

Method 8213

Digital Titrator with EDTA Method

Digital Titrator

(10 to 4000 mg/L as CaCO₃)

Scope and Application: For water, wastewater, and seawater



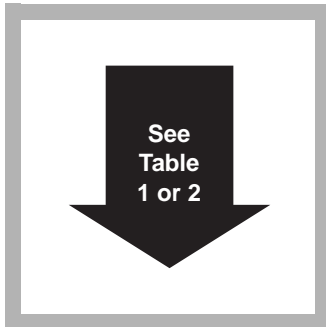
Tips and Techniques

- One German degree of hardness (G.d.h.) = 17.9 mg/L hardness as CaCO₃
- You can substitute a 0.1-g scoop of ManVer® 2 Hardness Indicator Powder or four drops of ManVer Hardness Indicator Solution for the ManVer 2 Hardness Indicator Powder Pillow.
- For added convenience when stirring, use the TitraStir apparatus (Cat. No. 19400-00, -10).
- mg/L Total Hardness as Ca = mg/L Total Hardness as CaCO₃ x 0.40
- mg/L Total Hardness as CaCO₃ = mg/L Ca as CaCO₃ + mg/L Mg as CaCO₃
- The magnesium concentration may be determined by subtracting the results of the calcium determination from the total hardness determination.

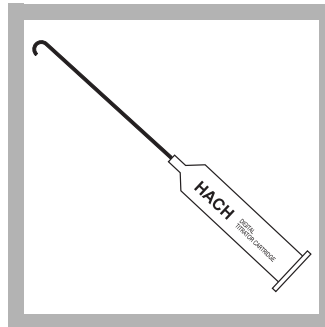


Digital Titration

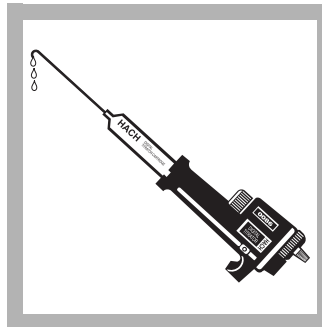
Method 8213



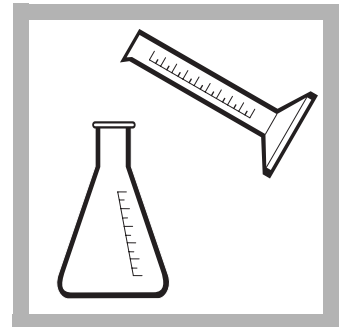
1. Select a sample size and an EDTA Titration Cartridge that corresponds to the expected calcium as calcium carbonate (CaCO₃) concentration. Use *Table 1* for concentrations in mg/L and *Table 2* for concentrations in German degrees of hardness.



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.

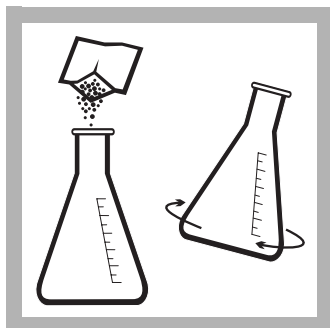


4. Use a graduated cylinder or pipet to measure the sample volume from *Table 1* or *Table 2*. Transfer the sample into a clean 250-mL Erlenmeyer flask. Dilute to about the 100-mL mark with deionized water, if necessary.

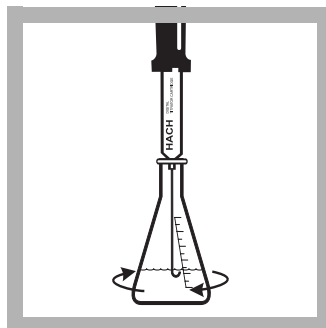
Hardness, Total



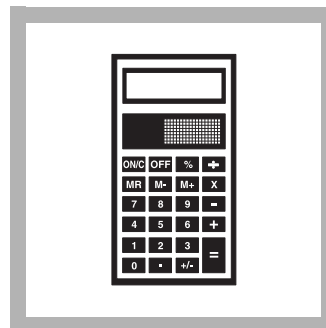
5. Add 2 mL of Buffer Solution, Hardness 1 and swirl to mix.



6. Add the contents of one ManVer 2 Hardness 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 red 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 Total Hardness as CaCO₃

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 indicator and prevent the color change at the end point.

