# Hardness, Calcium

DOC316.53.01157

## Titration Method with EDTA[1, 2]

**Method 8222**

**0–25,000 mg/L as $CaCO_3$**

**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

| |
|---|
| Magnesium is not included in the results but must be in the sample for a sharp endpoint. If the sample does not contain magnesium, add 1 to 2 drops of Magnesium Standard Solution, 10-g/L as $CaCO_3$, to the sample before the test is started. |
| As an alternative to the CalVer 2 Calcium Indicator Powder Pillow, use a 0.1-g scoop of CalVer 2 Calcium 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

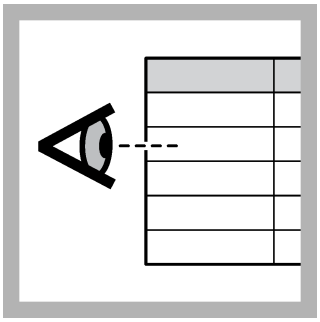
| Description | Quantity |
|---|---|
| CalVer 2 Calcium Indicator Powder Pillow | 1 |
| Potassium Hydroxide Standard Solution, 8 N | 1 mL |
| TitraVer Hardness Titrant (use a concentration that is applicable to the selected sample volume) | varies |
| Buret, Class A, 25 mL | 1 |
| Graduated cylinder (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 6 for order information.

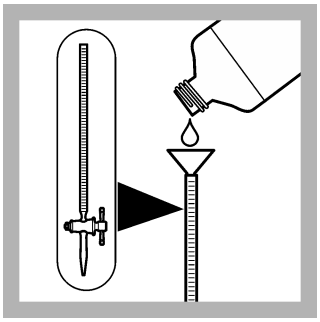
### Sample collection

- 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 room temperature 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

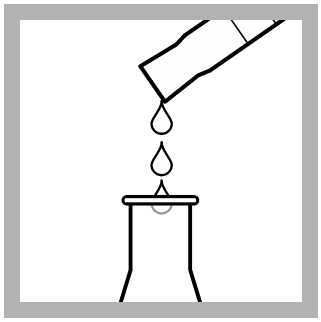


**1.** Select a sample volume and titrant from Table 1 on page 3.

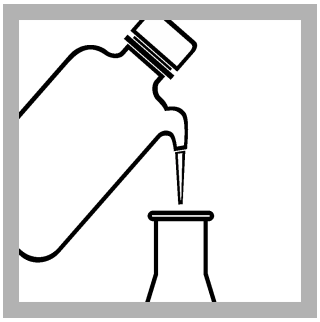


**2.** Fill a 25-mL buret to the zero mark with the titrant.

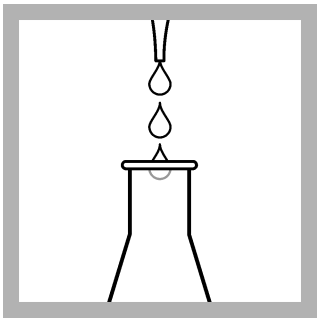
**3.** Use a graduated cylinder or a pipet[1] to measure the sample volume from Table 1 on page 3.



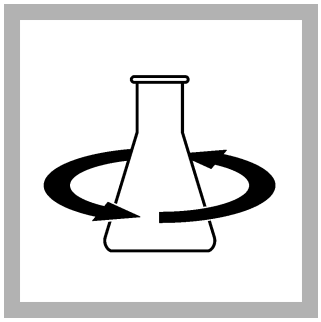
**4.** Pour the sample into a clean, 250-mL Erlenmeyer flask.



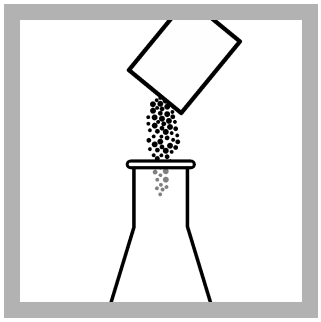
**5.** If the sample volume is less than 50 mL, dilute to approximately 50 mL with deionized water.



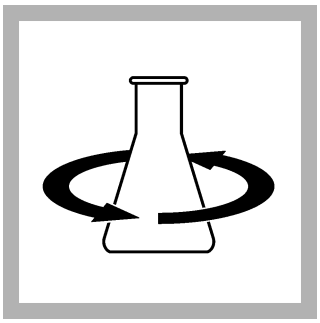
**6.** Add 1 mL of 8 N Potassium Hydroxide Standard Solution.



