

Titration Method with EDTA^{1,2}

Method 8226

0–25,000 mg/L as CaCO₃

Buret Titration

Scope and application: For water, wastewater and seawater.

¹ USEPA accepted when 0.020 N titrant is used.

² Adapted from *Standard Methods for the Examination of Water and Wastewater*.



Test preparation

Before starting

As an alternative to the ManVer 2 Hardness Indicator Powder Pillow, use 4 drops of Hardness 2 Indicator Solution or a 0.1-g scoop of ManVer 2 Hardness Indicator Powder.

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.

Items to collect

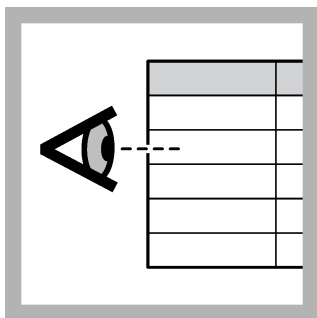
Description	Quantity
ManVer 2 Hardness Indicator Powder Pillow	1
Hardness 1 Buffer Solution	1 mL
TitraVer Hardness Titrant (use a concentration that is applicable to the selected sample volume)	varies
Buret, Class A, 25 mL	1
Graduated cylinder (use a size that is applicable to the selected sample volume), or TenSette pipet with tips	1
Erlenmeyer flask, 250 mL	1
Funnel, micro	1
Support stand with buret clamp	1
Water, deionized	varies

Refer to [Consumables and replacement items](#) on page 7 for order information.

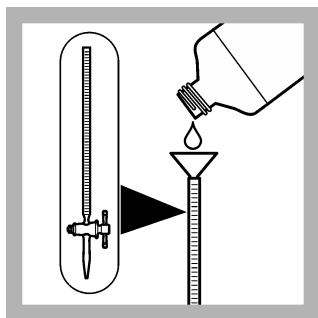
Sample collection and storage

- Collect samples in clean glass or plastic bottles that have been cleaned with a detergent and rinsed with 1:1 nitric acid and deionized water.
- To preserve samples for later analysis, adjust the sample pH to 2 or less with concentrated nitric acid (about 2 mL per liter). No acid addition is necessary if the sample is tested immediately.
- Keep the preserved samples at or below 6 °C (43 °F) for a maximum of 7 days.
- Before analysis, adjust the pH to 7 with sodium hydroxide solution.
- Correct the test result for the dilution caused by the volume additions.

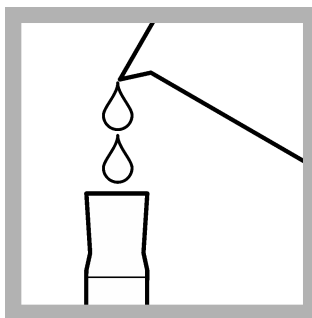
Test procedure



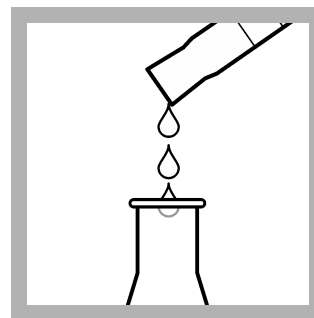
1. Select a sample volume and titrant from [Table 1](#) on page 3.



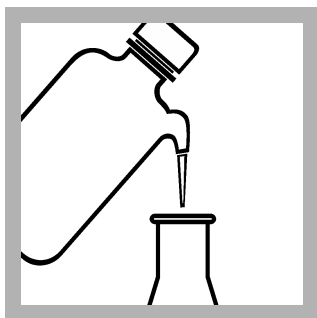
2. Fill a 25-mL buret to the zero mark with the titrant.



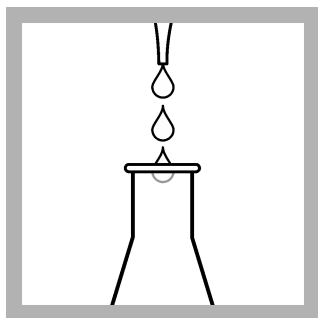
3. Use a graduated cylinder or pipet¹ to measure the sample volume from [Table 1](#) on page 3.



