

HARDNESS, CALCIUM (10 to 4000 mg/L as CaCO₃)

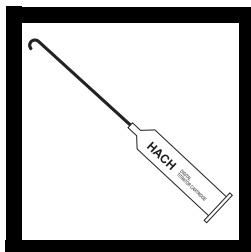
Using EDTA



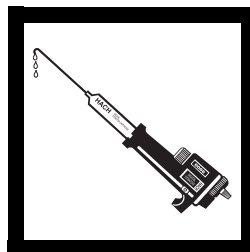
1. Select a sample size and an EDTA Titration Cartridge corresponding to the expected calcium as calcium carbonate (CaCO₃) concentration. Use *Table 1* for concentrations in mg/L or *Table 2* for concentrations in German degrees of hardness (G.d.h.).

Note: One German degree hardness equals 17.9 mg/L hardness as CaCO₃.

Note: If sample cannot be analyzed immediately, add 1.5 mL Nitric Acid per liter of sample to preserve the sample and to prevent adsorption of the calcium to the container walls. Store in a refrigerator. Samples preserved in this manner are stable for one week. Neutralize to pH 7 before running the test.

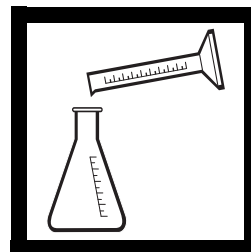


2. Insert a clean delivery tube into the titration cartridge. Attach the cartridge to the titrator body. See *General Description, Step-by-Step* for assembly instructions, if necessary.



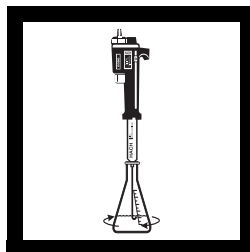
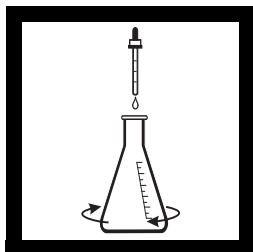
3. Turn the delivery knob to eject a few drops of titrant. Reset the counter to zero and wipe the tip.

Note: For added convenience use the *TitraStir® Stir Plate*. See *General Description, Step 3 in Step-by-Step*.



4. Use a graduated cylinder or pipet to measure the sample volume from *Table 1* or *Table 2*. Transfer the sample into a clean 250-mL Erlenmeyer flask. Dilute to about the 100-mL mark with deionized water, if necessary.

HARDNESS, CALCIUM, continued



$$\text{Total Digits Required} \times \text{Digit Multiplier}$$

$$= \text{mg/L Calcium Hardness as CaCO}_3$$

5. Add 2 mL of 8 N Potassium Hydroxide Standard Solution and swirl to mix.

Note: For samples of 50 mL or less, 1 mL may be added.

Note: Magnesium is not included in the results but must be present for a sharp end point. If it is known to be absent, add one to two drops of Magnesium Standard Solution, 10 g/L as CaCO₃.

6. Add the contents of one CalVer® 2 Calcium Indicator Powder Pillow (Cat. No. 852-99) and swirl to mix.

Note: A 0.1-gram scoop of CalVer 2 Calcium Indicator Powder (Cat. No. 281-14) may be substituted here.

7. Place the delivery tube tip into the solution and swirl the flask while titrating with EDTA from pink to blue. Record the number of digits required.

Note: Titrate slowly near the end point, because the reaction is slow, especially in cold samples.

8. Calculate the sample concentration using one of the formulas below:

Total Digits Required x Digit Multiplier (Table 1) = mg/L Calcium Hardness as CaCO₃

Total Digits Required x Digit Multiplier (Table 2) = G.d.h.

