Hardness, Total

DOC316.53.01045

Calcium and Magnesium; Chlorophosphonazo Rapid Liquid Method — Method 8374

4 to 1000 µg/L Ca and Mg as $CaCO_3$ (ULR) — Pour-Thru Cell

Scope and application: For boiler and ultrapure water.

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.

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	Pour-Thru Kit	Adapter
DR 6000	The flow path is to the right.	LZV899[1]	—
DR 3800		5940400	LZV585 (B)
DR 2800		5940400	LZV585 (B)
DR 2700		5940400	LZV585 (B)
DR 1900		LZV899	—
DR 5000	The flow path is toward the user.	LZV479	—
DR 3900		LZV899	—

Before starting

Clean the Pour-Thru Cell and all labware before the analysis, refer to Prepare analysis labware on page 4.
For the most accurate magnesium test results, keep the sample temperature between 21–29 °C (70–84 °F).
To test for calcium or magnesium contamination in the labware, do the test until the results are consistent. Use dedicated plasticware for this analysis.
To protect the Pour-Thru Cell from contamination when not in use, invert a small beaker over the top of the glass funnel.
If the test result is more than 750 µg/L, make a 1:1 dilution of the sample for best accuracy. Use ultra-pure (aldehyde-free) water for the dilution. Do the analysis again on the diluted sample and multiply the result by two.
Use "Alternate Forms" ("Chemical Forms" on some instruments) only when the sample is known to contain only Mg or Ca. This method does not distinguish between the two forms.
Refer to the instrument documentation for Pour-Thru cell and module assembly and installation. Make sure to install the Pour-Thru cell correctly.
Total hardness in mg/L equals mg/L Ca as $CaCO_3$ plus mg/L Mg as $CaCO_3$.
In bright light conditions (e.g., direct sunlight), close the cell compartment, if applicable, with the protective cover during measurements.
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.

[1] A cell cover (LZQ105) and a tube set (LZQ102) is also necessary.

Items to collect

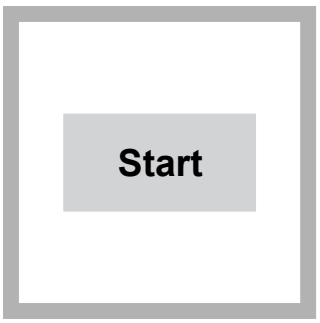
Description	Quantity
Chlorophosphonazo Indicator Solution	2 mL
CDTA Reagent for Ultra Low Range Hardness	2 drops
Water, Ultra-pure, Aldehyde-free	varies
Cylinder, graduated, 50 mL, polypropylene	1
Dispenser, adjustable volume, 1.0–5.0 mL	1
Flask, Erlenmeyer, PMP w/cap, 125-mL	1
Pour-Thru Cell Module (Refer to Instrument-specific information on page 1)	1

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

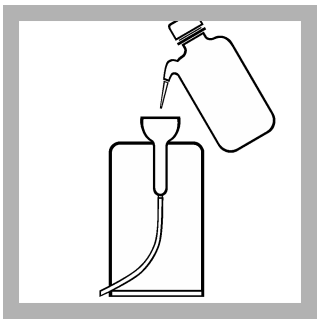
Sample collection

- Collect samples in clean plastic bottles with tight-fitting caps. Do not use glass bottles, which will contaminate the sample.
- Rinse the sample bottle several times with the sample to be collected.
- Seal the bottle to prevent contamination during the transport.
- Analyze the samples as soon as possible for best results.

Test procedure



1. Start program **227 Hardness Tot RL ULR**. For information about sample cells, adapters or light shields, refer to Instrument-specific information on page 1.

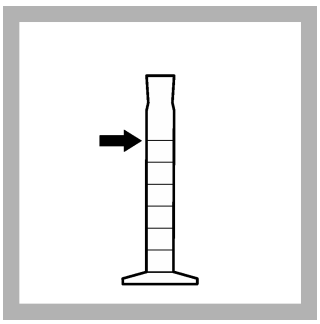


2. Flush the Pour-Thru Cell with 50 mL of ultra-pure water.

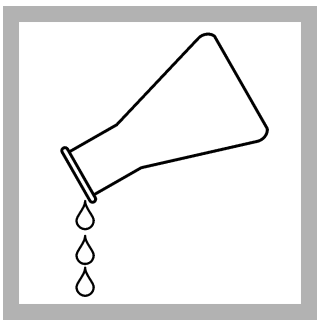
3. Fill a clean 125-mL plastic Erlenmeyer flask to the top with sample.

Collect the sample directly in the flask if possible.

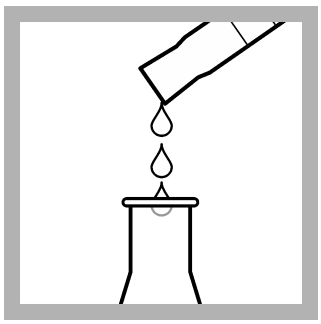
4. Rinse a clean 50-mL plastic graduated cylinder three times with sample.