Interfering Substance	Interference Levels and Treatments
Acidity	Does not interfere at 10,000 mg/L (as CaCO ₃).
Alkalinity	Does not interfere at 10,000 mg/L (as CaCO ₃).
Aluminum	A 0.5-gram scoop of potassium cyanide* (Cat. No. 767-14) raises the permissible aluminum level to 1 mg/L.
Barium	Titrate directly.
Cobalt	Interferes at all levels and must be absent or masked. A 0.5-gram scoop of potassium cyanide* (Cat. No. 767-14) removes interference from up to 100 mg/L cobalt.
Copper	Interferes at levels of 0.10 and 0.20 mg/L. A 0.5-gram scoop of potassium cyanide* (Cat. No. 767-14) removes interference from up to 100 mg/L copper.
Iron	Does not interfere up to 15 mg/L. Above this level it causes a red-orange to green end point which is sharp and usable up to 30 mg/L iron. Substitute a 0.0800 M CDTA (Cat. No. 14402-01) or 0.800 M CDTA (Cat. No. 14403-01) titration cartridge for the 0.0800 M EDTA or 0.800 M EDTA titration cartridges, respectively, if iron interference is probable.
Manganese	Titrate directly up to 20 mg/L but masks the end point above this level. Adding a 0.1-gram scoop of hydroxylamine hydrochloride monohydrate (Cat. No. 246-14) raises this level to 200 mg/L manganese.
Nickel	Interferes at all levels and must be absent or masked. A 0.5-gram scoop of potassium cyanide* (Cat. No. 767-14) removes interference from up to 100 mg/L nickel.
Orthophosphate	Causes a slow end point.
Polyphosphates	Polyphosphate must be absent for accurate results.
Polyvalent Metal Ions	Although less common than calcium and magnesium, other polyvalent metal ions cause the same hardness effects and will be included in the results.
Sodium Chloride	Saturated sodium chloride solutions do not give a distinct end point, but the titration can be run directly on sea water.
Strontium	Titrate directly.
Zinc	Titrate directly. A 0.5-gram scoop of potassium cyanide* (Cat. No. 767-14) removes interference from up to 100 mg/L zinc.
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.

* Metals masked with cyanide will not be included in the hardness result.

Hardness, Total

Adding the contents of one CDTA Magnesium Salt Powder Pillow removes metal interferences at or below the levels shown in *Table 3*.

Table 3

Metal	CDTA Removes Interference Below This Level
Aluminum	50 mg/L
Cobalt	200 mg/L
Copper	100 mg/L
Iron	100 mg/L
Manganese	200 mg/L
Nickel	400 mg/L
Zinc	300 mg/L

If more than one metal is present at or above the concentrations shown above, an additional CDTA Magnesium Salt Powder Pillow may be required.

Results obtained by this procedure include the hardness contributed by the metals. If the concentration of each metal is known, a correction can be applied to obtain the calcium and magnesium hardness concentration. The hardness (in mg/L as CaCO₃) contributed by each mg/L of metal is listed below, and can be subtracted from the total hardness value obtained above to determine the calcium and magnesium hardness. See *Table 4*.

Table 4

Metal	Hardness Contributed by Each mg/L of Metal
Aluminum	3.710
Barium	0.729
Cobalt	1.698
Copper	1.575
Iron	1.792
Manganese	1.822
Nickel	1.705
Strontium	1.142
Zinc	1.531

Sampling and Storage

Collect at least 100 mL of sample in a glass or polyethylene container. Samples may be held up to seven days before analysis if stored at 4 °C and acidified to pH 2 with concentrated nitric acid (Cat. No. 2540-49). Neutralize acidified sample to pH 7 with ammonium hydroxide (Cat. No. 14736-32) before testing.

When significant amounts of preservative are used, a volume correction should be made for the extra acid and base. Divide the total volume (sample + acid + base) by the volume of the sample, and multiply the result by the final test outcome.

Accuracy Check

Standard Additions Method (Sample Spike)

To verify analytical technique use 20 mL of the Calcium Standard Solution, 1000-mg/L as CaCO₃. Perform the procedure as described above. This solution will read 1000 mg/L or 55.9 G.d.h.

Perform this accuracy check when interferences are suspected.

1. Snap the neck off a Hardness Voluette Ampule Standard, 10,000-mg/L as CaCO₃.
2. Use a TenSette Pipet to add 0.1 mL of standard to the sample 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 M titrant, 100 digits of 0.0800 M titrant, 11 digits of 0.714 M, or 56 digits of 0.1428 M titrant. If these uniform increases do not occur, refer to *Section 3.2.2 Standard Additions* on page 46.

Summary of Method

After the sample is buffered to pH 10.1, ManVer 2 Hardness Indicator is added, and forms a red complex with a portion of the calcium and magnesium in the sample. EDTA titrant reacts first with the free calcium and magnesium ions, then with those bound to the indicator, causing it to change to a blue color at the end point.

Required Reagents

Description	Unit	Cat. No.
Total Hardness Reagent Set (about 100 tests)		22720-00
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
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
Flask, Erlenmeyer, 250-mL	each.....	505-46

Required Standards

Calcium Chloride Standard Solution, 1000-mg/L as CaCO ₃	1000 mL.....	121-53
Calcium Standard Solution, Voluette® Ampule, 10,000-mg/L as CaCO ₃ , 10-mL	16/pkg.....	2187-10



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