

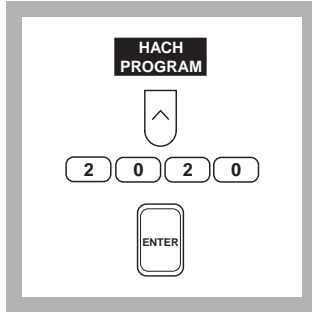


Method 8030

Calcium and Magnesium; Calmagite Colorimetric Method

(0 to 4.00 mg/L Ca and Mg as CaCO₃)

Scope and Application: For water, wastewater, and seawater. The estimated detection limit for program numbers 2010 and 2020 is 0.03 mg/L CaCO₃.



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

Select the stored program for magnesium hardness by pressing **2020** 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.

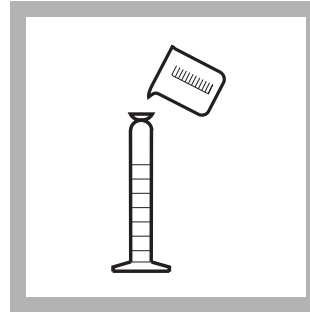
Note: The Flow Cell and Sipper Modules can be used for this procedure if rinsed with deionized water between samples.



2. The display will show:

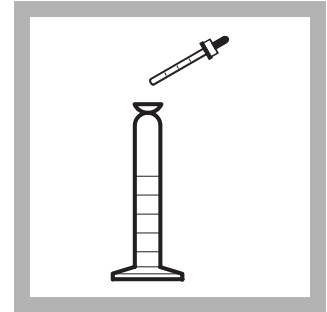
**HACH PROGRAM:
2020 Hardness, Mg**

The wavelength (λ), **522 nm**, is automatically selected.

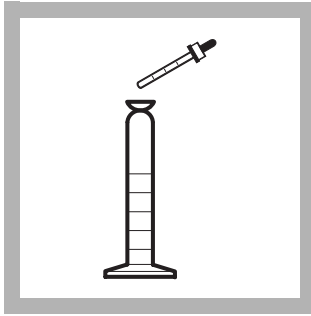


3. Pour 100 mL of sample into a 100-mL graduated mixing cylinder.

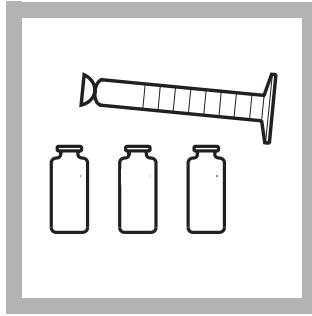
Note: For the most accurate magnesium test results the sample temperature should be 21-29 °C (70-84 °F).



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

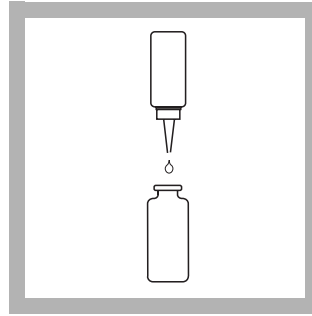


5. Add 1.0 mL of Alkali Solution for Calcium and Magnesium Test using a 1.0-mL measuring dropper. Stopper. Invert several times to mix.

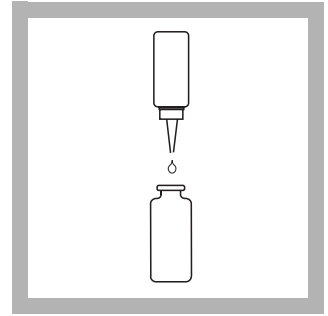


6. Pour 25 mL of the solution into each of three sample cells.

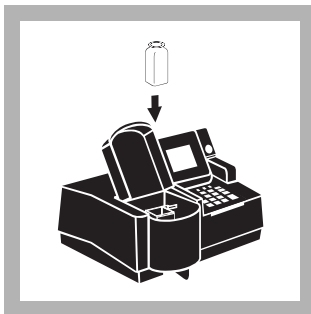
Note: The test will detect any calcium or magnesium contamination in the mixing cylinder, measuring droppers or sample cells. To test cleanliness, repeat the test multiple times until you obtain consistent results.



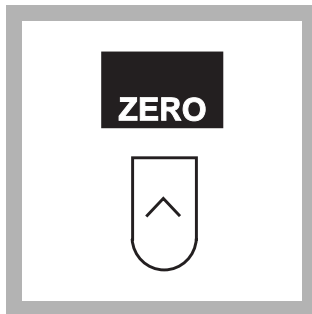
7. Add one drop of 1 M EDTA Solution to one cell (the blank). Swirl to mix.



