Manganese, Low Range

DOC316.53.01461

1-(2-Pyridylazo)-2-Naphthol PAN Method[1]

Method 8149

0.01 to 0.70 mg/L Mn

Powder Pillows

Scope and application: For water and wastewater; digestion is necessary for total manganese determinations.

[1] Adapted from Goto, K., et al., Talanta, 24, 652-3 (1977).

Test preparation

Before starting

To make sure that all forms of the metal are measured, digest the sample with heat and acid. Use the mild or vigorous digestion. Refer to the Water Analysis Guide for more information.
Always do tests in sample cells. Do not put the instrument in the sample or pour the sample into the cell holder.
Make sure that the sample cells are clean and there are no scratches where the light passes through them.
Rinse the sample cell and cap with the sample three times before the sample cell is filled.
Make sure that there are no fingerprints or liquid on the external surface of the sample cells. Wipe with a lint-free cloth before measurement.
Cold waters can cause condensation on the sample cell or bubbles in the sample cell during color development. Examine the sample cell for condensation or bubbles. Remove condensation with a lint-free cloth. Invert the sample cell to remove bubbles.
Install the instrument cap over the cell holder before ZERO or READ is pushed.
After the test, immediately empty and rinse the sample cell. Rinse the sample cell and cap three times with deionized water.
Rinse all glassware with a 1:1 (50%) nitric acid solution. Rinse again with deionized water.
Review the Safety Data Sheets (MSDS/SDS) for the chemicals that are used. Use the recommended personal protective equipment.
The alkaline cyanide solution contains cyanide. Make sure to read the Safety Data Sheets and obey the safety precautions.
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.

Items to collect

Description	Quantity
Alkaline Cyanide Reagent	24 drops
Water, deionized	10 mL
Ascorbic Acid Powder Pillow	2
PAN Indicator Solution, 0.1%	24 drops
Sample cells, 25-mm (10-mL)	2

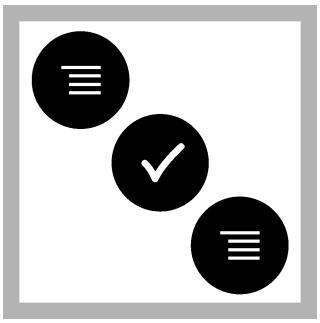
Refer to Consumables and replacement items on page 5 for order information.

Sample collection and storage

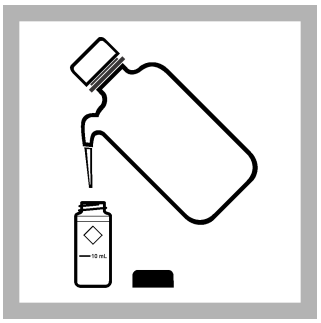
- Collect samples in clean glass or plastic bottles that have been cleaned with 6 N (1:1) hydrochloric acid and rinsed with deionized water.
- To preserve samples for later analysis, adjust the sample pH to less than 2 with concentrated nitric acid (approximately 2 mL per liter). No acid addition is necessary if the sample is tested immediately.

- Keep the preserved samples at room temperature for a maximum of 6 months.
- Before analysis, adjust the pH to 4–5* with 5 N sodium hydroxide solution.
- Correct the test result for the dilution caused by the volume additions.

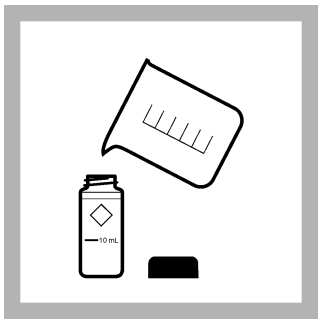
Powder pillow procedure



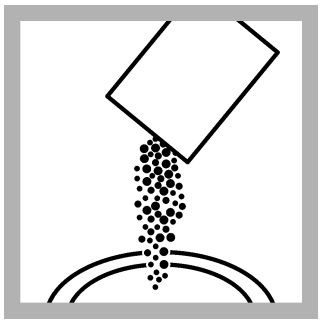
1. Set the instrument to manganese (Mn). Refer to the instrument documentation.



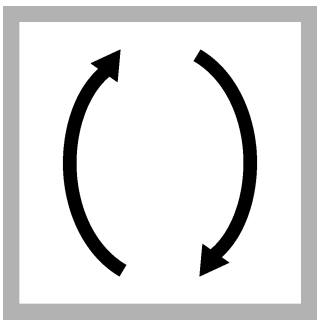
2. Prepare the blank: Fill a sample cell to the 10-mL mark with deionized water.



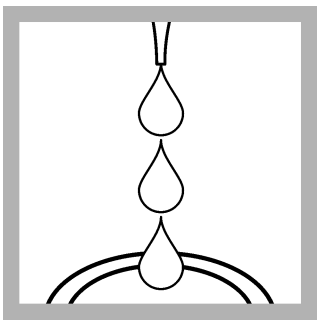
3. Prepare the sample: Fill a sample cell to the 10-mL mark with sample.



