

## EDTA Titration Method

Method 10253

100 to 200,000 mg/L as CaCO<sub>3</sub>

Digital Titrator

Scope and application: For oil and gas field waters.



### 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<sub>3</sub>, to the sample before the test is started.

As an alternative to the CalVer 2 Calcium Indicator Power Pillow (85299), use two CalVer 2 Calcium Indicator Power Pillows (94799) or 0.1 g scoop of CalVer 2 Calcium Indicator Powder.

The optional TitraStir Titration Stand can hold the Digital Titrator 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 or 2 mL |
| 0.800 M EDTA Titration Cartridge   | 1         |
| Digital Titrator   | 1         |
| Delivery tube for Digital Titrator   | 1         |
| Graduated cylinder (use a size that is applicable to the selected sample volume) | 1         |
| Erlenmeyer flask, 250 mL   | 1         |
| Water, deionized   | varies    |

Refer to [Consumables and replacement items](#) on page 6 for order information.

#### Sample collection and storage

- Collect samples in clean glass or plastic bottles that have been cleaned with 1:1 nitric acid and rinsed with deionized water.
- To preserve samples for later analysis, adjust the sample pH to less than 2 with concentrated nitric acid (approximately 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.

## Determine the sample volume

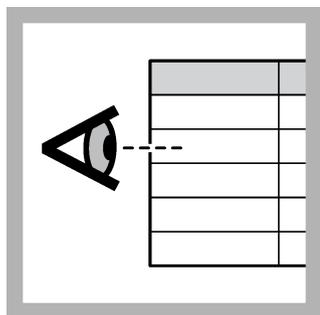
Use the steps that follow to make an estimate of the sample volume to use in the test procedure.

1. Add approximately 75–100 mL of deionized water to a clean titration flask.
2. Use a TenSette pipet to add 0.2 mL of the sample to the titration flask. Swirl to mix.
3. Add 1 mL of 8 N Potassium Hydroxide Standard Solution. Swirl to mix.
4. Add the contents of one CalVer 2 Calcium Indicator Powder Pillow to the flask. Swirl to mix. The sample color becomes red.
5. Titrate the solution quickly with the 0.800 M EDTA Titration Cartridge until the color changes from red to pure blue. Record the number of digits on the counter.
6. Find the sample volume to use in the test procedure from [Table 1](#).
7. Rinse the flask fully with deionized water.

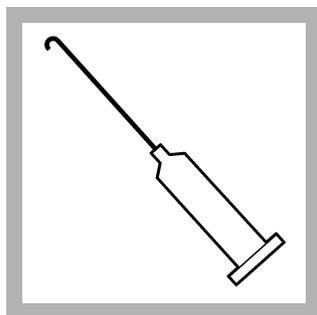
**Table 1 Determine the sample volume**

| Number of digits | Sample volume (mL) |
|------------------|--------------------|
| 200              | 0.2                |
| 100              | 0.5                |
| 50               | 1                  |
| 25               | 2                  |
| 10               | 5                  |
| 5                | 10                 |
| 1                | 20                 |

## Test procedure



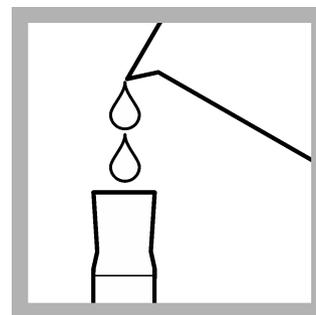
1. Select a sample volume and titration cartridge from [Table 2](#) on page 3. Refer to [Determine the sample volume](#) on page 2.



2. Insert a clean delivery tube into the 0.800 M EDTA Titration Cartridge. Attach the cartridge to the Digital Titrator.



3. Hold the Digital Titrator with the cartridge tip up. Turn the delivery knob to eject air and a few drops of titrant. Reset the counter to zero and clean the tip.



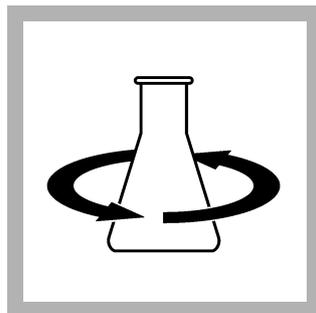
4. Use a graduated cylinder to measure the sample volume from [Table 2](#) on page 3.



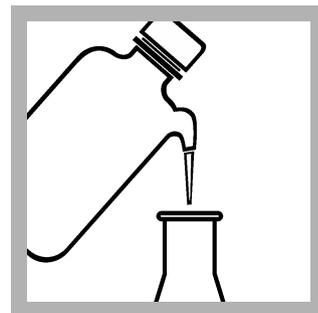
5. Pour the sample into a clean, 250-mL Erlenmeyer flask.