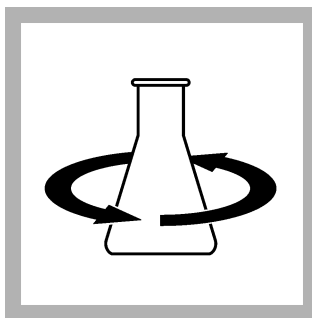
4. Pour the sample into a clean, 250-mL Erlenmeyer flask.



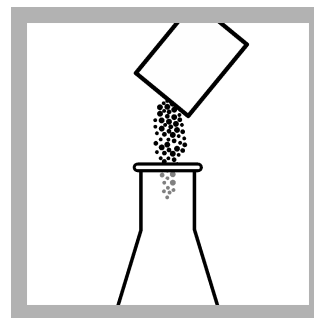
5. If the sample volume is less than 50 mL, dilute to approximately 50 mL with deionized water.



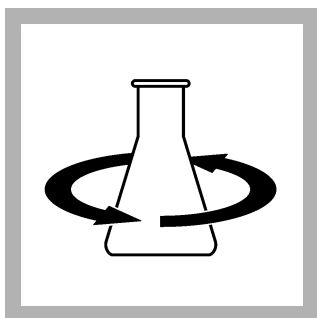
6. Add 1 mL of Hardness 1 Buffer Solution.



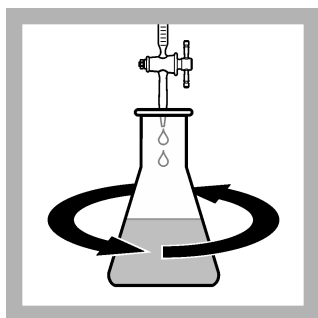
7. Swirl to mix.



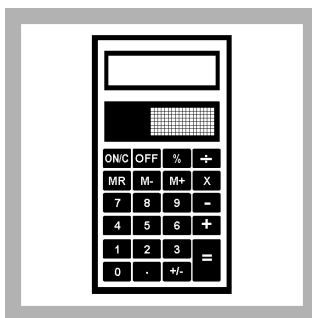
8. Add the contents of one ManVer 2 Hardness Indicator Powder Pillow.



9. Swirl to mix.



10. Put the flask under the buret. Swirl the flask. Add titrant until the color changes from red to pure blue.



11. Use the multiplier in [Table 1](#) on page 3 to calculate the concentration. $\text{mL of titrant} \times \text{multiplier} = \text{mg/L total hardness as CaCO}_3$.

Sample volumes and multipliers

Select a range in [Table 1](#), then read across the table row to find the applicable information for this test. Use the multiplier to calculate the concentration in the test procedure.

¹ Titration accuracy has a direct relation to the accuracy of the sample volume measurement. For smaller volumes, it is recommended to use a pipet to increase accuracy.

Example: A 50-mL sample was titrated with 0.020 N titrant and 12 mL of titrant was used at the endpoint. The concentration is $12 \text{ mL} \times 20 = 240 \text{ mg/L}$ total hardness as CaCO_3 .

Table 1 Sample volumes and multipliers

Range (mg/L)	Sample volume (mL)	Titration—TitraVer hardness	Multiplier
0–500	50	0.020 N	20
400–1000	25	0.020 N	40
1000–2500	10	0.020 N	100
2000–5000	5	0.020 N	200
1000–5000	50	0.200 N	200
4000–10,000	25	0.200 N	400
10,000–25,000	10	0.200 N	1000


Conversions

To change the units or chemical form of the test result, multiply the test result by the factor in [Table 2](#).