Table 1

Range (mg/L as CaCO ₃)	Sample Volume (mL)	Titration Cartridge (M EDTA)	Catalog Number	Digit Multiplier
10-40	100	0.0800	14364-01	0.1
40-160	25	0.0800	14364-01	0.4
100-400	100	0.800	14399-01	1.0
200-800	50	0.800	14399-01	2.0
500-2000	20	0.800	14399-01	5.0
1000-4000	10	0.800	14399-01	10.0

Table 2

Range (G.d.h.)	Sample Volume (mL)	Titration Cartridge (M EDTA)	Catalog Number	Digit Multiplier
1-4	100	0.1428	14960-01	0.01
4-16	25	0.1428	14960-01	0.04
10-40	50	0.714	14959-01	0.1
25-100	20	0.714	14959-01	0.25
>100	10	0.714	14959-01	0.5

HARDNESS, CALCIUM, continued

Hardness Relationships

mg/L Ca = Ca Hardness, mg/L as CaCO₃ x 0.40

Accuracy Check

Standard Additions Method

This accuracy check should be performed when interferences are suspected or to verify analytical technique.

1. Snap the neck off a Hardness Standard Solution Voluette® Ampule, 10,000 mg/L as CaCO₃.
2. Use a TenSette® Pipet to add 0.1 mL of standard to the solution titrated in *step 7*. Resume titration back to the same end point. Record the number of digits required.
3. Repeat, using two more additions of 0.1 mL. Titrate to the end point after each addition.
4. Each 0.1 mL addition of standard should require 10 additional digits of 0.800 N titrant or 100 digits of 0.0800 N titrant (11 digits of 0.714 M or 56 digits of 0.1428 M titrant). If these uniform increases do not occur, refer to *Appendix A, Accuracy Check and Standard Additions*.

HARDNESS, CALCIUM, continued

Interferences

WARNING:

Potassium cyanide is toxic. Always add it after the potassium hydroxide. Excess potassium cyanide does not affect results. All cyanide wastes should be disposed of by adding an excess of strongly alkaline sodium hypochlorite solution (bleach) with stirring. Use good ventilation. Allow to stand for 24 hours before disposal.

- Some transition and heavy metals complex the indicators and prevent the color change at the end point. Adding a 0.5-g scoop of potassium cyanide (KCN) after the addition of potassium hydroxide removes interference from the following metals at the levels listed (in an undiluted 100-mL sample), see *Table 3*.

Table 3

Metal	Max. Tolerance Level* with KCN	Max. Tolerance Level* without KCN present
Cobalt	20 mg/L	none
Copper	100 mg/L	0.10 mg/L
Nickel	200 mg/L	0.5 mg/L
Zinc	100 mg/L	5 mg/L

* Proportionally higher levels of these elements are tolerable in smaller sample sizes since their effect is diluted when bringing the volume to 100 mL. Because Tables 1 and 2 have sample volumes of 10-100 mL, the interference concentrations may be greater in your sample and have no effect because of sample dilution.

- Iron interferes above 8 mg/L in undiluted samples. Above this level, it causes a red-orange to green end point which is sharp and usable up to 20 mg/L iron.
- Manganese interferes above 5 mg/L.
- Aluminum causes a slow end point, but up to 200 mg/L can be tolerated by allowing enough time for color change.

HARDNESS, CALCIUM, continued

- Magnesium interference up to 200 mg/L is prevented by formation of magnesium hydroxide at the high test pH, but higher levels prevent a distinct end point.
- Orthophosphate causes a slow end point, but does not interfere if the calcium phosphate that forms is allowed enough time to redissolve during the titration. Polyphosphate must be absent for accurate results.
- Barium and strontium are titrated with calcium but seldom present in natural waters in significant amounts.
- Acidity and alkalinity at 10,000 mg/L as CaCO₃ do not interfere.
- Saturated sodium chloride solutions do not give a distinct end point, but the titration can be run directly on sea water.
- Samples at about 20 °C (68 °F) or colder should be titrated slowly near the end point to allow enough time for the color change.
- Highly buffered samples or extreme sample pH may exceed the buffering capacity of the reagents and require sample pretreatment.

Summary of Method

The sample is made alkaline (pH 12-13) with potassium hydroxide to precipitate magnesium as magnesium hydroxide. CalVer 2 Indicator is added and combines with any calcium to form a pink-red color. As EDTA is added, it reacts with the free calcium ions present. When no free calcium ions remain, the EDTA then removes the calcium complexed with the indicator, causing a color change to blue.

