Hardness, Calcium and Magnesium

DOC316.53.01043

Calmagite Colorimetric Method

Method 8030

0.05 to 4.00 mg/L Ca and Mg as $CaCO_3$

Scope and application: For water, wastewater and seawater.

Test preparation

Instrument specific information

Table 1 shows all of the instruments that have the program for this test. The table also shows sample cell and orientation requirements for reagent addition tests, such as powder pillow or bulk reagent tests.

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

Table 1 Instrument-specific information

Instrument	Sample cell orientation	Sample cell
DR 6000 DR 3800 DR 2800 DR 2700 DR 1900	The fill line is to the right.	2495402 
DR 5000 DR 3900	The fill line is toward the user.	
DR 900	The orientation mark is toward the user.	2401906 

Before starting

Install the instrument cap on the DR 900 cell holder before ZERO or READ is pushed.
For the most accurate magnesium test results, keep the sample temperature between 21–29 °C (70–84 °F).
This test detects any calcium or magnesium contamination in the mixing cylinder, measuring droppers or sample cells. To test cleanliness, repeat the test until the results are consistent.
Total hardness in mg/L equals mg/L Ca as $CaCO_3$ plus mg/L Mg as $CaCO_3$.
Traces of EDTA or EGTA that remain from previous tests will give incorrect results. Rinse sample cells thoroughly before each use.
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.

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Items to collect

Description	Quantity
Alkali Solution, for calcium and magnesium tests	1 mL
Calcium and Magnesium Indicator Solution	1 mL
EDTA Solution, 1 M	1 drop
EGTA Solution	1 drop
Cylinder, graduated mixing, 100-mL	1
Dropper, measuring, 0.5-mL and 1.0-mL	2
Sample cells (For information about sample cells, adapters or light shields, refer to Instrument specific information on page 1.)	3

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

Sample collection and storage

- Collect samples in clean plastic bottles that have been cleaned with 6 N (50%) hydrochloric acid and rinsed with deionized water. Rinse the bottle three times with sample before collection.
- To preserve samples for later analysis, adjust the sample pH to less than 2 with 50% nitric acid (about 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 3–8 with 5 N sodium hydroxide solution.
- Correct the test result for the dilution caused by the volume additions.

Calmagite procedure

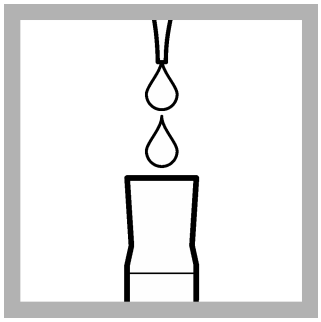


1. Start program **225 Hardness, Mg**. For information about sample cells, adapters or light shields, refer to Instrument specific information on page 1.

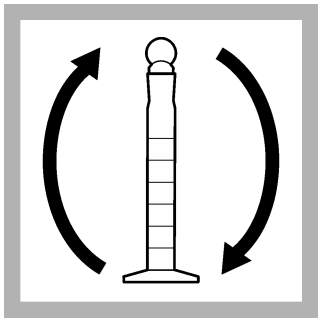
Note: *Although the program name can be different between instruments, the program number does not change.*



2. Pour 100 mL of sample into a 100-mL graduated mixing cylinder.

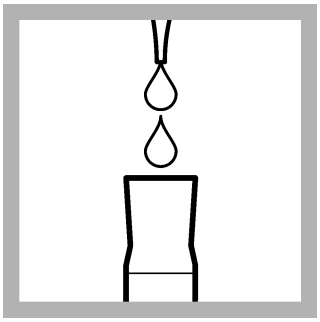


3. Use a 1.0 mL dropper to add 1.0 mL of Calcium and Magnesium Indicator Solution.

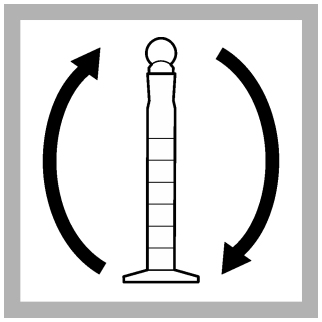


4. Put the stopper on the mixing cylinder. Invert the mixing cylinder several times to mix.

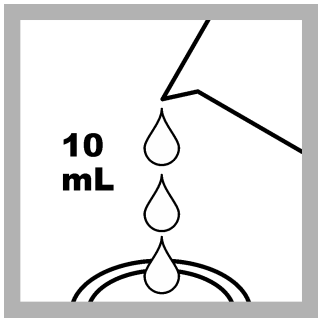
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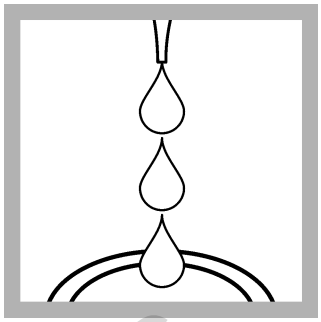
5. Use a 1.0 mL dropper to add 1.0 mL of Alkali Solution for Calcium and Magnesium Test.



