Hardness, Total, Sequential

DOC316.53.01159

Titration Method with EDTA[1,2]

0–25,000 mg/L as $CaCO_3$

Method 8338

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

The first titration gives the results for calcium hardness and the second titration gives total hardness. The difference between the values is the magnesium hardness level. All the concentration results are in mg/L as $CaCO_3$. Refer to Conversions on page 4 for conversions to other units.
As an alternative to the CalVer 2 Calcium Indicator Powder Pillow, use a 0.1-g scoop of CalVer 2 Calcium Indicator Powder.
As an alternative to the ManVer 2 Hardness Indicator Powder Pillow, use 2 drops of Hardness 2 Indicator Solution.
The optional TitraStir Titration Stand can hold the buret and stir the sample.
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
CalVer 2 Calcium Indicator Powder Pillow	1
Potassium Hydroxide Standard Solution, 8 N	1 mL
Hardness 1 Buffer Solution	1 mL
ManVer 2 Hardness Indicator Powder Pillow	1
Sulfuric Acid Standard Solution, 5.25 N	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

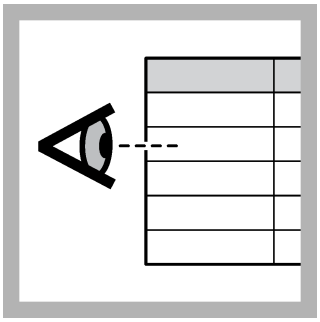
Refer to Consumables and replacement items on page 7 for order information.

Sample collection and storage

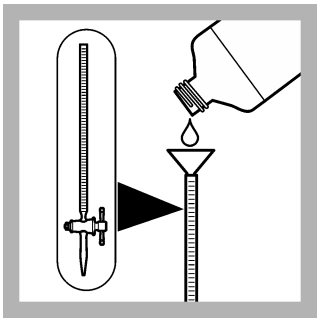
- Collect samples in clean glass or plastic bottles that have been cleaned with a detergent and rinsed with 1:1 nitric acid and deionized water.

- 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 6 months.
- Before analysis, adjust the pH to 7 with Potassium Hydroxide Standard Solution.
- Correct the test result for the dilution caused by the volume additions.

Test procedure

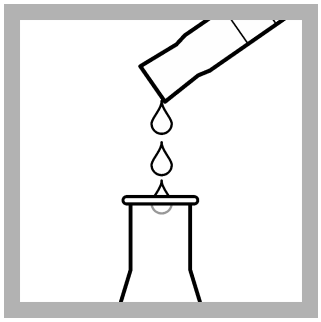


1. Select a sample volume and titrant from Table 1 on page 4.

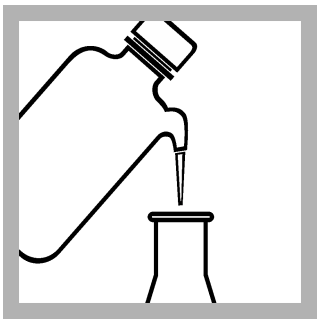


2. Fill a 25-mL buret to the zero mark with the titrant.

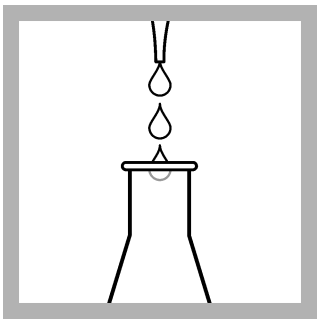
3. Use a graduated cylinder or a pipet[1] to measure the sample volume from Table 1 on page 4.



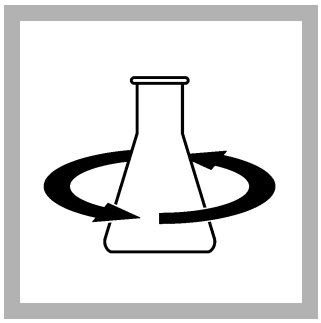
4. Pour the sample into a clean, 250-mL Erlenmeyer flask.



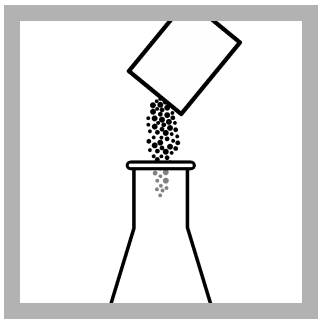
5. If the sample volume is less than 50 mL, dilute to approximately 50 mL with deionized water.



