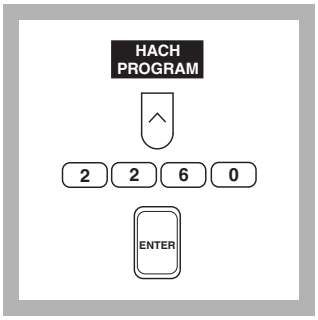
MANGANESE

Method 8149 **PAN Method***

Powder Pillows **LR (0 to 0.700 mg/L)**

Scope and Application: *For water and wastewater; digestion is required for determining total manganese. See Section 1 for digestion procedure. The estimated detection limit for program number 2260 is 0.005 mg/L total Mn.*

* Adapted from Goto, K., et al., *Talanta*, 24, 752-3 (1977)



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

Select the stored program number for low range manganese by pressing **2260** with the numeric keys.

Press: **ENTER**

Note: *If samples cannot be analyzed immediately, see Sample Collection, Storage and Preservation following these steps. Adjust the pH of preserved samples before analysis.*

Note: *The Flow Cell and Sipper Modules can be used with this procedure if rinsed well with deionized water between the blank and prepared sample.*

2. The display will show:

HACH PROGRAM: 2260
Manganese, LR

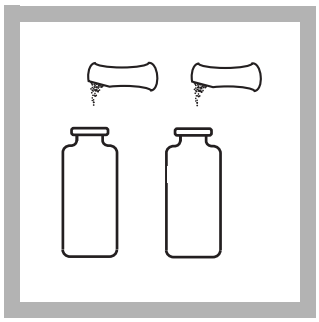
The wavelength (λ), **560 nm**, is automatically selected.

3. Pour 10.0 mL of deionized water into a sample cell (the blank).

Note: *Rinse all glassware with 1:1 Nitric Acid Solution. Rinse again with deionized water.*

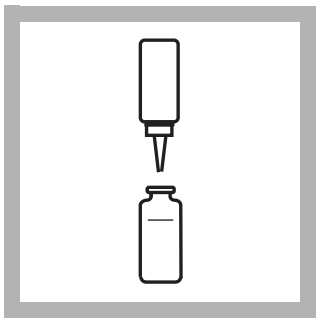
4. Pour 10.0 mL of sample into another sample cell (the prepared sample).

Note: *For proof of accuracy, use a 0.500-mg/L manganese standard solution (see the Accuracy Check* section*) in place of the sample.*



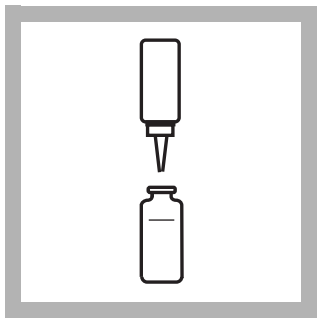
5. Add the contents of one Ascorbic Acid Powder Pillow to each cell. Swirl to mix.

Note: *For samples containing hardness greater than 300-mg/L $CaCO_3$, add ten drops of Rochelle Salt Solution to the sample after addition of the Ascorbic Acid Powder Pillow.*



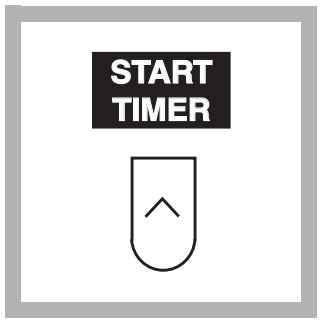
6. Add 12 drops of Alkaline-Cyanide Reagent Solution to each cell. Swirl to mix.

Note: *A cloudy or turbid solution may form in some samples after addition of the Alkaline-Cyanide Reagent Solution. The turbidity should dissipate after Step 7.*



7. Add 12 drops of PAN Indicator Solution, 0.1%, to each sample cell. Swirl to mix.

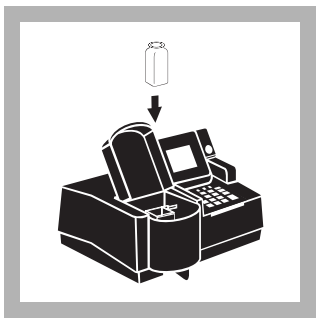
Note: *An orange color will develop in the sample if manganese is present.*



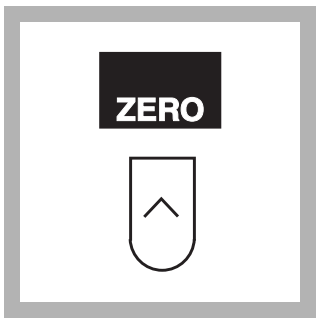
8. Press the soft key under ***START TIMER***.