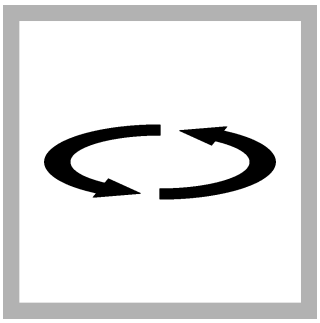
6. Put the stopper on the mixing cylinder. Invert the mixing cylinder several times to mix.



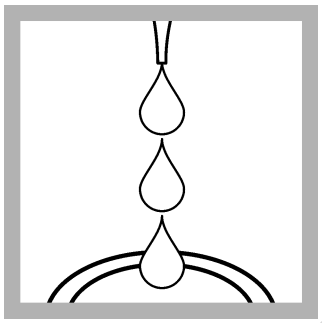
7. Pour 10 mL of the solution into each of three sample cells.



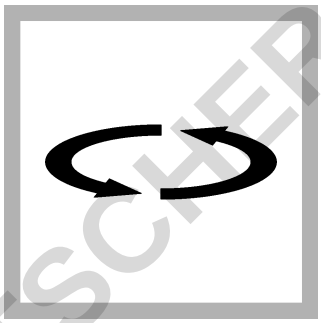
8. Blank preparation: Add one drop of 1 M EDTA solution to the first sample cell.



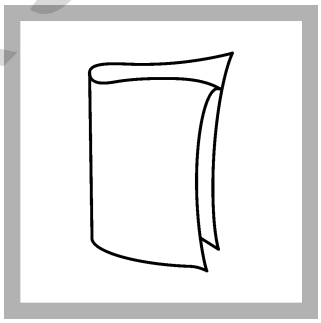
9. Swirl to mix.



10. Magnesium sample: Add one drop of EGTA Solution to the second sample cell.



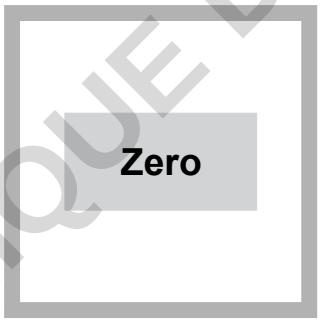
11. Swirl to mix.



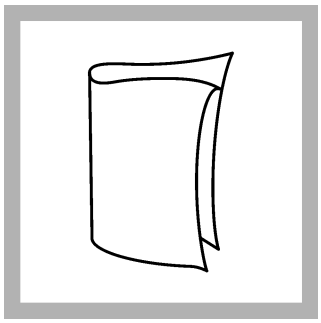
12. Clean the blank sample cell.



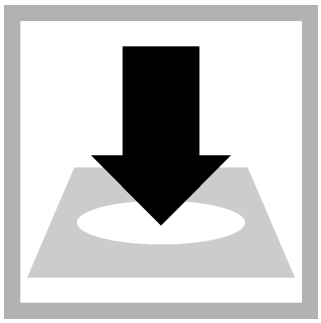
13. Insert the blank into the cell holder.