REQUIRED REAGENTS

Description	Unit	Cat. No.
Calcium Hardness Reagent Sets (about 100 tests)		
1-16 G.d.h. includes: (1) 282-32, (1) 852-99, (1) 14960-01		24473-00
10-100+ G.d.h. includes: (1) 282-32, (1) 852-99, (1) 14959-01		24474-00
10-160 mg/L includes: (1) 282-32, (1) 852-99, (1) 14364-01		24472-00
100-4,000 mg/L includes: (1) 282-32, (1) 852-99, (1) 14399-01		24475-00

HARDNESS, CALCIUM, continued

CalVer® 2 Indicator Powder Pillows.....	100/pkg.....	852-99
Potassium Hydroxide Standard Solution, 8.00 N.....	100 mL MDB*.....	282-32
Water, deionized.....	4 L.....	272-56

Select one or more based on sample concentration:

EDTA Titration Cartridge, 0.0800 M.....	each.....	14364-01
EDTA Titration Cartridge, 0.1428 M.....	each.....	14960-01
EDTA Titration Cartridge, 0.714 M.....	each.....	14959-01
EDTA Titration Cartridge, 0.800 M.....	each.....	14399-01

REQUIRED APPARATUS

Digital Titrator.....	each.....	16900-01
Flask, Erlenmeyer, 250 mL.....	each.....	505-46

Select one or more based on sample concentration:

Cylinder, graduated, 10 mL.....	each.....	508-38
Cylinder, graduated, 25 mL.....	each.....	508-40
Cylinder, graduated, 50 mL.....	each.....	508-41
Cylinder, graduated, 100 mL.....	each.....	508-42

OPTIONAL REAGENTS

Calcium and Magnesium Total Hardness Reagent Set (about 100 tests)	22721-00
Includes: (2) 282-32, (1) 424-32, (1) 851-99, (1) 947-99, (1) 14364-01, (1) 14399-01	

Description	Unit	Cat. No.
Calcium Chloride Standard Solution, 1000 mg/L as CaCO ₃	1000 mL.....	121-53
CalVer® 2 Calcium Indicator Powder.....	113 g.....	281-14
Calcium Standard Solution Voluette® Ampules, 10,000 mg/L as CaCO ₃ , 10-mL	16/pkg.....	2187-10
Magnesium Standard Solution, 10 g/L CaCO ₃	29 mL SCDB.....	1022-33
Nitric Acid, ACS	500 mL.....	152-49
Nitric Acid Solution, 1:1.....	500 mL.....	2540-49
Potassium Cyanide, ACS	125 g.....	767-14

OPTIONAL APPARATUS

Bottle, wash, poly, 500-mL.....	each.....	620-11
Clamp, 2-prong, extension, 38-mm	each.....	21145-00
Clamp Holder.....	each.....	326-00
Demineralizer Assembly, 473 mL	each.....	21846-00
Delivery Tubes, with 180° hook	5/pkg.....	17205-00
Delivery Tubes, 90° with hook	5/pkg.....	41578-00
pH Paper, 1.0 to 11 pH	5 rolls/pkg.....	391-33
Pipet, TenSette®, 0.1 to 1.0 mL	each.....	19700-01

* Marked Dropper Bottle (MDB). Contact Hach for larger sizes.

HARDNESS, CALCIUM, continued

Pipet Tips for 19700-01 TenSette® Pipet	50/pkg.....	21856-96
Pipet, volumetric, Class A, 10-mL.....	each.....	14515-38
Pipet, volumetric, Class A, 20-mL.....	each.....	14515-20
Pipet, volumetric, Class A, 25-mL.....	each.....	14515-40
Pipet, volumetric, Class A, 50-mL.....	each.....	14515-41
Pipet, volumetric, Class A, 100-mL.....	each.....	14515-42
Pipet Filler, safety bulb.....	each.....	14651-00
<i>sens^{ion}</i> ™ 1 Basic Portable pH Meter with electrode.....	each.....	51700-10
Spoon, measuring, 0.1-gram	each.....	511-00
Spoon, measuring, 0.5-gram	each.....	907-00
Support Ring Stand.....	each.....	563-00
TitraStir® Stir Plate, 115 Vac	each.....	19400-00
TitraStir® Stir Plate, 230 Vac	each.....	19400-10
Voluette® Ampule Breaker Kit.....	each.....	21968-00