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



9. Place the blank into the cell holder. Close the light shield.

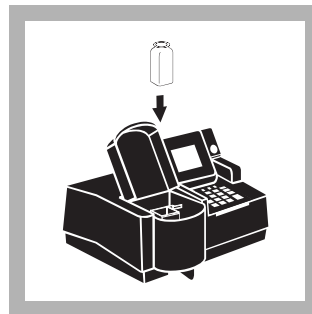


10. Press the soft key under **ZERO**.

The display will show:

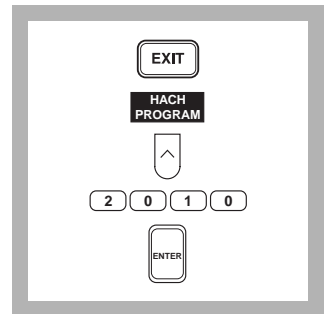
0.00 mg/L CaCO₃

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 magnesium as calcium carbonate (or chosen units) will be displayed. This value is the amount of magnesium in the sample expressed as CaCO₃.

Note: Results can be expressed as magnesium (Mg²⁺). Press the soft keys under **OPTIONS** and then **FORM**: to scroll through the available options.



12. Without removing the cell, press the **EXIT** key, followed by the soft key under **NEW PROGRAM**. At the program number prompt, select the stored program number for calcium hardness by pressing **2010** with the numeric keys.

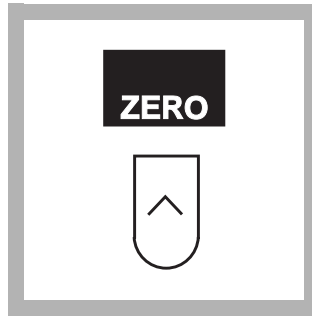
Press: **ENTER**



13. The display will show:

**HACH PROGRAM:
2010 Hardness, Ca**

The wavelength (λ), **522 nm**, is automatically selected.

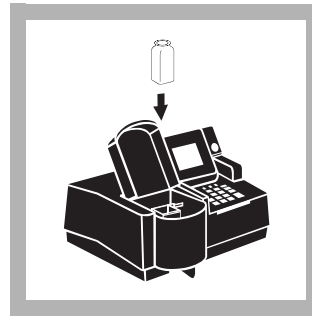


14. Press the soft key under **ZERO**.

The display will show:

0.00 mg/L CaCO₃

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.



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

Close the light shield. Results in mg/L calcium as calcium carbonate (or chosen units) will be displayed. The result is the amount of calcium in the sample expressed as CaCO₃.

Note: Result can be expressed as calcium (Ca). Press the soft keys under **OPTIONS** and then **FORM**: to scroll through the available options. Press **ENTER** to return to the read screen.

Note: mg/L hardness equals mg/L Ca as CaCO₃ plus mg/L Mg as CaCO₃.

Interferences

Table 1 Interfering Substances and Suggested Treatments

Interfering Substance	Interference Levels and Treatments
Chromium (3+)	Above 0.25 mg/L
Copper (2+)	Above 0.75 mg/L
EDTA, chelated	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 using.
Iron (2+)	Above 1.4 mg/L
Iron (3+)	Above 2.0 mg/L
Manganese (2+)	Above 0.20 mg/L
Zinc (2+)	Above 0.050 mg/L
Calcium >1.0 mg/L; Mg >0.25 mg/L	For the most accurate calcium test result, rerun the test 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 needed if either is below those respective concentrations.

Sample Collection, Storage and Preservation

Collect samples in acid-washed plastic bottles. Adjust the sample pH to 2 or less with nitric acid (about 5 mL per liter). Cool samples to 4 °C. Preserved samples can be stored up to six months. Before analysis, adjust the sample pH to between 3 and 8 with 5.0 N Sodium Hydroxide Standard Solution. Correct the test results for volume additions; see Section 1.2.2 *Correcting for Volume Additions*.

