.



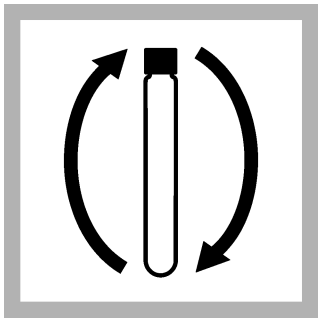
3. Pour the homogenized sample into a 250-mL beaker and stir slowly with a magnetic stir plate.
If the sample does not have suspended solids, ignore this step.



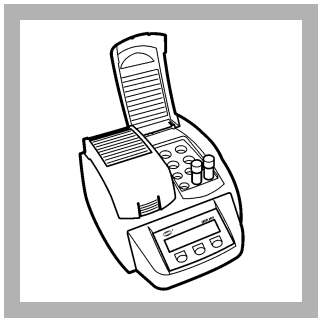
4. Prepare the sample: Use a pipet to add 0.5 mL of the homogenized sample to a test vial.



5. Prepare the blank: Use a pipet to add 0.5 mL of deionized water to a second test vial.

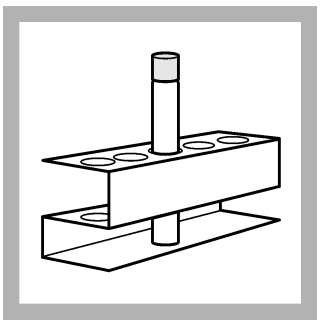


6. Put the caps on the vials and close tightly. Invert the vials several times to mix.

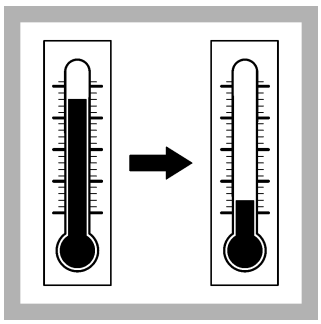


7. Insert the vials in the preheated DRB200 reactor. Close the cover.

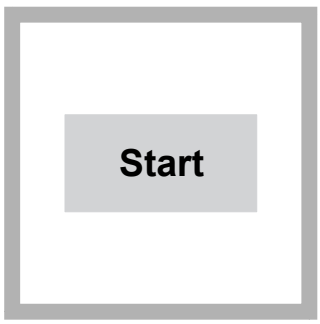
8. Keep the vials in the reactor for 1 hour. Increase the digestion time for difficult to digest compounds to a maximum of 4 hours. Digest the blank vial for the same time as the sample.



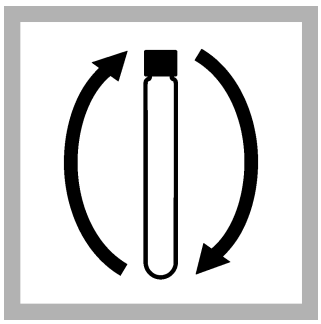
9. After the timer expires, let the vials cool in a test tube rack for 2 minutes. If the solution develops a colorless upper layer and a purple lower layer, invert the vials several times to mix. Use finger cots to touch hot vials.



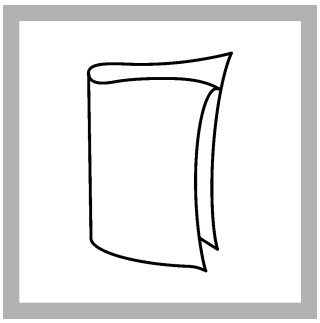
10. Put the vials in a cool water bath or hold the vials under cold tap water until the temperature of the vials decreases to room temperature.



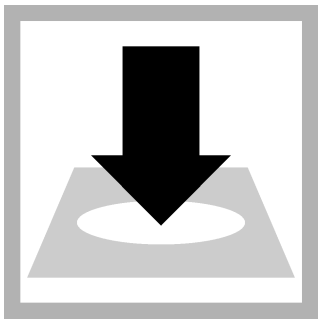
11. Start program **432 COD Mn III**. For information about sample cells, adapters or light shields, refer to Instrument-specific information on page 1.



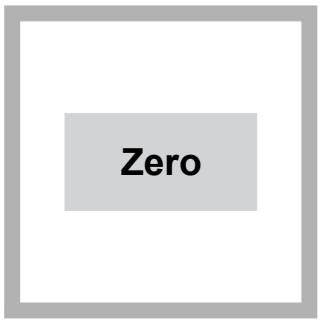
12. Invert the vials several times to mix.