14. Push **ZERO**. The display shows 0.00 mg/L $CaCO_3$.

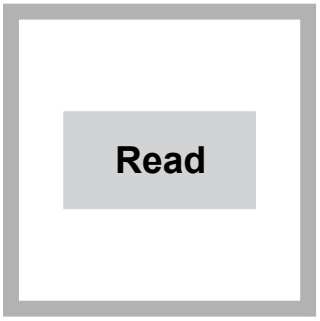


15. Clean the prepared sample cell.

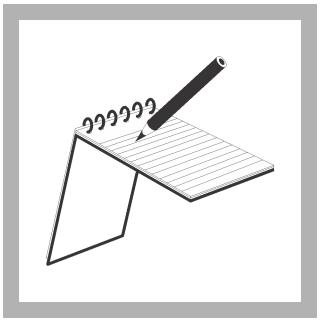


16. Magnesium sample: Insert the prepared magnesium sample cell into the cell holder.

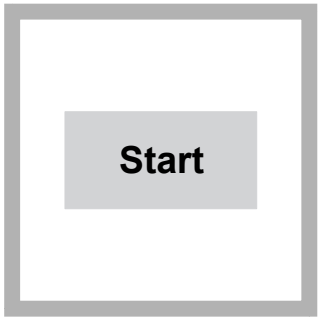
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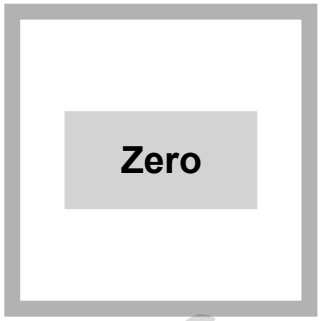
17. Push **READ**. Results show in mg/L magnesium as calcium carbonate. This value is the amount of magnesium in the sample expressed as $CaCO_3$.



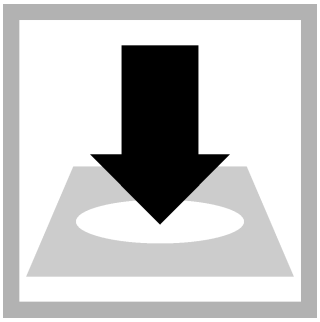
18. Do not remove the sample cell from the instrument. Record or select **STORE** to save the magnesium results before the next step.



19. Exit the magnesium program. Start program **220 Hardness, Ca**.



20. Push **ZERO**. The display shows 0.00 mg/L $CaCO_3$.



21. Calcium sample: Insert the third sample cell into the cell holder.



22. Push **READ**. Results show in mg/L calcium as calcium carbonate. This value is the amount of calcium in the sample expressed as $CaCO_3$.

Interferences

Interfering substance	Interference level
Ca > 1.0 mg/L; Mg > 0.25 mg/L	For the most accurate calcium test result, run the test again on a diluted sample if the calcium is over 1.0 and the magnesium is over 0.25 mg/L as $CaCO_3$. No retesting is necessary if either is below those respective concentrations.
Chromium (Cr^{3+})	Above 0.25 mg/L
Copper (Cu^{2+})	Above 0.75 mg/L
EDTA	Above 0.2 mg/L as $CaCO_3$
EDTA or EGTA	Traces remaining in sample cells from previous tests will give erroneous results. Rinse cells thoroughly before use.
Iron (Fe^{2+})	Above 1.4 mg/L
Iron (Fe^{3+})	Above 2.0 mg/L
Manganese (Mn^{2+})	Above 0.20 mg/L
Zinc (Zn^{2+})	Above 0.050 mg/L

Accuracy check

Standard solution method

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

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Items to collect:

- 2.00 mg/L (as $CaCO_3$) Calcium Standard Solution

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 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 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
220	2.00 mg/L Ca	1.90–2.10 mg/L Ca	0.05 mg/L Ca
225	2.00 mg/L Mg	1.92–2.08 mg/L Mg	0.05 mg/L Mg

Summary of method

The colorimetric method for measuring hardness supplements the conventional titrimetric method because the colorimetric method can measure very low levels of calcium and magnesium. Also, some metals that interfere in the titrimetric method may not interfere when the sample is diluted to bring it within the range of this test. The indicator dye is calmagite, which forms a purplish-blue color in a strongly alkaline solution and changes to red when it reacts with free calcium or magnesium.

Calcium and magnesium determinations are made by chelation of calcium with EGTA to remove the red color from calcium and then chelation of calcium and magnesium with EDTA to remove the red color from both calcium and magnesium. The measurement of the red color in the different states is used to measure the calcium and magnesium concentrations. The measurement wavelength is 522 nm for spectrophotometers or 520 nm for colorimeters.

Consumables and replacement items

Required reagents

Description	Quantity/test	Unit	Item no.
Hardness Reagent Set, includes:	—	100 tests	2319900
Alkali Solution, for calcium and magnesium tests	1 mL	100 mL MDB	2241732
Calcium and Magnesium Indicator Solution	1 mL	100 mL MDB	2241832
EDTA Solution, 1 M	1 drop	50 mL SCDB	2241926
EGTA Solution	1 drop	50 mL SCDB	2229726

Required apparatus

Description	Quantity/test	Unit	Item no.
Mixing cylinder, graduated, 100-mL , tall form	1	each	2088642
Dropper, measuring, 0.5-mL and 1.0-mL plastic	2	20/pkg	2124720

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Optional reagents and apparatus

Description	Unit	Item no.
Nitric Acid, concentrated	500 mL	15249
Sodium Hydroxide Standard Solution, 5.0 N	100 mL MDB	245032
Paper, pH, 0–14 pH range	100/pkg	2601300

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02/2015, Edition 10