6. Add 1 mL of 8 N Potassium Hydroxide Standard Solution.

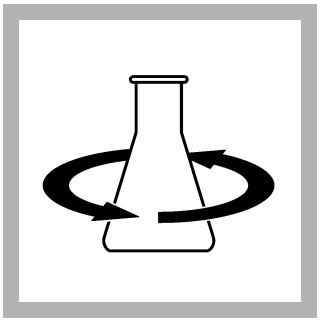


7. Swirl to mix.

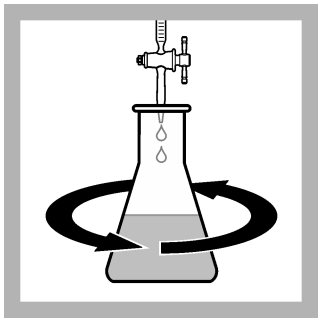


8. Add the contents of one CalVer 2 Calcium Indicator Powder Pillow.

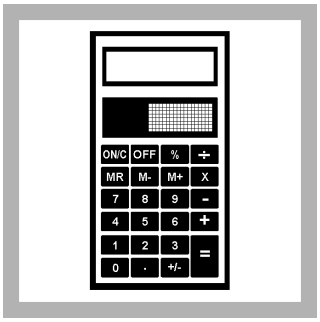
[1] Titration accuracy has a direct relation to the accuracy of the sample volume measurement. For smaller volumes, it is recommended to use a pipet to increase accuracy.



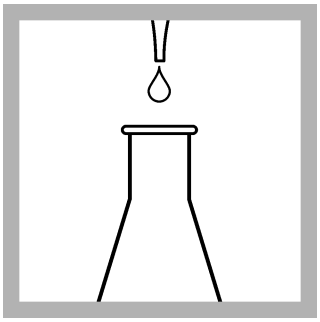
9. Swirl to mix.



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

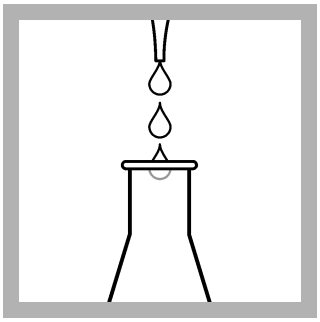


11. Use the multiplier in Table 1 on page 4 to calculate the concentration. mL of titrant × multiplier = mg/L Ca as $CaCO_3$.

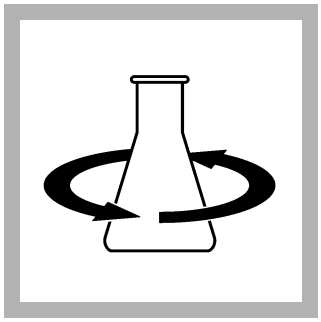


12. Add 5.25 N Sulfuric Acid Standard Solution, 1 drop at a time until the color changes from pure blue to purple and then to red.

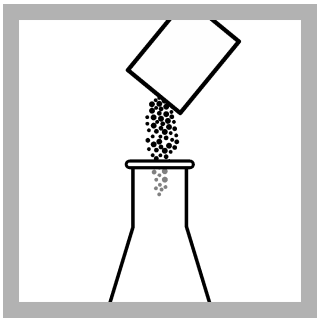
Swirl the flask to make sure that all the precipitated magnesium hydroxide has dissolved.



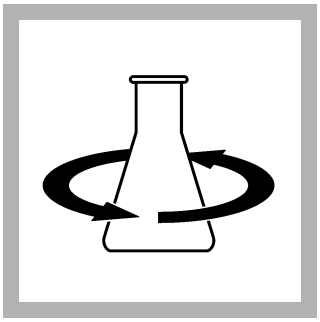
13. Add 1 mL of Hardness 1 Buffer Solution.



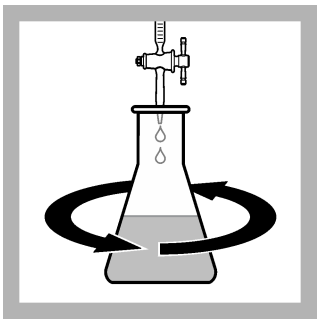
14. Swirl to mix.