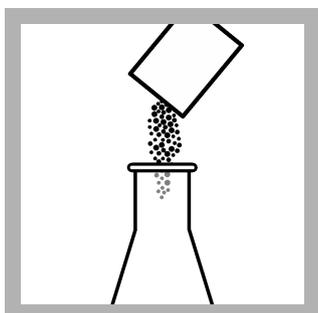
6. If the sample volume is 100 mL, add 2 mL of 8 N Potassium Hydroxide Standard Solution. If the sample volume is 50 mL or less, add 1 mL of 8 N Potassium Hydroxide Standard Solution.



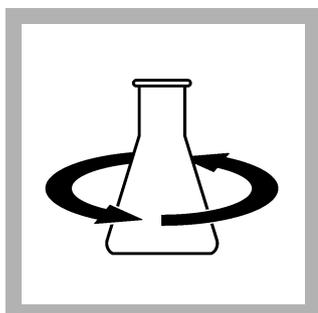
7. Swirl to mix.



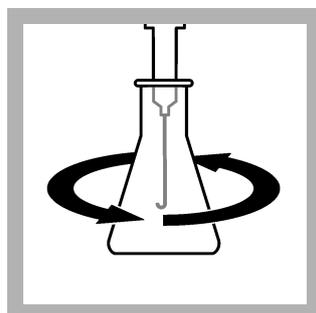
8. If the sample volume is less than 100 mL, dilute to approximately 100 mL with deionized water.



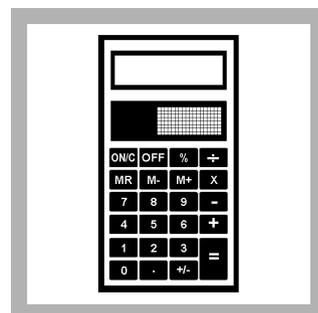
9. Add the contents of one CalVer 2 Calcium Indicator Powder Pillow.



10. Swirl to mix.



11. Put the end of the delivery tube fully into the solution. Swirl the flask. Turn the knob on the Digital Titrator to add titrant to the solution. Continue to swirl the flask. Add titrant until the color changes from red to pure blue. Record the number of digits on the counter.



12. Use the multiplier in [Table 2](#) on page 3 to calculate the concentration. Digits used  $\times$  digit multiplier = mg/L Ca as  $\text{CaCO}_3$ .

## Sample volumes and digit multipliers

Select a range in [Table 2](#), then read across the table row to find the applicable information for this test. Use the digit multiplier to calculate the concentration in the test procedure.

**Note:** Refer to [Determine the sample volume](#) on page 2 to find a sample volume for this test.

**Example:** A 50-mL sample was titrated with the 0.800 M EDTA Titration Cartridge and the counter showed 250 digits at the endpoint. The concentration is 250 digits  $\times$  2 = 500 mg/L Ca as  $\text{CaCO}_3$ .

**Table 2 Sample volumes and digit multipliers**

| Range (mg/L as $\text{CaCO}_3$ ) | Sample volume (mL) | Digit multiplier |
|----------------------------------|--------------------|------------------|
| 100–400                          | 100                | 1                |
| 200–800                          | 50                 | 2                |
| 500–2000                         | 20                 | 5                |
| 1000–4000                        | 10                 | 10               |

**Table 2 Sample volumes and digit multipliers (continued)**

| Range (mg/L as CaCO <sub>3</sub> ) | Sample volume (mL) | Digit multiplier |
|------------------------------------|--------------------|------------------|
| 2000–8000                          | 5                  | 20               |
| 5000–20,000                        | 2                  | 50               |
| 10,000–40,000                      | 1                  | 100              |
| 20,000–80,000                      | 0.5                | 200              |
| 50,000–200,000                     | 0.2                | 500              |

## Conversion units

To change the units or chemical form of the test result, multiply the test result by the factor in [Table 3](#).

**Table 3 Conversions**

| mg/L Ca as CaCO <sub>3</sub> to... | multiply by... | Example   |
|------------------------------------|----------------|---|
| mg/L as Ca                         | 0.40           | 1000 mg/L as CaCO <sub>3</sub> x 0.40 = 400 mg/L Ca |
| German degrees hardness (Gdh)      | 0.056          | 1000 mg/L as CaCO <sub>3</sub> x 0.056 = 56 Gdh     |
| Grains per gallon (gpg)            | 0.058          | 1000 mg/L as CaCO <sub>3</sub> x 0.058 = 58 gpg     |

## Interferences

| <b>⚠ WARNING</b>   |  |
|--|--|
|  | 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 4](#) shows the substances that can interfere with this test.