Table 2 Conversions

mg/L as CaCO_3 to...	multiply by...	Example
mg/L as Ca	0.40	$1000 \text{ mg/L as CaCO}_3 \times 0.40 = 400 \text{ mg/L Ca}$
mg/L as Mg	0.243	$1000 \text{ mg/L as CaCO}_3 \times 0.243 = 243 \text{ mg/L Mg}$
Grains per gallon (gpg)	0.058	$1000 \text{ mg/L as CaCO}_3 \times 0.058 = 58 \text{ gpg}$
German degrees hardness (Gdh)	0.056	$1000 \text{ mg/L as CaCO}_3 \times 0.056 = 56 \text{ Gdh}$

Interferences

⚠ WARNING	
	Chemical hazard. Potassium cyanide is toxic. Make sure to add potassium cyanide to the sample after the Hardness 1 Buffer Solution has been added. Keep cyanide solutions at more than pH 11 to prevent exposure to hydrogen cyanide gas. Dispose of reacted solutions according to local, state and federal regulations.

An interfering substance can prevent the color change at the titration endpoint. A smaller sample volume can often dilute the interfering substance to a level at which the substance does not interfere. [Table 3](#) shows the substances that can interfere with this test.

Table 3 Interferences

Interfering substance	Interference level
Acidity	10,000 mg/L acidity as CaCO_3 does not interfere.
Alkalinity	10,000 mg/L alkalinity as CaCO_3 does not interfere.
Aluminum	Interferes when the sample contains more than 0.20 mg/L aluminum. Add 0.5 grams of potassium cyanide after the Hardness 1 Buffer Solution during the test procedure to remove the interference from a maximum of 1 mg/L aluminum. As an alternative, add a CDTA powder pillow to remove the interference.
Barium	Barium is titrated at the same time with calcium and interferes with this test, but it is unusual to find high levels of Barium in natural waters.
Chloride	The chloride level in seawater does not interfere. Solutions that are saturated with chloride do not show a sharp endpoint.

Table 3 Interferences (continued)

Interfering substance	Interference level
Cobalt	Interferes directly at all levels. Add 0.5 grams of potassium cyanide after the Hardness 1 Buffer Solution during the test procedure to remove the interference from a maximum of 20 mg/L cobalt. As an alternative, add a CDTA powder pillow to remove the interference.
Copper	Interferes when the sample contains 0.1 mg/L copper. Add 0.5 grams of potassium cyanide after the Hardness 1 Buffer Solution during the test procedure to remove the interference from a maximum of 100 mg/L copper. As an alternative, add a CDTA powder pillow to remove the interference.
Iron	More than 8 mg/L iron causes an orange-red to green endpoint. Results are accurate to 20 mg/L iron with this endpoint. For more accurate endpoints in solutions that have higher levels of iron, use HexaVer Hardness Titrant (CDTA) and not TitraVer Hardness Titrant (EDTA).
Manganese	Interferes when the sample contains more than 5 mg/L manganese. Add a 0.10-gram scoop of Hydroxylamine Hydrochloride Monohydrate to increase the interference level to 200 mg/L manganese.
Nickel	Interferes directly at all levels. Add 0.5 grams of potassium cyanide after the Hardness 1 Buffer Solution during the test procedure to remove the interference from a maximum of 200 mg/L nickel. As an alternative, add a CDTA powder pillow to remove the interference.
Orthophosphate	Forms calcium phosphate and causes a slow endpoint. If sufficient time is given to let the calcium phosphate dissolve during the titration, the orthophosphate will not interfere with the test.
Polyphosphates	Interferes at all levels.
Polyvalent metal ions	Although less common than calcium and magnesium, other polyvalent metal ions are titrated with the calcium and magnesium and are included in the results.
Strontium	Strontium is titrated at the same time with calcium and magnesium and interferes with this test, but it is unusual to find high levels of Strontium in natural waters.
Zinc	Interferes directly and is included in the test result. Add 0.5 grams of potassium cyanide after the Hardness 1 Buffer Solution during the test procedure to remove the interference from a maximum of 100 mg/L zinc. As an alternative, add a CDTA powder pillow to remove the interference.
Highly buffered samples or extreme sample pH	Can prevent the correct pH adjustment (of the sample) by the reagents. Sample pretreatment may be necessary. Before analysis, adjust the pH to 7.

Use CDTA to remove metal interferences

Add one CDTA Magnesium Salt Powder Pillow to remove the interference from metals at or below the levels shown in [Table 4](#). If more than one metal is in the sample at or more than the concentration in [Table 4](#), add an additional CDTA Magnesium Salt Powder Pillow.