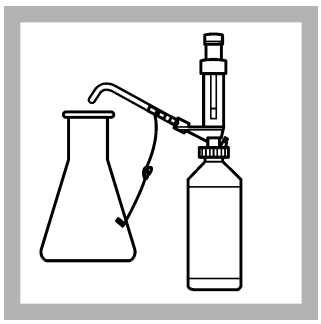
5. Fill the cylinder to the 50-mL mark with sample from the flask.



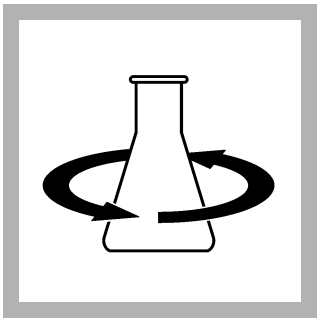
6. Discard the remaining contents of the flask.



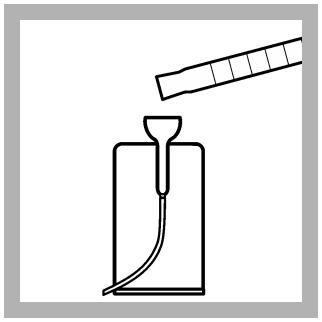
7. Pour the contents of the 50-mL cylinder back into the original flask.



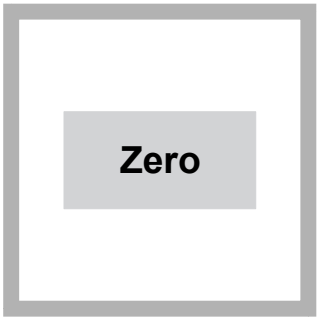
8. Use the bottle-top dispenser to add 2.0 mL of Chlorophosphonazo Reagent to the sample.



9. Swirl to mix.

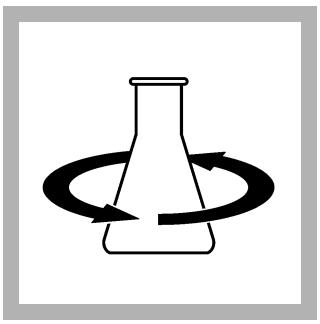


10. Use a clean, dry, plastic 25-mL graduated cylinder to pour approximately half (25 mL) of the sample into the Pour-Thru Cell.

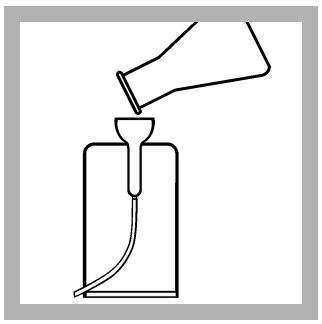


11. When the flow stops, push **ZERO**. The display shows 0 µg/L $CaCO_3$.

12. Add 2 drops of CDTA Reagent for Ultra Low Range Hardness to the remaining sample in the flask.
Complete the next 3 steps within 2 minutes.

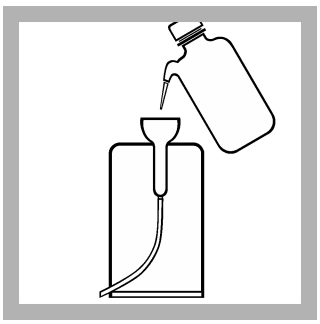


13. Swirl to mix.

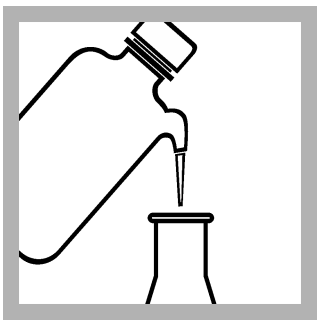


14. Pour the remaining sample into the Pour-Thru Cell.

15. Push **READ**. Results show in µg/L $CaCO_3$.



16. Rinse the Pour-Thru Cell with at least 75 mL of ultra-pure water immediately after use.



17. Rinse the flask with ultra-pure water. Put a cap on the flask when finished.

Interferences

Table 2 shows the results of interference studies that used various hardness standard solutions between 0 and 500 µg/L as $CaCO_3$. Various cations and anions were added to the hardness standard solutions at levels in the range applicable for ultra-pure water

applications. An ion was considered an interference when the measured hardness concentration changed by ±10%.