**Table 4 Interferences**

| Interfering substance | Interference level  |
|-----------------------|---|
| Acidity               | 10,000 mg/L acidity as CaCO <sub>3</sub> does not interfere.  |
| Alkalinity            | 10,000 mg/L alkalinity as CaCO <sub>3</sub> 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                | Interferes directly and is included in the test result. Most produced and flowback water samples contain barium at high concentrations. If the barium concentration is known, it can be subtracted from the calcium test result. Multiply the barium concentration as mg/L Ba by 0.729 to get mg/L Ba as CaCO <sub>3</sub> , then subtract this number from the calcium as CaCO <sub>3</sub> test result. |
| Chloride              | The chloride level in seawater does not interfere. Solutions that are saturated with chloride do not show a sharp endpoint.   |
| Cobalt                | Interferes directly and is included in the test result. 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.   |
| 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.   |

**Table 4 Interferences (continued)**

| Interfering substance                        | Interference level   |
|--|--|
| 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. Most produced and flowback water samples contain iron at very high concentrations. Use a small sample volume to decrease the iron interference when the sample contains more than 100 mg/L iron. If the iron concentration in a small sample volume is more than 100 mg/L, add one CDTA powder pillow to decrease the interference. |
| 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                                    | Interferes directly and is included in the test result. Most produced and flowback water samples contain strontium at high concentrations. If the strontium concentration is known, it can be subtracted from the calcium test result. Multiply the strontium concentration as mg/L Sr by 1.142 to get mg/L Sr as CaCO <sub>3</sub> , then subtract this number from the calcium as CaCO <sub>3</sub> test result.   |
| 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)

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 Voluette Ampule Standard Solution, 10,000-mg/L as CaCO<sub>3</sub>
- Ampule Breaker
- Pipet, TenSette, 0.1–1.0 mL and pipet tips

1. Use the test procedure to measure the concentration of the sample.
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 number of digits on the counter.
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 number of digits on the counter.
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 number of digits on the counter.
8. Compare the actual result to the correct result. The correct result for this titration is 10 digits of the 0.800 M EDTA Titration Cartridge 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.

## 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, barium (as long as both strontium and calcium are present) and strontium in the sample. 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. |
|---|---------------|------------|----------|
| Calcium Hardness Reagent Set, HR, includes: | —             | each       | 2447500  |
| CalVer 2 Calcium Indicator Powder Pillows   | 1             | 100/pkg    | 85299    |
| Potassium Hydroxide Standard Solution, 8 N  | 1–2 mL        | 100 mL MDB | 28232H   |
| EDTA titration cartridge, 0.800 M           | varies        | each       | 1439901  |
| Water, deionized                            | varies        | 4 L        | 27256    |

### Required apparatus

| Description   | Quantity/test | Unit   | Item no. |
|---|---------------|--------|----------|
| 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    |
| Digital Titrator  | 1             | each   | 1690001  |
| Delivery tube for Digital Titrator, J-hook tip                | 1             | 5/pkg  | 1720500  |
| Flask, Erlenmeyer, 250 mL                                     | 1             | each   | 50546    |
| Pipet, TenSette <sup>®</sup> , 0.1–1.0 mL                     | 1             | each   | 1970001  |
| Pipet tips, for TenSette <sup>®</sup> Pipet, 0.1–1.0 mL       | 1             | 50/pkg | 2185696  |

### Recommended standards

| Description  | Unit   | Item no. |
|--|--------|----------|
| Calcium Hardness Standard Solution, 10,000-mg/L as CaCO <sub>3</sub> , 10-mL Voluette ampule | 16/pkg | 218710   |
| Hardness Quality Control Standard, high range  | 500 mL | 2833349  |

### Optional reagents and apparatus

| Description   | Unit    | Item no. |
|---|---------|----------|
| Ampule Breaker, 10-mL Voluette <sup>®</sup> Ampules                                       | each    | 2196800  |
| CalVer <sup>®</sup> 2 Calcium Indicator Powder  | 113 g   | 28114H   |
| CDTA Magnesium Salt Powder Pillow   | 100/pkg | 1408099  |
| Delivery tube for Digital Titrator, 90-degree bend for use with TitraStir Titration Stand | 5/pkg   | 4157800  |

**Optional reagents and apparatus (continued)**

| <b>Description</b>  | <b>Unit</b> | <b>Item no.</b> |
|---|-------------|-----------------|
| Magnesium Standard Solution, 10 g/L as CaCO <sub>3</sub>    | 29 mL       | 102233          |
| Nitric Acid, concentrated                                   | 500 mL      | 15249           |
| Nitric Acid Solution, 1:1                                   | 500 mL      | 254049          |
| Pipet filler, safety bulb                                   | each        | 1465100         |
| Pipet, volumetric, Class A, 10 mL                           | each        | 1451538         |
| Pipet, volumetric Class A, 20 mL                            | each        | 1451520         |
| Pipet, volumetric, Class A, 25 mL                           | each        | 1451540         |
| Potassium Cyanide, ACS                                      | 100 g       | 76714           |
| Potassium Hydroxide, 8 N                                    | 500 mL      | 28249           |
| Sampling bottle with cap, low density polyethylene, 500 mL  | 12/pkg      | 2087079         |
| Sampling bottle, with cap, low density polyethylene, 250 mL | 12/pkg      | 2087076         |
| Spoon, measuring, 0.1 g                                     | each        | 51100           |
| Stir bar, octagonal   | each        | 2095352         |
| TitraStir <sup>®</sup> Titration Stand, 115 VAC             | each        | 1940000         |
| TitraStir <sup>®</sup> Titration Stand, 230 VAC             | each        | 1940010         |



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