The results given with CDTA Magnesium Salt include the hardness from these metals. If the concentration of each metal is known, a correction can be made to get the hardness from calcium and magnesium only. The hardness value from different metal ions is shown in [Table 5](#).

Metal hardness = (mg/L of metal in the sample) x (hardness equivalence factor)

Calcium and magnesium hardness = (total hardness) – (metal hardness)

Table 4 Interference level with one CDTA pillow

Interfering substance	Interference level
Aluminum	50 mg/L
Cobalt	200 mg/L
Copper	100 mg/L
Iron	100 mg/L

Table 4 Interference level with one CDTA pillow (continued)

Interfering substance	Interference level
Manganese	200 mg/L
Nickel	400 mg/L
Zinc	300 mg/L

Table 5 Hardness equivalence factors (mg/L as CaCO₃)

Interfering substance	Hardness equivalence factor
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

Accuracy check

Standard additions method (sample spike)—0.020 N titrant

Use the standard additions method to validate the test procedure, reagents, apparatus, technique and to find if there is an interference in the sample.

Items to collect:

- Calcium Hardness Standard Solution, 10,000 mg/L as CaCO₃, 10-mL Voluette ampule
 - Ampule Breaker
 - Pipet, TenSette, 0.1–1.0 mL and pipet tips
1. Use the test procedure to measure the concentration of the sample with the 0.020 N titrant.
 2. Use a TenSette pipet to add 0.1 mL of the standard solution to the titrated sample.
 3. Titrate the spiked sample to the endpoint. Record the mL of titrant added.
 4. Add one more 0.1-mL addition of the standard solution to the titrated sample.
 5. Titrate the spiked sample to the endpoint. Record the mL of titrant added.
 6. Add one more 0.1-mL addition of the standard solution to the titrated sample.
 7. Titrate the spiked sample to the endpoint. Record the mL of titrant added.
 8. Compare the actual result to the correct result. The correct result for this titration is 1.0 mL of titrant for each 0.1-mL addition of the standard solution. If much more or less titrant was used, there can be a problem with user technique, reagents, apparatus or an interference.

Standard additions method (sample spike)—0.200 N titrant

Use the standard additions method to validate the test procedure, reagents, apparatus, technique and to find if there is an interference in the sample.

Items to collect:

- Calcium Hardness Standard Solution, 10,000 mg/L as CaCO₃, 10-mL Voluette ampule

-
- Ampule Breaker
 - Pipet, TenSette, 0.1–1.0 mL and pipet tips
1. Use the test procedure to measure the concentration of the sample with the 0.200 N titrant.
 2. Use a TenSette pipet to add 1.0 mL of the standard solution to the titrated sample.
 3. Titrate the spiked sample to the endpoint. Record the mL of titrant added.
 4. Add one more 1.0-mL addition of the standard solution to the titrated sample.
 5. Titrate the spiked sample to the endpoint. Record the mL of titrant added.
 6. Add one more 1.0-mL addition of the standard solution to the titrated sample.
 7. Titrate the spiked sample to the endpoint. Record the mL of titrant added.
 8. Compare the actual result to the correct result. The correct result for this titration is 1.0 mL of titrant for each 1.0-mL addition of the standard solution. If much more or less titrant was used, there can be a problem with user technique, reagents, apparatus or an interference.

Standard solution method—0.020 N titrant

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

Items to collect:

- Calcium Chloride Standard Solution, 1000 mg/L as CaCO_3
 - Pipet, TenSette, 1.0–10.0 mL and pipet tips
1. Use the test procedure to measure the concentration of the standard solution. Use 25.0 mL of the standard solution and the 0.020 N titrant.
 2. Compare the actual result to the correct result. The correct result for this titration is 25 mL of titrant.

