

Method 8204

Digital Titrator with EDTA Method (10 to 4000 mg/L as CaCO₃)

Digital Titrator

Scope and Application: For water, wastewater, and seawater



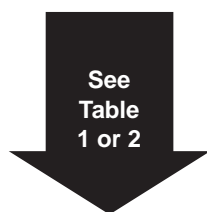
Tips and Techniques

- One German degree of hardness (G.d.h.) = 17.9 mg/L hardness as CaCO₃
- You can substitute a 0.1-g scoop of CalVer® 2 Calcium Indicator Powder for the CalVer 2 Calcium Indicator Powder Pillow.
- For added convenience when stirring, use the TitraStir apparatus (Cat. No. 19400-00, -10).
- mg/L Ca = Ca Hardness, mg/L as CaCO₃ x 0.40

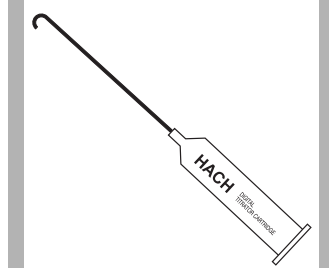


Digital Titration

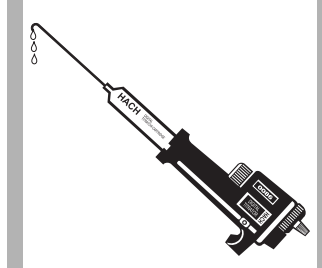
Method 8204



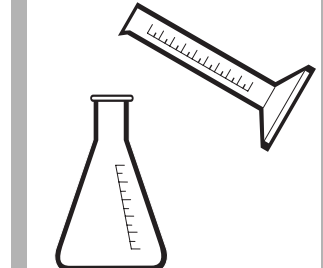
1. Select a sample size and an EDTA Titration Cartridge that corresponds to the expected calcium as calcium carbonate (CaCO₃) concentration. Use *Table 1* for concentrations in mg/L and *Table 2* for concentrations in German degrees of hardness.



2. Insert a clean delivery tube into the titration cartridge. Attach the cartridge to the titrator body.

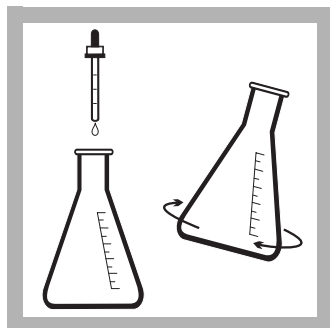


3. Turn the delivery knob to eject a few drops of titrant. Reset the counter to zero and wipe the tip.



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.

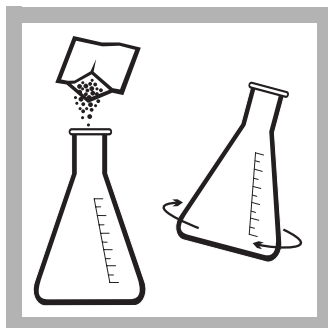
Hardness, Calcium



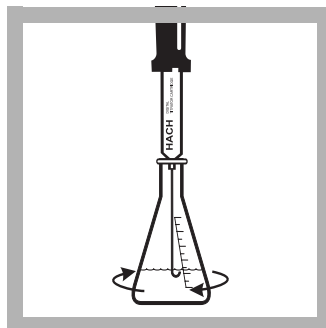
5. Add 2 mL of 8 N Potassium Hydroxide Standard Solution and swirl.

For samples 50 mL and less, add 1 mL.

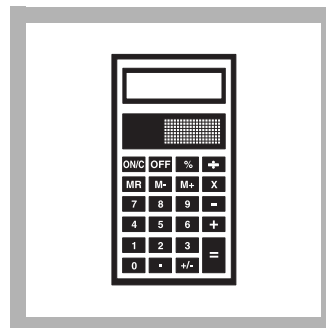
Magnesium is not included in the results but must be present for a sharp end point. If magnesium is absent, add one to two drops of Magnesium Standard Solution, 10-g/L as CaCO_3 .



6. Add the contents of one CalVer 2 Calcium Indicator Powder Pillow and swirl to mix.



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.



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

Total Digits Required x Digit Multiplier from *Table 1* = mg/L Calcium Hardness as CaCO_3

Total Digits Required x Digit Multiplier from *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

Interferences

WARNING:
Potassium cyanide is toxic. Always add it after the potassium hydroxide. Excess potassium cyanide does not affect results. Dispose of all cyanide wastes 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) (Cat. No. 767-14) after adding 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 because their effect is diluted when bringing the volume to 100 mL. Because *Table 1* and *Table 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

Interfering Substance	Interference Levels and Treatments
Acidity	The test can tolerate 10,000 mg/L acidity.
Alkalinity	The test can tolerate 10,000 mg/L alkalinity and can be run directly in sea water.
Aluminum	Interferes by causing a slow end point but up to 200 mg/L aluminum can be tolerated by allowing sufficient time for the color change.
Barium	Barium is titrated along with calcium but is seldom found in natural waters in significant amounts.
Iron	Interferes above 8 mg/L by causing an orange red to green end point. Accurate results can still be obtained up to about 20 mg/L iron with this end point.
Magnesium	Interference from magnesium is prevented up to 200 mg/L by the formation of magnesium hydroxide at the high test pH but higher levels prevent a distinct end point.
Manganese	Interferes above 5 mg/L.
Orthophosphate	Causes a slow end point but does not interfere if the calcium phosphate that forms is allowed time to redissolve during the titration.
Polyphosphates	Interfere directly and must be absent.
Sodium Chloride	Saturated solutions do not give a distinct end point.
Strontium	Strontium is titrated along with calcium but is seldom found in natural waters in significant amounts.
Temperature	Samples at about 20°C (68°F) or colder should be titrated slowly near the end point to allow sufficient time for the color change.
Highly buffered samples or extreme sample pH	May exceed the buffering capacity of the reagents and require sample pretreatment; see <i>Section 3.3 Interferences</i> on page 50.

Sampling and Storage

If sample cannot be analyzed immediately, add 1.5 mL Nitric Acid (Cat. No. 2540-49) per liter of sample to preserve the sample and to prevent adsorption of the calcium to the container walls. Store in a refrigerator at 4 °C or below; samples preserved in this manner are stable for one week. Neutralize acidified sample to pH 7 with ammonium hydroxide (Cat. No. 14736-32) before testing.

Hardness, Calcium

Accuracy Check

Standard Additions Method

Perform this accuracy check when interferences are suspected or to verify analytical technique.

1. Snap the neck off a Hardness Voluette Ampule Standard, 10,000-mg/L as CaCO_3 .
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 3.2.2 *Standard Additions*.

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.		24473-00
10–100+ G.d.h.		24474-00
10–160 mg/L.....		24472-00
100–4,000 mg/L.....		24475-00
Water, deionized	4 L	272-56

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

Required Standards

Calcium Standard Solution, Voluette® Ampule, 10,000-mg/L as CaCO_3 , 10-mL 16/pkg.....	2187-10
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FOR TECHNICAL ASSISTANCE, PRICE INFORMATION AND ORDERING:
In the U.S.A. – Call toll-free 800-227-4224
Outside the U.S.A. – Contact the HACH office or distributor serving you.
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HACH COMPANY
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