Method Performance

Precision

Standard: 1.50 mg/L as CaCO₃

Program	95% Confidence Limits
2010	1.45–1.55 mg/L as CaCO ₃
2020	1.47–1.53 mg/L as CaCO ₃

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

Estimated Detection Limit

Program	EDL
2010	0.03 mg/L as CaCO ₃
2020	0.03 mg/L as CaCO ₃

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: 2010

Portion of Curve	ΔAbs	ΔConcentration
0.010 Abs	0.010	0.054 mg/L as CaCO ₃
2 mg/L	0.010	0.054 mg/L as CaCO ₃
3.6 mg/L	0.010	0.079 mg/L as CaCO ₃

Program Number: 2020

Portion of Curve	ΔAbs	ΔConcentration
0.010 Abs	0.010	0.029 mg/L as CaCO ₃
2 mg/L	0.010	0.032 mg/L as CaCO ₃
3.6 mg/L	0.010	0.049 mg/L as CaCO ₃

See Section 1.5.3 *Sensitivity Explained* for more information.

Calibration Standard Preparation

To perform a hardness calibration using the Calmagite Colorimetric method, prepare calibration standards containing 0.5, 2.0, 2.5, 3.0, 3.5, and 4.0 mg/L Ca as CaCO₃ as follows:

- a. Into six different 100-mL Class A volumetric flasks, pipet 1.00, 4.00, 5.00, 6.00, 7.00, and 8.00 mL of a 50-mg/L Calcium Chloride Standard Solution as CaCO₃ (Cat. No. 21277-16) using Class A glassware.
- b. Dilute to the mark with deionized water. Mix well.

Also prepare calibration standards containing 0.41, 1.65, 2.06, 2.47, 2.88 and 3.30 mg/L Mg as CaCO₃ as follows:

- a. Into a 100-mL Class A volumetric flask, pipet 10.00 mL of 1000-mg/L Magnesium Standard Solution as Mg (Cat. No. 14794-42) using Class A glassware to prepare a 100 mg/L standard (412 mg/L Mg as CaCO₃).
- b. Into six different 1000-mL Class A volumetric flasks, pipet 1.00, 4.00, 5.00, 6.00, 7.00, and 8.00 mL of the 100-mg/L magnesium standard using Class A glassware.
- c. Dilute to the mark with deionized water. Mix well.

Using the Calmagite Colorimetric method and the instructions described in the *User-Entered Programs* section of the *DR/4000 Spectrophotometer Instrument Manual*, generate a calcium calibration curve from the calcium standards prepared above and a magnesium calibration curve from the magnesium standards prepared above.

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 (those listed the table above) that interfere in the titrimetric method may be inconsequential when diluting the sample 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 contacting free calcium or magnesium. Calcium and magnesium determinations are made by chelating calcium with EGTA to destroy any red color due to calcium and then chelating the calcium and magnesium with EDTA to destroy the red color due to both calcium and magnesium. By measuring the red color in the different states, calcium and magnesium concentrations are determined.

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 3.

Pollution Prevention and Waste Management

For information on pollution prevention and waste management, refer to *Section 3*.

HARDNESS, continued

REQUIRED REAGENTS AND STANDARDS

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

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	SCDB	22419-26
EGTA Solution	1 drop	50 mL	SCDB	22297-26

REQUIRED EQUIPMENT AND SUPPLIES

Cylinder, 100-mL, graduated mixing	1	each	1896-42
Dropper, measuring, 0.5 and 1.0 mL.....	2	20/pkg	21247-20
DR/4000 1-Inch Cell Adapter	1	each	48190-00

OPTIONAL REAGENTS AND STANDARDS

Calcium Chloride Standard Solution, 50-mg/L as CaCO ₃	946 mL	21277-16
Magnesium Standard Solution, 1000-mg/L as Mg	100 mL	14794-42
Nitric Acid, ACS	500 mL	152-49
Sodium Hydroxide Standard Solution, 5.0 N.....	100 mL	2450-32

OPTIONAL EQUIPMENT AND SUPPLIES

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
Flask, volumetric, Class A, 100-mL	each	14574-42
Flask, volumetric, Class A, 1000-mL, with stopper.....	each	14574-53
Pipet, volumetric, Class A, 1.00-mL	each	14515-35
Pipet, volumetric, Class A, 4.00-mL	each	14515-04
Pipet, volumetric, Class A, 5.00-mL	each	14515-37
Pipet, volumetric, Class A, 6.00-mL	each	14515-06
Pipet, volumetric, Class A, 7.00-mL	each	14515-07
Pipet, volumetric, Class A, 8.00-mL	each	14515-08
Pipet, volumetric, Class A, 10.00-mL	each	14515-38
Thermometer, pocket, -10 to 110 °C.....	each	1877-01



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