Table 2 Interfering substances

Interfering substance	Interference level
Aluminum	Negative interference above 150 µg/L
Ammonium	No interference at or below 1000 µg/L
Copper	Positive interference above 250 µg/L
Formaldehyde	No interference at or below 47,000 µg/L
Nitrate	Positive interference above 250 µg/L
Potassium	No interference at or below 1000 µg/L
Silicon	Positive interference above 1000 µg/L
Sodium	Negative interference above 79,000 µg/L

Prepare analysis labware

Fully clean all containers used in this test to remove possible traces of calcium or magnesium. Use plastic containers for all analysis and storage. Before analysis, clean the Pour-Thru cell and all labware as follows:

1. Clean all containers by normal means, then rinse with ultra-pure water.
2. Fill and soak all containers for 10 minutes with a 1:25 dilution of Chlorophosphonazo Reagent in ultra-pure water.

   Note: *If containers are rinsed and capped after each use, only occasional soaking is necessary.*
3. Rinse well with ultra-pure water.
4. Keep containers tightly closed and dedicate them for ULR Hardness only.
5. Fill the Pour-Thru cell with this same mixture of chlorophosphonazo and water. Let the mixture soak in the cell for several minutes.
6. Rinse the Pour-Thru Cell with ultra-pure water.
7. Use a wash bottle to fully rinse the inside of the bottle-top dispenser cap and inlet tubing with a large volume of ultra-pure water.
8. Put the inlet tubing of the bottle-top dispenser into a beaker of ultra-pure water and depress the plunger 10-15 times to rinse the dispenser.

   Note: *For best results, pour a small amount of reagent into the beaker of rinse water.*
9. Remove the dispenser from the water and depress the plunger until all of the water has been expelled. Shake off any excess water on the dispenser.
10. Install the dispenser on the Chlorophosphonazo Reagent bottle and tighten the cap.

Accuracy check

Standard additions method (sample spike)

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

Items to collect:

- 50,000-µg/L (50-mg/L) as $CaCO_3$ Calcium Chloride Standard Solution
- Flask, volumetric, 50-mL plastic
- 20-mL volumetric pipet, Class A and pipet filler safety bulb
- Pipet, TenSette®, 0.1–1.0 mL and tips
- Ultrapure water

1. Prepare a 20,000-µg/L (20-mg/L) hardness standard solution as follows:
   a. Use a pipet to add 20 mL of a 50-mg/L Calcium Chloride Standard solution into a 50-mL plastic volumetric flask.
   b. Dilute to the mark with ultrapure water. Mix well. Prepare this solution daily.
2. Use the test procedure to measure the concentration of the sample, then keep the (unspiked) sample in the instrument.
3. Go to the Standard Additions option in the instrument menu.
4. Select the values for standard concentration, sample volume and spike volumes.
5. Prepare three spiked samples: use the TenSette pipet to add 0.2 mL, 0.4 mL and 0.6 mL of the prepared standard solution, respectively, to three 50-mL portions of fresh sample. Mix well.
6. 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.
7. Select **Graph** to compare the expected results to the actual results.

   Note: *If the actual results are significantly different from the expected results, make sure that the sample volumes and sample spikes are measured accurately. The sample volumes and sample spikes that are used should agree with the selections in the standard additions menu. If the results are not within acceptable limits, the sample may contain an interference.*

Standard solution method

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

Items to collect:

- 0.50-mg/L (500-µg/L) as $CaCO_3$ Calcium Chloride 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 small 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
227	500 µg/L $CaCO_3$	495–505 µg/L	8 µg/L Ca

Summary of Method

Calcium and magnesium mix equally with the Chlorophosphonazo Indicator to give a complex with color which absorbs light very strongly at 669 nm. One drop of the CDTA reagent breaks up this complex. The decrease in color is proportional to the amount of calcium and magnesium in the sample (as $CaCO_3$). The measurement wavelength is 669 nm.

Consumables and replacement items

Required reagents

Description	Quantity/test	Unit	Item no.
Chlorophosphonazo Indicator Solution	2 mL	500 mL	2589549
CDTA Reagent for Ultra Low Range Hardness	2 drops	30 mL SCDB	2589723

Required apparatus

Description	Quantity/test	Unit	Item no.
Cylinder, graduated, 50 mL, polypropylene	1	each	108141
Dispenser, adjustable volume, 1.0–5.0 mL	2	each	2563137
Flask, Erlenmeyer, Polymethylpentene, screw cap, 125 mL	2	each	2089843

Recommended standards

Description	Unit	Item no.
Calcium Standard Solution, 50 mg/L as $CaCO_3$	946 mL	2127716
Calcium Standard Solution, 0.50 mg/L as $CaCO_3$	946 mL	2058016
Water, Ultra-pure, Aldehyde-free	500 mL	2594649

Optional reagents and apparatus

Description	Unit	Item no.
Pipet, TenSette®, 0.1–1.0 mL	each	1970001
Pipet tips for TenSette® Pipet, 0.1–1.0 mL	50/pkg	2185696
Pipet, volumetric Class A, 20 mL	each	1451520
Pipet filler, safety bulb	each	1465100
Flask, volumetric, 50 mL, polypropylene	each	1406041

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