

Hardness, Total

DOC316.53.01045

Calcium and Magnesium;
Chlorophosphonazo Rapid Liquid Method
ULR (4 to 1000 µg/L Ca and Mg as CaCO₃)

Method 8374

Pour-Thru Cell

Scope and Application: For boiler and ultra pure water.



Test preparation

How to use instrument-specific information

The *Instrument-specific information* table displays requirements that may vary between instruments. To use this table, select an instrument then read across to find the corresponding information required to perform this test.

Table 163 Instrument-specific information

Instrument	Pour-thru Kit	Cell orientation	Adapter
DR 6000	LQV175.99.20002	Arrow faces right	—
DR 5000	LZV479	—	—
DR 3900	LQV157.99.10002	Align cell flow arrows with arrows on cell compartment	—
DR 3800, DR 2800, DR 2700	5940400	1-inch (round) path aligned with arrow on the adapter	LZV585 (B)

Before starting the test:

Pre-clean the Pour-Thru Cell and all labware as specified in *Treating analysis labware*.

For the most accurate magnesium test results, keep the sample temperature between 21–29 °C (70–84 °F).

The test will detect any calcium or magnesium contamination in the mixing cylinder, measuring droppers, or sample cells. To test cleanliness, repeat the test until results are consistent.

Protect the Pour-Thru Cell from contamination when not in use by inverting a small beaker over the top of the glass funnel.

If the sample concentration is greater than 750 µg/L, a 1:1 dilution of the sample is recommended for greatest accuracy. Use ultra-pure (aldehyde-free) water for the dilution. Repeat the analysis on the diluted sample and multiply the resulting concentration by two.

Alternate forms should only be used when the sample is known to contain only Mg or Ca. This method does not distinguish between the two forms.

Refer to the instrument User Manual for Pour-Thru cell and module assembly and installation.

Use dedicated plasticware for this analysis.

In bright light conditions (e.g. direct sunlight) it may be necessary to close the DR 2800 or DR 2700 cell compartment with the protective cover during measurements.

Total hardness in mg/L equals mg/L Ca as CaCO₃ plus mg/L Mg as CaCO₃.

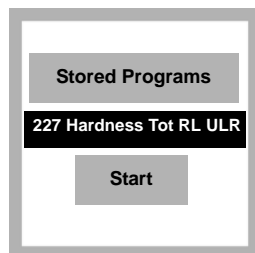
Ensure the pour-thru cell is completely seated in the sample cell compartment.

Collect the following items:

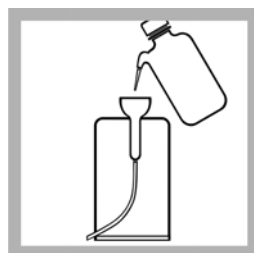
Description	Quantity
Chlorophosphonazo Indicator Solution	2 mL
CDTA Reagent for Ultra Low Range Hardness	1 drop
Water, Ultra-pure	Varies
Cylinder, graduated, 50-mL, poly	1
Dispenser, Adjustable Volume	1
Flask, Erlenmeyer, PMP w/cap, 125-mL	1
Pour-Thru Cell Module (see Instrument-specific information table)	1

See [Consumables and replacement items](#) for reorder information.

Chlorophosphonazo rapid liquid method



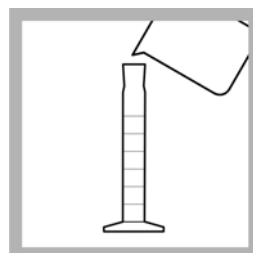
1. Select the test.
Insert an adapter if required ([Instrument-specific information](#)).



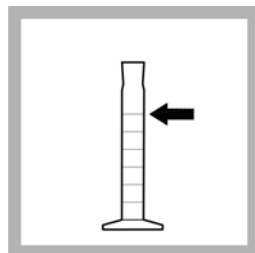
2. Flush the Pour-Thru Cell with 50 mL of ultra-pure water.



3. Fill a clean, 125-mL plastic Erlenmeyer flask to overflowing with sample.
Collect sample directly in the flask if possible.



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



5. Fill the rinsed cylinder to the 50-mL mark with sample from the flask. Discard remaining contents of the flask.



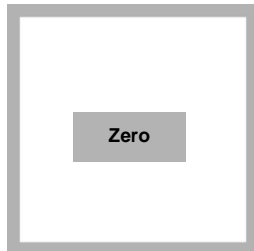
6. Pour the contents of the 50-mL cylinder back into the flask.



7. Add 2.0 mL of Chlorophosphonazo Reagent to the sample with the Dispenser. Swirl to mix.



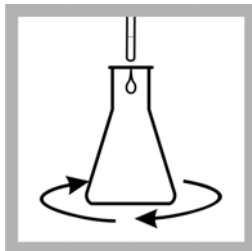
8. Pour approximately half (25 mL) of the sample into the Pour-Thru Cell. Use a clean, dry, plastic 25-mL graduated cylinder to measure the sample.

Chlorophosphonazo rapid liquid method (continued)

9. After the flow stops, **ZERO** the instrument.

The display will show:

0 $\mu\text{g/L CaCO}_3$

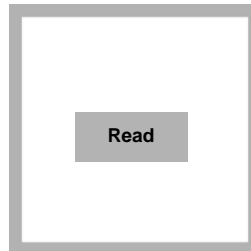


10. Add one drop of CDTA Reagent for Ultra Low Range Hardness to the remaining sample in the flask. Swirl to mix.

Complete steps 11 and 12 within one to two minutes.