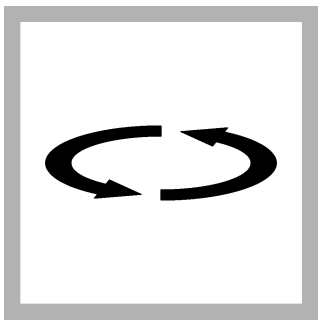
4. Add the contents of one Ascorbic Acid Powder Pillow to each sample cell.



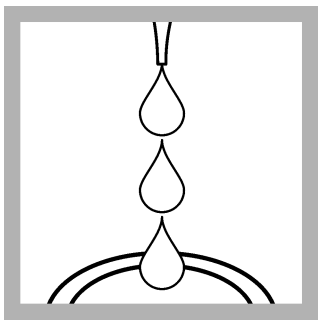
5. Put the stopper on the sample cells. Invert several times to dissolve the powder.



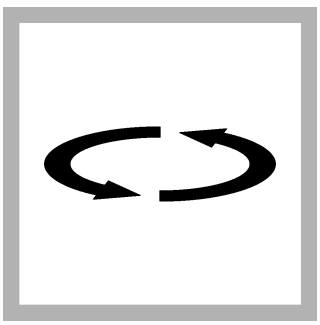
6. Add 12 drops of Alkaline Cyanide Reagent Solution to each sample cell.



7. Swirl to mix.
The solution may start to show turbidity. This should dissipate in the next step.



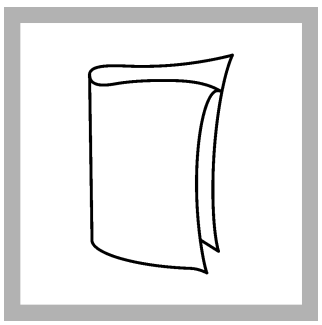
8. Add 12 drops of 0.1% PAN Indicator Solution to each sample cell.



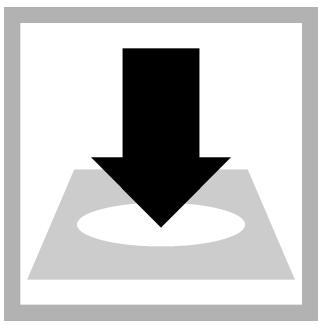
9. Swirl to mix.
An orange color will show if manganese is in the sample.

10. Set and start a timer for 2 minutes. A 2-minute reaction time starts.

If the sample contains more than 5 mg/L iron, wait 10 minutes.

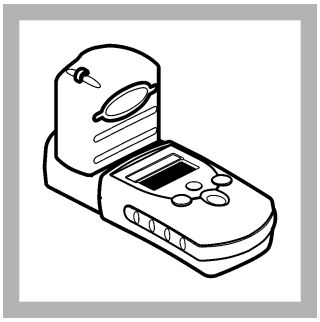


11. When the timer expires, clean the blank sample cell.

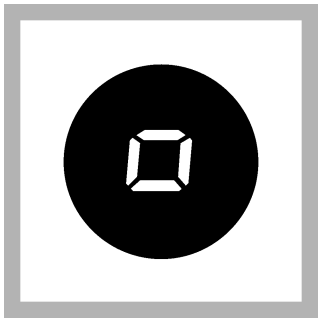


12. Insert the blank into the cell holder. Point the diamond mark on the sample cell toward the keypad.

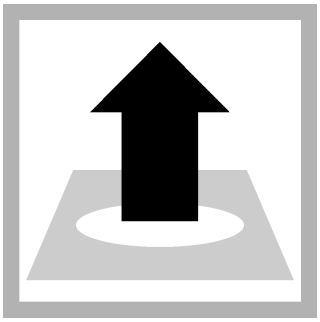
* Do not adjust to more than pH 5 because the manganese can be lost as a precipitate.



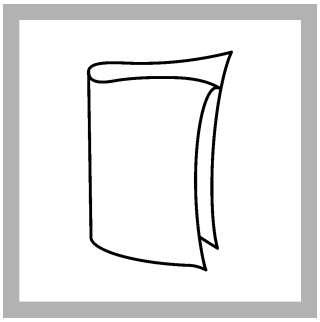
13. Install the instrument cap over the cell holder.



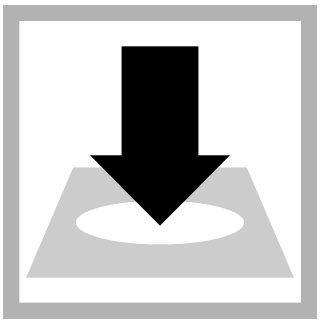
14. Push **ZERO**. The display shows “0.00”.



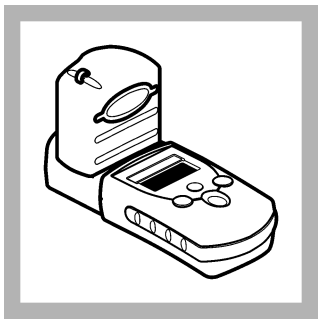
15. Remove the sample cell from the cell holder.



16. Clean the prepared sample cell.



17. Insert the prepared sample into the cell holder. Point the diamond mark on the sample cell toward the keypad.



18. Install the instrument cap over the cell holder.

19. Push READ. Results show in mg/L manganese (Mn). To change the result to MnO_4–, multiply the result by 2.16. To change the result to $KMnO_4$, multiply the result by 2.88.