Standard solution method—0.200 N titrant

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

Items to collect:

- Calcium Hardness Standard Solution, 10,000 mg/L as CaCO_3 , 10-mL Voluette ampule
 - Ampule Breaker
 - Pipet, TenSette, 1.0–10.0 mL and pipet tips
1. Use the test procedure to measure the concentration of the standard solution. Use 10.0 mL of the standard solution and the 0.200 N titrant.
 2. Compare the actual result to the correct result. The correct result for this titration is 10 mL of titrant.

Summary of method

A buffer solution (an organic amine and one of its salts) is added to the sample to adjust the pH to 10.1. An organic dye, calmagite, is then added as the indicator for the test. The organic dye reacts with calcium and magnesium ions to give a red-colored complex. The EDTA (ethylenediaminetetraacetic acid) titrant is added, which reacts with all of the free calcium and magnesium ions in the sample. After the EDTA has reacted with all of the free magnesium ions, the EDTA removes the magnesium ions from the indicator. The indicator color then changes from red to blue.

Consumables and replacement items

Required reagents

Description	Quantity/Test	Unit	Item no.
Hardness (Total) Reagent Set (approximately 100 tests):	—	each	2447600
ManVer 2 Hardness Indicator Powder Pillows	1 pillow	100/pkg	85199
Buffer Solution, Hardness 1	1 mL	1 L	42432
TitraVer® Hardness Titrant, 0.020 N	varies	1 L	20553
Hardness (Total) Reagent Set (approximately 100 tests):	—	each	2447700
ManVer 2 Hardness Indicator Powder Pillows	1 pillow	100/pkg	85199
Buffer Solution, Hardness 1	1 mL	1 L	42432
TitraVer® Hardness Titrant, 0.200 N	varies	500 mL	102149

Required apparatus

Description	Quantity/test	Unit	Item no.
Buret clamp, double	1	each	32800
Buret, Class A, 25 mL	1	each	2636540
Support stand	1	each	56300
Funnel, micro	1	each	2584335
Graduated cylinders—Select one or more for the sample volume:			
Cylinder, graduated, 5 mL	1	each	50837
Cylinder, graduated, 10 mL	1	each	50838
Cylinder, graduated, 25 mL	1	each	50840
Cylinder, graduated, 50 mL	1	each	50841
Cylinder, graduated, 100 mL	1	each	50842
Tensette® pipets and pipet tips—Select one or more for the sample volume:			
Pipet, TenSette®, 0.1–1.0 mL	1	each	1970001
Pipet tips, TenSette® Pipet, 0.1–1.0 mL	varies	50/pkg	2185696
Pipet, TenSette®, 1.0–10.0 mL	1	each	1970010
Pipet tips, TenSette® Pipet, 1.0–10.0 mL	varies	50/pkg	2199796
Flask, Erlenmeyer, 250 mL	1	each	50546

Recommended standards

Description	Unit	Item no.
Calcium Chloride Standard Solution, 1000 mg/L as CaCO ₃	1 L	12153
Calcium Hardness Standard Solution, 10,000 mg/L as CaCO ₃ , 10-mL Voluette ampule	16/pkg	218710

Optional reagents and apparatus

Description	Unit	Item no.
Ampule Breaker, 10-mL Voluette® Ampules	each	2196800
CDTA Magnesium Salt Powder Pillow	100/pkg	1408099

Optional reagents and apparatus (continued)

Description	Unit	Item no.
Delivery tube for Digital Titrator, 90-degree bend	5/pkg	4157800
ManVer Hardness Indicator Solution	100 mL	42532
ManVer 2 Hardness Indicator Powder	113 g	28014
Nitric Acid, concentrated	500 mL	15249
Nitric Acid Solution, 1:1	500 mL	254049
Potassium Cyanide, ACS	100 g	76714
Sampling bottle, with cap, low density polyethylene, 250 mL	12/pkg	2087076
Sodium Hydroxide Solution, 5 N	50 mL	245026
Spoon, measuring, 0.1 g	each	51100
Spoon, measuring, 0.5 g	each	90700
Stir bar, octagonal	each	2095352



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.
On the Worldwide Web – www.hach.com; E-mail – techhelp@hach.com

HACH COMPANY
WORLD HEADQUARTERS
Telephone: (970) 669-3050
FAX: (970) 669-2932