A 2-minute reaction period will begin.

Note: *If the sample contains high amounts of iron (greater than 5 mg/L), allow ten minutes for complete color development.*



9. When the timer beeps, place the blank into the cell holder. Close the light shield.

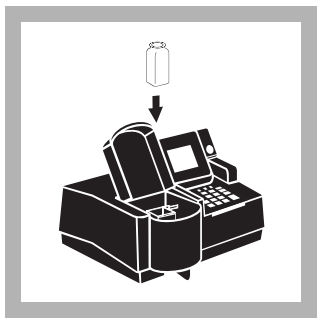


10. Press the soft key under ***ZERO***.

The display will show:

0.000 mg/L Mn

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.*



11. Place the prepared sample into the cell holder. Close the light shield. Results in mg/L manganese (or chosen units) will be displayed.

Interferences

The following do not interfere up to the indicated concentrations:

Interfering Substance	Interference Levels and Treatments
Aluminum	20 mg/L
Cadmium	10 mg/L
Calcium	1000 mg/L as $CaCO_3$
Cobalt	20 mg/L
Copper	50 mg/L
Iron	25 mg/L
Lead	0.5 mg/L
Magnesium	300 mg/L as $CaCO_3$
Nickel	40 mg/L
Zinc	15 mg/L

Sample Collection, Storage and Preservation

Collect samples in a clean glass or plastic container. Adjust the pH to 2 or less with concentrated nitric acid (about 2 mL per liter). Preserved samples can be stored up to six months at room temperature. Adjust the pH to between 4.0 to 5.0 with 5.0 N Sodium Hydroxide before analysis. Correct the test result for volume additions; see Section *1.2.2 Correcting for Volume Additions.*

Accuracy Check

Standard Additions Method

a. Leave the unspiked sample in the sample compartment. Verify that the units displayed are in mg/L. Select standard additions mode by pressing the soft keys under ***OPTIONS, (MORE)*** and then ***STD ADD***.

b. Press **ENTER** to accept the default sample volume (mL), 10.

c. Press **ENTER** to accept the default standard concentration (mg/L), 10.0.

d. Press the soft key under ***ENTRY DONE***.

e. Snap the neck off a Manganese Voluette Ampule Standard, 10 mg/L Mn.

f. Use the TenSette Pipet to add 0.1, 0.2 mL and 0.3 mL of standard, respectively to three 10-mL samples and mix each thoroughly.

g. Analyze each standard addition sample as described above. Accept the standard additions reading by pressing the soft key under ***READ*** each time. Each addition should reflect approximately 100% recovery.

h. After completing the sequence, the display will show the extrapolated concentration value and the "best-fit" line through the standard additions data points, accounting for matrix interferences.

i. See Section *1.4.1 Standard Additions* for more information.

Standard Solution Method
Prepare a 0.5-mg/L manganese standard solution by pipetting 2.0 mL of Manganese Voluette Standard Solution, 250-mg/L Mn, into a 1000-mL volumetric flask. Dilute to the mark with deionized water. This solution should be prepared daily. Perform the manganese procedure as described above.

To adjust the calibration curve using the reading obtained with the 0.5-mg/L standard solution, press the soft keys under ***OPTIONS, (MORE)*** then ***STD: OFF.*** Press **ENTER** to accept the default concentration, the value of which will depend on the selected units. If an alternate concentration is used, enter the actual concentration and press enter to return to the read screen. See Section *1.5.5 Adjusting the Standard Curve* for more information.

Method Performance

Precision
Standard: 0.500 mg/L Mn

Program	95% Confidence Limits
2260	0.498–0.502 mg/L Mn

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

Estimated Detection Limit

Program	EDL
2260	0.005 mg/L Mn

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: 2260

Portion of Curve:	ΔAbs	ΔConcentration
Entire Range	0.010	0.0057 mg/L

See Section *1.5.3 Sensitivity Explained* for more information.