Interferences

Interfering substance	Interference level
Aluminum	20 mg/L
Cadmium	10 mg/L
Calcium	1000 mg/L as $CaCO_3$
Cobalt	20 mg/L
Copper	50 mg/L
Hardness	For samples that contain more than 300 mg/L hardness as $CaCO_3$, add 4 drops of Rochelle Salt Solution to the sample after the Ascorbic Acid Powder Pillow is added.
Iron	25 mg/L (If the sample contains more than 5 mg/L iron, increase the reaction period to 10 minutes.)
Lead	0.5 mg/L
Magnesium	300 mg/L as $CaCO_3$
Nickel	40 mg/L
Zinc	15 mg/L

Accuracy check

Standard additions method

Use the standard additions method to validate the test procedure, reagents and instrument and to find if there is an interference in the sample.

Items to collect:

- Manganese PourRite® Ampule Standard, 10 mg/L Mn
- Ampule breaker
- Pipet, TenSette®, 0.1–1.0 mL and tips

1. Prepare three spiked samples: use the TenSette pipet to add 0.1 mL, 0.2 mL and 0.3 mL of the standard solution, respectively, to three 10-mL portions of fresh sample. Mix well.
2. Use the test procedure to measure the concentration of each of the spiked samples. Start with the smallest sample spike. Measure each of the spiked samples in the instrument.
3. Compare the expected result to the actual result. The expected manganese concentration increase is approximately 0.10 mg/L Mn for each 0.1 mL of standard that is added.

Standard solution method

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

Items to collect:

- Manganese Voluette Standard Solution, 250 mg/L Mn
- 1-L volumetric flask, Class A
- 2.0-mL volumetric pipet, Class A and pipet filler
- Deionized water

1. Prepare a 0.5 mg/L-manganese standard solution as follows:
   a. Use a pipet to add 2.0 mL of the 250-mg/L manganese standard solution into the volumetric flask.
   b. Dilute to the mark with deionized water. Mix well. Prepare this solution daily.
2. Use the test procedure to measure the concentration of the prepared standard solution.
3. Compare the expected result to the actual result. The expected result is 0.5 mg/L Mn.

   Note: *The factory calibration can be adjusted slightly with the standard calibration 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 slight variations in the reagents or instruments.*

Method performance

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

Precision (95% confidence interval)
0.50 ± 0.02 mg/L Mn

Summary of method

The PAN method is a highly sensitive and rapid procedure to measure low levels of manganese. The ascorbic acid reagent reduces all oxidized forms of manganese to Mn^{2+}. The alkaline-cyanide reagent masks potential interferences. PAN Indicator then forms an orange-colored complex with Mn^{2+}.

Consumables and replacement items

Required reagents

Description	Quantity/Test	Unit	Item no.
Manganese Reagent Set, 10 mL, includes:	—	50 tests	2651700
Alkaline Cyanide Reagent	12 drops	50 mL SCDB	2122326
Ascorbic Acid Powder Pillow	2	100/pkg	1457799
PAN Indicator Solution, 0.1%	12 drops	50 mL SCDB	2122426
Water, deionized	varies	4 L	27256

Recommended standards and apparatus

Description	Unit	Item no.
Sample cells, 10-mL round, 25 mm x 60 mm	6/pkg	6/pkg
Manganese Standard Solution, 10-mg/L Mn, 2 mL PourRite® Ampule	20/pkg	2605820
Manganese Standard Solution, 250-mg/L Mn, 10-mL Voluette® Ampule	16/pkg	1425810
Ampule Breaker, 10-mL Voluette® Ampules	each	2196800
PourRite® Ampule Breaker, 2-mL	each	2484600
Metals Drinking Water Standard, HR for Cu, Fe, Mn	500 mL	2833649

Optional reagents and apparatus

Description	Unit	Item no.
Mixing cylinder, graduated, 25-mL	each	2088640
Flask, volumetric, Class A, 1000-mL glass	each	1457453
Manganese Standard Solution, 2-mL PourRite® Ampule, 25 mg/L	20/pkg	2112820
Nitric Acid, concentrated	500 mL	15249
Paper, pH, 0–14 pH range	100/pkg	2601300
Pipet filler, safety bulb	each	1465100
Pipet, TenSette®, 0.1–1.0 mL	each	1970001
Pipet, TenSette®, 1.0–10.0 mL	each	1970010
Pipet tips for TenSette® Pipet, 0.1–1.0 mL	50/pkg	2185696
Pipet tips for TenSette® Pipet, 0.1–1.0 mL	1000/pkg	2185628
Pipet tips for TenSette® Pipet, 1.0–10.0 mL	50/pkg	2199796
Pipet tips for TenSette® Pipet, 1.0–10.0 mL	250/pkg	2199725
Pipet, volumetric, Class A, 2-mL	each	1451536
Rochelle Salt Solution	29 mL	172533
Sodium Hydroxide Standard Solution, 5.0 N	100 mL MDB	245032

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