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



12. **READ** the results in $\mu\text{g/L CaCO}_3$.



13. Using a wash bottle, rinse the Pour-Thru Cell with at least 75 mL of ultra-pure water immediately after use.

Rinse the flask with ultra-pure water. Cap when finished.

Interferences

Table 164 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
Potassium	No interference at or below 1000 µg/L
Silicon	Positive interference above 1000 µg/L
Sodium	Negative interference above 79,000 µg/L

Treating analysis labware

Clean all containers used in this test thoroughly to remove any traces of calcium or magnesium. If possible, use plastic containers for all analysis and storage. Clean containers by normal means, then rinse with ultra-pure (aldehyde-free) water. Fill and soak for 10 minutes with a 1:25 dilution of Chlorophosphonazo Reagent in ultra-pure water. Rinse well with ultra-pure water. Keep containers tightly closed and dedicate them for ULR Hardness only. If containers are rinsed and capped after each use, only occasional soaking is necessary. Fill the Pour-Thru cell with this same mixture of chlorophosphonazo and water and let stand for several minutes. Rinse with ultra-pure water.

Avoid contamination of the Chlorophosphonazo Reagent bottle when placing the Repipet dispenser on the bottle. Rinse the inlet tubing and inside of the dispenser cap with copious amounts of ultra-pure water using a wash bottle. Place the inlet tubing into a beaker of ultra-pure water and depress the plunger 10–15 times to rinse the inside of the dispenser. (For best results, pour a small amount of reagent into the beaker of rinse water.) 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, place the dispenser on the bottle and tighten.

Sample collection, preservation and storage

- Do not use glass containers.
- Collect samples in clean plastic containers, preferably with screw-type closures.
- Rinse containers several times with the water to be analyzed before collecting the final sample.
- Seal to avoid contamination during transport.
- Analyze as soon as possible.

Accuracy check

Required for accuracy check:

- Calcium Chloride Standard Solution, 50 mg/L (50,000 µg/L) as CaCO₃
- TenSette® Pipet and Pipet Tips

Standard additions method (sample spike)

1. Prepare a 20,000 µg/L (20 mg/L) CaCO₃ standard by pipetting 20 mL of 50 mg/L CaCO₃ standard solution into a 50 mL plastic volumetric flask. Dilute the solution with 50 mL of ultra-pure water.
2. After reading test results, leave the sample cell (unspiked sample) in the instrument.
3. Select Options>More>Standard Additions from the instrument menu.

- Default values for standard concentration, sample volume and spike volumes can be accepted or edited. Accept the default values then read the unspiked sample measurement. After values are accepted, the unspiked sample reading will appear in the top row. See the user manual for more information.
- Use the TenSette Pipet to prepare spiked samples: add 0.2 mL, 0.4 mL, and 0.6 mL of the prepared 20,000 µg/L standard to three 50 mL portions of fresh sample.
- Follow the test procedure for each of the spiked samples, starting with the 0.2 mL sample spike. Measure each of the spiked samples in the instrument.
- Select **GRAPH** to view the results. Select **IDEAL LINE** (or best-fit) to compare the standard addition results to the theoretical 100% recovery.

Standard solution method

Note: Refer to the instrument user manual for specific software navigation instructions.

- Using a 0.50 mg/L (500 µg/L as CaCO₃) Calcium Chloride Standard Solution, perform the procedure using the standard in place of the sample.
- To adjust the calibration curve using the reading obtained with the 0.50-mg/L Standard Solution, select Options>More>Standard Adjust from the instrument menu.
- Turn on the Standard Adjust feature and accept the displayed concentration. If an alternate concentration is used, enter the concentration and adjust the curve to that value.

Method performance

Program	Standard	Precision 95% Confidence Limits of Distribution	Sensitivity Concentration change per 0.010 Abs change
227	0.500 mg/L Cr ⁶⁺	495–505 µg/L	8µg/L Ca

Summary of method

Calcium and magnesium combine equivalently with the Chlorophosphonazo Indicator to form a colored complex which absorbs light very strongly at 669 nm. One drop of the CDTA reagent breaks up this complex, and the resultant decrease in color is proportional to the amount of calcium and magnesium (as CaCO₃) in the sample. Test results are measured at 669 nm.

Consumables and replacement items

Required reagents

Description	Quantity/Test	Unit	Catalog number
Chlorophosphonazo Indicator Solution	2 mL	500 mL	2589549
CDTA Reagent for Ultra Low Range Hardness	1 drop	10 mL SCDB	2589636

Required apparatus

Description	Quantity	Unit	Catalog number
Cylinder, graduated, 50 mL, poly	1	each	108141
Dispenser, variable-volume	1	each	2563137
Flask, Erlenmeyer, PMP w/cap, 125 mL	1	each	2089843

Hardness, Total

Recommended standards

Description	Unit	Catalog number
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	Catalog number
Pipet, TenSette® 0.1–1.0 mL	each	1970001
Pipet Tips, for TenSette Pipet 1970001	50/pkg	2185696
Pipet, volumetric, Class A, 20 mL	each	1451520
Pipet filler, Safety bulb	each	1465100
Flask, volumetric, polypropylene, 50 mL	each	1406041



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