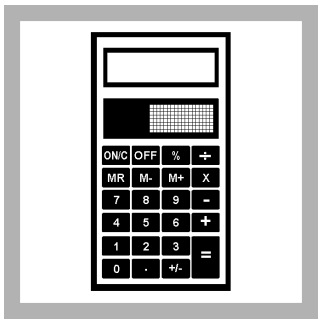
15. Add the contents of one ManVer 2 Hardness Indicator Powder Pillow.



16. Swirl to mix.



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



18. Use the multiplier in Table 1 on page 4 to calculate the concentration. mL of titrant × multiplier = 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.

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 mL × 20 = 240 mg/L Ca as $CaCO_3$.

Table 1 Sample volumes and multipliers

Range (mg/L)	Sample volume (mL)	Titrant—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 mg/L as $CaCO_3$ x 0.40 = 400 mg/L Ca
mg/L as Mg	0.243	1000 mg/L as $CaCO_3$ x 0.243 = 243 mg/L Mg
Grains per gallon (gpg)	0.058	1000 mg/L as $CaCO_3$ x 0.058 = 58 gpg
German degrees hardness (Gdh)	0.056	1000 mg/L as $CaCO_3$ × 0.056 = 56 Gdh

Hardness relationships

- mg/L Mg Hardness as $CaCO_3$ = mg/L Total Hardness as $CaCO_3$ – mg/L Ca Hardness as $CaCO_3$
- mg/L $MgCO_3$= mg/L Mg Hardness as $CaCO_3$ × 0.842
- mg/L Mg = mg/L $MgCO_3$ × 0.29

Interferences

⚠WARNING

Chemical hazard. Do not use potassium cyanide to remove interferences because it will form deadly hydrogen cyanide gas when the sulfuric acid solution is added.

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 at all levels. Add a CDTA powder pillow to remove the interference. Refer to Use CDTA to remove metal interferences on page 5.
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.

Table 3 Interferences (continued)

Interfering substance	Interference level
Chloride	The chloride level in seawater does not interfere. Solutions that are saturated with chloride do not show a sharp endpoint.
Cobalt	Interferes at all levels. Add a CDTA powder pillow to remove the interference. Refer to Use CDTA to remove metal interferences on page 5.
Copper	Interferes when the sample contains 0.10 and 0.20 mg/L copper.
Heavy metals	Some transition and heavy metals react with the indicator and prevent the color change at the end point.
Iron	Iron does not interfere until 15 mg/L. More than this level will cause a red-orange to green endpoint, which is sharp and usable with a maximum of 30 mg/L iron.
Manganese	Interferes when the sample contains more than 20 mg/L manganese. Add a 0.1-gram scoop of hydroxylamine hydrochloride to increase this level to 200 mg/L manganese.
Nickel	Interferes at all levels. Add a CDTA powder pillow to remove the interference. Refer to Use CDTA to remove metal interferences on page 5.
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 interferes with this test, but it is unusual to find high levels of Strontium in natural waters.
Zinc	Interferes at all levels. Add a CDTA powder pillow to remove the interference. Refer to Use CDTA to remove metal interferences on page 5.

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
Manganese	200 mg/L
Nickel	400 mg/L
Zinc	300 mg/L

Table 5 Hardness equivalence factors (mg/L as $CaCO_3$)

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 $CaCO_3$, 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 standard solution. Use 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 $CaCO_3$, 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 standard solution. Use 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

This test procedure is a combination of the calcium and total hardness procedures. Refer to each method for more information.

Consumables and replacement items

Required reagents

Description	Quantity/Test	Unit	Item no.
Calcium and Total Hardness Reagent Set (approximately 100 tests):	—	each	2448200
Buffer Solution, Hardness 1	1 mL	100 mL MDB	42432
CalVer 2 Calcium Indicator Powder Pillows	1 pillow	100/pkg	94799
ManVer 2 Hardness Indicator Powder Pillows	1 pillow	100/pkg	92899
Potassium Hydroxide Standard Solution, 8 N	1 mL	100 mL MDB	28232H
Sulfuric Acid Standard Solution, 5.25 N	varies	100 mL MDB	244932
TitraVer® Hardness Titrant, 0.020 N	varies	1 L	20553
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
Hydroxylamine Hydrochloride	113 g	24614
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
Bottle, sampling, with cap, low density polyethylene, 250 mL	12/pkg	2087076
Spoon, measuring, 0.1 g	each	51100
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
TitraStir® Titration Stand, 115 VAC	each	1940000
TitraStir® Titration Stand, 230 VAC	each	1940010

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