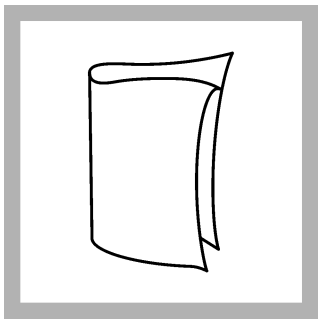
13. Clean the blank vial.



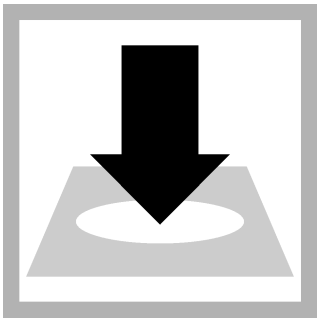
14. Insert the blank vial into the 16-mm cell holder.



15. Push **ZERO**. The display shows 0 mg/L COD Mn.



16. Clean the sample vial.



17. Insert the sample vial into the 16-mm cell holder.

18. Push **READ**. Results show in mg/L COD Mn.

Interferences

Inorganic materials can also be oxidized by trivalent manganese and cause a positive interference when present in significant concentrations. Chloride is the most common interference. To determine if the level of chloride in the sample causes an interference, prepare a KHP standard solution that contains the same concentration of chloride that is in the sample. Compare the expected result (without chloride) to the actual result. If chloride in the sample causes an interference, calibrate the instrument with COD standard solutions that contain the chloride concentration in the samples.

Other inorganic interferences (e.g., nitrite, ferrous iron, sulfide) are not usually present in significant amounts. If necessary, determine the concentration of these interferences with separate methods, then adjust the final COD test results accordingly. If the interference is very high, dilute the sample to decrease or remove the interference.

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

Accuracy check

Standard solution method

Use the standard solution method to validate the test procedure, the reagents and the instrument.

Items to collect:

- COD Standard Solution, 800-mg/L

1. Use the test procedure to measure the concentration of the standard solution.
2. Compare the expected result to the actual result.

   Note: *The factory calibration can be adjusted slightly with the standard adjust option so that the instrument shows the expected value of the standard solution. The adjusted calibration is then used for all test results. This adjustment can increase the test accuracy when there are small variations in the reagents or instruments.*

Method performance

The method performance data that follows was derived from laboratory tests that were measured on a spectrophotometer during ideal test conditions. Users can get different results under different test conditions.

Program	Standard	Precision (95% confidence interval)	Sensitivity Concentration change per 0.010 Abs change
432	600 mg/L COD	576–624 mg/L COD	8 mg/L COD

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" (*Standard Methods for the Examination of Water and Wastewater*, 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 that is based on the oxidation of Potassium Acid Phthalate (KHP). A different response can be seen in analyzing various wastewaters. The KHP calibration is adequate for most applications. The highest degree of accuracy occurs 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 get a direct mg/L COD reading or to generate a correction factor for the precalibrated KHP response. For samples that are difficult to oxidize, extend the sample digestion time up to 4 hours. The measurement wavelength is 510 nm for spectrophotometers or 520 nm for colorimeters.

Consumables and replacement items

Required reagents

Description	Quantity/test	Unit	Item no.
Manganese III COD Reagent Vials	1	25/pkg	2623425
Water, deionized	varies	4 L	27256

Required apparatus

Description	Quantity/test	Unit	Item no.
Blender, 2-speed, 120 VAC option	1	each	2616100
Blender, 2-speed, 240 VAC option	1	each	2616102
DRB200 Reactor, 110 VAC option, 15 x 16-mm wells	1	each	LTV082.53.40001
DRB200 Reactor, 220 VAC option, 15 x 16-mm wells	1	each	LTV082.52.40001
Pipet, TenSette®, 0.1–1.0 mL	1	each	1970001
Pipet tips, for TenSette® Pipet, 0.1–1.0 mL	2	50/pkg	2185696
Test tube rack	1	each	1864100

Recommended standards

Description	Unit	Item no.
COD Standard Solution, 800 mg/L	200 mL	2672629
Oxygen Demand Standard (BOD, COD, TOC), 10-mL ampules	16/pkg	2833510
Wastewater Influent Standard Solution, Mixed Parameter, for NH_3-N, NO_3-N, PO_4^{3-}, COD, SO_4^{2-}, TOC	500 mL	2833149

Optional reagents and apparatus

Description	Unit	Item no.
Finger cots	2/pkg	1464702
Paper, pH, 0–14 pH range	100/pkg	2601300
Titrator Strips, Quantab®, for low range chloride	40 tests	2744940
Sulfuric Acid, concentrated, ACS	500 mL	97949

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