Calibration Standard Preparation

To perform a manganese calibration using the PAN method, prepare a 5.00-mg/L Mn stock solution by pipetting 5.00 mL of a 1000-mg/L Manganese Standard Solution (Cat. No. 12791-42) into a 1000-mL volumetric flask using Class A glassware. Dilute to the mark with deionized water and mix thoroughly.

Prepare calibration standards containing 0.100, 0.200, 0.300, 0.400, 0.500, 0.600, and 0.700-mg/L Mn as follows:

a. Into seven different 100-mL Class A volumetric flasks, pipet 2.00, 4.00, 6.00, 8.00, 10.00, 12.00, and 14.00 mL of the 5.00-mg/L Mn stock solution using Class A glassware.

b. Dilute to the mark with deionized water. Mix thoroughly.

c. Using the PAN 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

The PAN method is a highly sensitive and rapid procedure for detecting low levels of manganese. An ascorbic acid reagent is used initially to reduce all oxidized forms of manganese to Mn^{2+}. An alkaline-cyanide reagent is added to mask any potential interferences. PAN Indicator is then added to combine with the Mn^{2+} to form an orange-colored complex.

Safety

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

Pollution Prevention and Waste Management

The alkaline cyanide solution contains cyanide. Cyanide solutions should be collected for disposal as a reactive (D001) waste. Be sure cyanide solutions are stored in a caustic solution with pH >11 to prevent release of hydrogen cyanide gas. See Section *1* for more information on proper disposal of these materials.

REQUIRED REAGENTS AND STANDARDS

	Cat. No.
Manganese Reagent Set, 10 mL (50 tests)	26517-00

Includes: (1) 14577-99, (1) 21223-26, (1) 21224-26

Description	Quantity Required per test	Unit	Cat. No.
Alkaline Cyanide Reagent	30 drops	50 mL SCDB	21223-26
Ascorbic Acid Powder Pillows	2 pillows	100/pkg	14577-99
PAN Indicator Solution, 0.1%	42 drops	50 mL SCDB	21224-26
Water, deionized	10 mL	4 liters	272-56

REQUIRED EQUIPMENT AND SUPPLIES

DR/4000 1-Inch Cell Adapter	1	each	48190-00

OPTIONAL REAGENTS AND STANDARDS

Hydrochloric Acid Solution	500 mL	884-49
Manganese Standard Solution, 1000-mg/L Mn	100 mL	12791-42
Manganese Standard Solution, 2-mL ampule, 10-mg/L Mn	20/pkg	26058-20
Manganese Standard Solution, 2-mL Voluette Ampule, 25-mg/L Mn	20/pkg	21128-20
Manganese Standard Solution, 10-mL Voluette ampule, 250-mg/L Mn	16/pkg	14258-10
Nitric Acid Solution, 1:1	500 mL	2540-49
Rochelle Salt Solution	29 mL DB	1725-33
Sodium Hydroxide Solution, 50%	500 mL	2180-49
Nitric Acid, ACS	500 mL	152-49

OPTIONAL EQUIPMENT AND SUPPLIES

Ampule Breaker Kit	each	21968-00
Beaker, 1000-mL	each	500-53
DR/4000 Carousel Module Kit	each	48070-02
DR/4000 Flow Cell Module Kit, 1-inch	each	48070-04
DR/4000 Flow Cell Module Kit, 1-cm	each	48070-05
DR/4000 Sipper Module Kit, 1-inch	each	48090-03
Dropper, 0.5 and 1 mL marks	20/pkg	21247-20
Flask, volumetric, Class A, 100-mL	each	14574-42
Flask, volumetric, Class A, 1000-mL	each	14574-53
Pipet, TenSette, 0.1 to 1.0 mL	each	19700-01
Pipet Tips, for 19700-01 TenSette Pipet	50/pkg	21856-96
Pipet, volumetric, Class A, 2.00-mL	each	14515-36
Pipet, volumetric, Class A, 4.00-mL	each	14515-04
Pipet, volumetric, Class A, 5.0-mL	each	14515-37
Pipet, volumetric, Class A, 6.0-mL	each	14515-06
Pipet, volumetric, Class A, 7.0-mL	each	14515-07
Pipet, volumetric, Class A, 8.0-mL	each	14515-08
Pipet, volumetric, Class A, 10.0-mL	each	14515-38
Pipet Filler, safety bulb	each	14651-00

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