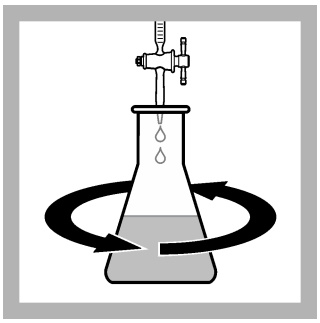
**7.** Swirl to mix.



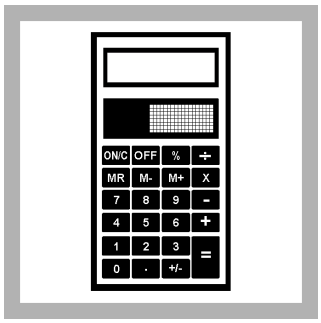
**8.** Add the contents of one CalVer 2 Calcium Indicator Powder Pillow.



**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. mL of titrant × multiplier = mg/L Ca 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 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 units

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 Ca 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 |
| German degrees hardness (Gdh) | 0.056 | 1000 mg/L as $CaCO_3$ × 0.056 = 56 Gdh |
| Grains per gallon (gpg) | 0.058 | 1000 mg/L as $CaCO_3$ x 0.058 = 58 gpg |

## Interferences

**⚠WARNING**

Chemical hazard. Potassium cyanide is toxic. Make sure to add potassium cyanide to the sample after the 8 N Potassium Hydroxide Standard 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 | Causes a slow endpoint. The sample can contain a maximum of 200 mg/L aluminum if sufficient time is given for the color change. |
| 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. |
| Cobalt | Interferes directly. Add 0.5 grams of potassium cyanide after the 8 N Potassium Hydroxide Standard Solution during the test procedure to remove the interference from a maximum of 20 mg/L cobalt. |

**Table 3 Interferences (continued)**

| Interfering substance | Interference level |
|---|---|
| Copper | Interferes at 0.1 mg/L copper. Add 0.5 grams of potassium cyanide after the 8 N Potassium Hydroxide Standard Solution during the test procedure to remove the interference from a maximum of 100 mg/L copper. |
| 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. |
| Magnesium | The formation of magnesium hydroxide at the high test pH prevents interference from 200 mg/L magnesium. Samples with more than 200 mg/L magnesium do not give a distinct endpoint. |
| Manganese | Interferes at more than 5 mg/L manganese. |
| Nickel | Interferes at 0.5 mg/L nickel. Add 0.5 grams of potassium cyanide after the 8 N Potassium Hydroxide Standard Solution during the test procedure to remove the interference from a maximum of 200 mg/L nickel. |
| 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 | Interfere directly and are included in the test result. |
| 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. |
| Temperature | Samples at 20 °C (68 °F) or colder should be titrated slowly near the endpoint to give sufficient time for the color change. |
| Zinc | Interferes at 5 mg/L zinc. Add 0.5 grams of potassium cyanide after the 8 N Potassium Hydroxide Standard Solution during the test procedure to remove the interference from a maximum of 100 mg/L zinc. |
| Highly buffered samples or extreme sample pH | Can prevent the correct pH adjustment (of the sample) by the reagents. Sample pretreatment may be necessary. |

## 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

Potassium hydroxide is added to the sample to adjust the pH to 12 to 13, which causes a magnesium hydroxide precipitate to form. CalVer 2 Calcium Indicator is then added, which reacts with calcium to give a red color. The EDTA titrant is added, which reacts with all the free calcium. After the EDTA has reacted with all of the free calcium ions, the

EDTA removes the calcium 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 (Calcium) Reagent Set (approximately 100 tests): | — | each | 2447000 |
| CalVer 2 Calcium Indicator Powder Pillows | 1 pillow | 100/pkg | 85299 |
| Potassium Hydroxide Standard Solution, 8 N | 1 mL | 100 mL MDB | 28232H |
| 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 |
| Bottle, sampling, with cap, low density polyethylene, 250 mL | 12/pkg | 2087076 |
| CalVer® 2 Calcium Indicator Powder | 113 g | 28114H |
| Magnesium Standard Solution, 10-g/L as $CaCO_3$ | 29 mL | 102233 |

**Optional reagents and apparatus (continued)**

| Description | Unit | Item no. |
|---|---|---|
| Nitric Acid, concentrated | 500 mL | 15249 |
| Nitric Acid Solution, 1:1 | 500 mL | 254049 |
| Potassium Cyanide, ACS | 100 g | 76714 |
| Potassium Hydroxide Standard Solution, 8 N | 500 mL | 28249 |
| Spoon, measuring, 0.1 g | each | 51100 |
| Stir bar, octagonal | each | 2095352 |
| TitraStir® Titration Stand, 115 VAC | each | 1940000 |
| TitraStir® Titration Stand, 230 VAC | each | 1940010 |

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