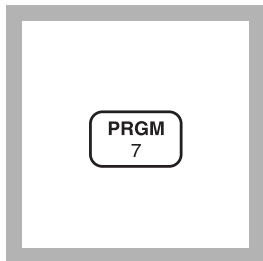


HARDNESS (0 to 4.00 mg/L Ca and Mg as CaCO₃) For water, wastewater, seawater**Calcium and Magnesium; Calmagite Colorimetric Method**

1. Enter the stored program number for magnesium hardness (as CaCO₃).

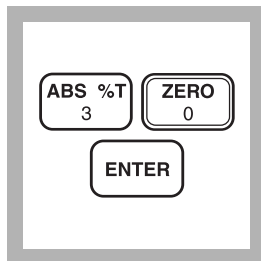
Press: **PRGM**

The display will show:

PRGM ?

Note: Adjust the pH of stored samples before analysis.

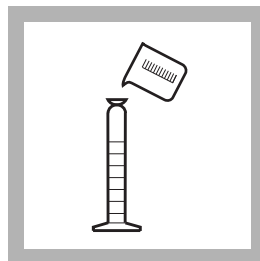
Note: For most accurate results, perform a Reagent Blank Correction using deionized water (see Section 1).



2. Press: **30 ENTER**

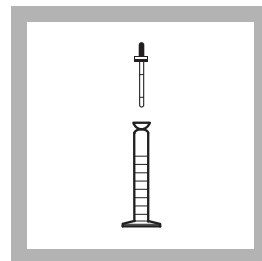
The display will show **mg/L, CaCO₃** and the **ZERO** icon.

Note: For alternate forms (Mg, MgCO₃), press the **CONC** key.

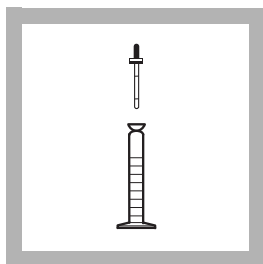


3. Pour 100 mL of sample into a 100-mL graduated mixing cylinder.

Note: The sample temperature should be 21-29 °C (70-84 °F).

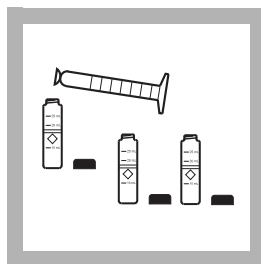


4. Add 1.0 mL of Calcium and Magnesium Indicator Solution using a 1.0-mL measuring dropper. Stopper. Invert several times to mix.



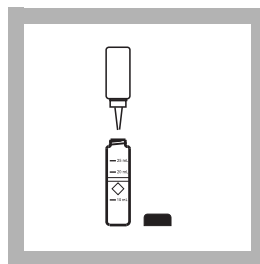
5. Add 1.0 mL of Alkali Solution for Calcium and Magnesium Test using a 1.0-mL measuring dropper. Stopper. Invert several times to mix.

Note: If the sample turns read after adding Alkali Solution, dilute sample 1:1 and repeat analysis.

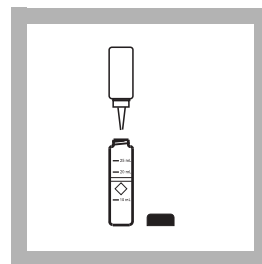


6. Pour 10 mL of the solution into each of three sample cells.

Note: The test will detect any calcium or magnesium contamination in the mixing cylinder, measuring droppers or sample cells. To test cleanliness, repeat the test multiple times until you obtain consistent results.

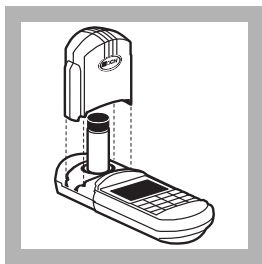


7. Add one drop of 1 M EDTA Solution to one cell (the blank). Swirl to mix.

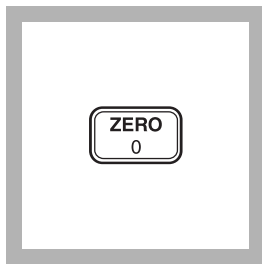


8. Add one drop of EGTA Solution to another cell (the prepared sample). Swirl to mix.

HARDNESS, continued

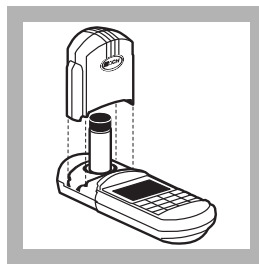


9. Place the blank into the cell holder. Tightly cover the sample cell with the instrument cap.

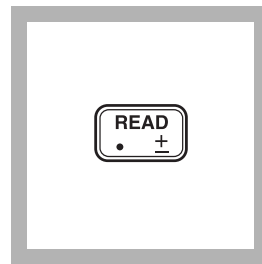


10. Press: **ZERO**
The cursor will move to the right, then the display will show:
0.00 mg/L CaCO₃

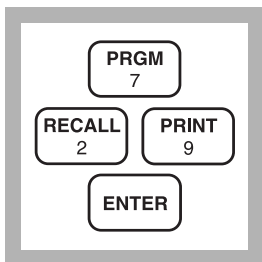
Note: If Reagent Blank Correction is on, the display may flash "limit". See Section 1.



11. Place the prepared sample into the cell holder. Tightly cover the sample cell with the instrument cap.



12. Press: **READ**
The cursor will move to the right, then the result in mg/L magnesium hardness (as CaCO₃) will be displayed.



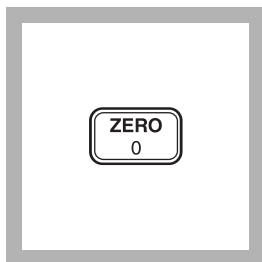
13. Without removing the cell, press:

PRGM 29 ENTER

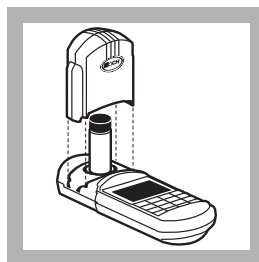
The display will show:

PRGM ?

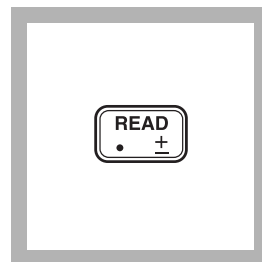
*Note: For alternate forms (Ca) press the **CONC** key.*



14. Press: **ZERO**
The cursor will move to the right, then the display will show:
0.00 mg/L CaCO₃



15. Place the third sample cell into the cell holder.



16. Press: **READ**
The cursor will move to the right, then the result in mg/L calcium hardness (as CaCO₃) will be displayed.

Note: Standard Adjust may be performed using a prepared standard (see Section 1).

Note: mg/L total hardness = mg/L Ca as CaCO₃ + mg/L Mg as CaCO₃.

Sampling and Storage

Collect samples in acid-washed plastic bottles. Adjust the sample pH to 2 or less with nitric acid (about 5 mL per liter). Preserved samples can be stored up to six months. Adjust the sample pH to

HARDNESS, continued

between 3 and 8 with 5.0 N Sodium Hydroxide Standard Solution just before analysis. Correct the test results for volume additions; see *Correction for Volume Additions* in *Section 1* for more information.

Accuracy Check

Using a 2.00 mg/L (as CaCO₃) standard solution as sample, perform the hardness procedure described above. The results should be 2.00 mg/L calcium (as CaCO₃).

Method Performance

Precision

In a single laboratory using a standard solution of 2.00 mg/L Mg as CaCO₃ and 1.88 mg/L Ca as CaCO₃ with the instrument, a single operator obtained a standard deviation of ± 0.09 mg/L Mg as CaCO₃ and ± 0.08 mg/L Ca as CaCO₃.

Estimated Detection Limit

The estimated detection limit for program 30 is 0.13 mg/L magnesium hardness and 0.08 mg/L calcium hardness. For more information on the estimated detection limit, see *Section 1*.

Interferences

For the most accurate hardness test result, the test should be rerun on a diluted sample if the calcium is over 1.0 or the magnesium is over

0.25 mg/L as CaCO₃. No retesting is needed if either is below those respective concentrations.

The following cause a detectable error in test results.

Interfering Substance	Level at Which Substance Interferes
Cr ³⁺	0.25 mg/L
Cu ²⁺	0.75 mg/L
EDTA, chelated	0.2 mg/L as CaCO ₃
Fe ²⁺	1.4 mg/L
Fe ³⁺	2.0 mg/L
Mn ²⁺	0.20 mg/L
Zn ²⁺	0.050 mg/L

Traces of EDTA or EGTA remaining in sample cells from previous tests will give erroneous results. Rinse cells thoroughly before use.

HARDNESS, continued

Summary of Method

The colorimetric method for measuring hardness supplements the conventional titrimetric method because it can measure very low levels of calcium and magnesium. Also some interfering metals (those listed above) in the titrimetric method are inconsequential in the colorimetric method when diluting the sample to bring it within the range of this test.

The indicator dye, calmagite, forms a purplish-blue color in a strongly alkaline solution and changes to red when it reacts with free calcium or magnesium. Calcium is chelated with EGTA to destroy any red color due to calcium and then the sample is chelated with EDTA to destroy the red color due to both calcium and magnesium. Measuring the red color in the different stages of chelation gives results as the calcium and magnesium hardness concentrations.

REQUIRED REAGENTS

	Cat. No.
Hardness Reagent Set (100 Tests)	23199-00
Includes: (1) 22417-32, (1) 22418-32, (1) 22419-26, (1) 22297-26	

Description	Quantity Required		Unit	Cat. No.
	Per Test			
Alkali Solution for Calcium and Magnesium Test	1 mL.....	100 mL	MDB.....	22417-32
Calcium and Magnesium Indicator Solution	1 mL.....	100 mL	MDB.....	22418-32
EDTA Solution, 1 M.....	1 drop.....	50 mL.....		22419-26
EGTA Solution	1 drop.....	50 mL.....		22297-26

REQUIRED APPARATUS

Cylinder, 100-mL mixing	1	each.....	1896-42
Dropper, measuring, 0.5 and 1.0 mL	2	20/pkg.....	21247-20
Sample Cell, 10-20-25 mL, w/cap	3	6/pkg.....	24019-06

OPTIONAL REAGENTS

Calcium Standard Solution, 2.0 mg/L as CaCO ₃	946 mL.....	20581-16
Nitric Acid, ACS.....	500 mL.....	152-49
Nitric Acid Solution, 1:1	500 mL.....	2540-49
Sodium Hydroxide Standard Solution 5.0 N	100 mL MDB.....	2450-32

OPTIONAL APPARATUS

pH Meter, <i>sensio</i> TM 1, portable, with electrode	each.....	51700-10
Thermometer, -20 to 110 °C.....	each.....	26357-02