Hardness, Calcium

DOC316.53.01318

EDTA Titration Method

Method 10253

100 to 200,000 mg/L as $CaCO_3$

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 $CaCO_3$, 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.

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Determine the sample volume

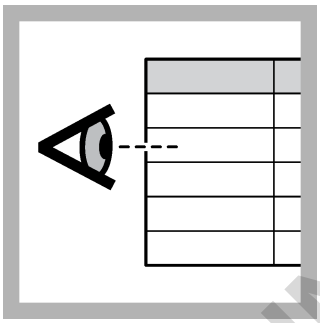
Use the steps that follow to make an estimate of the sample volume to use in the test procedure.

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.

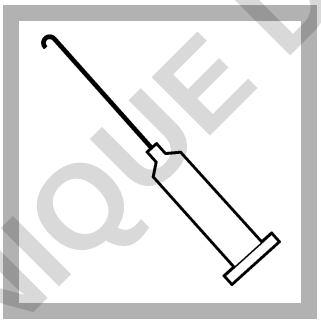
Table 1 Determine the sample volume

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

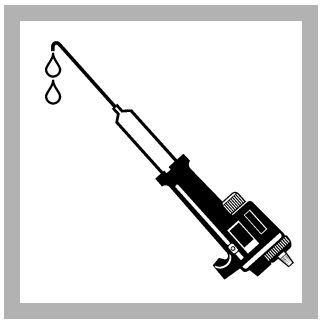
Test procedure



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.

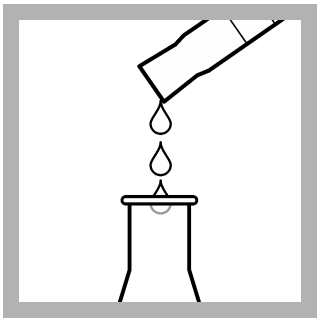


3. Hold the Digital Titrator with the cartridge tip up. Turn the delivery knob to eject air and a few drops of titrant. Reset the counter to zero and clean the tip.

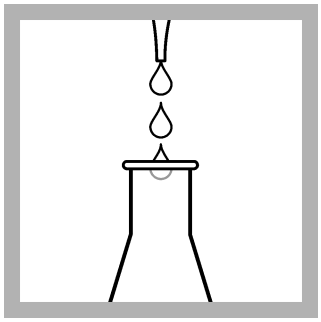


4. Use a graduated cylinder to measure the sample volume from Table 2 on page 3.

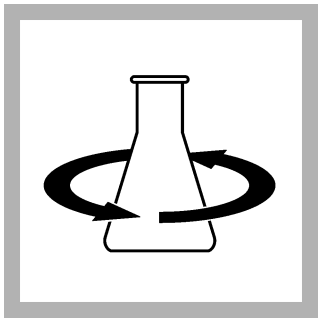
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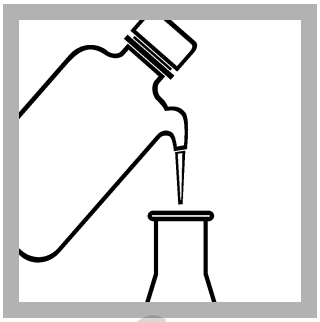
5. Pour the sample into a clean, 250-mL Erlenmeyer flask.



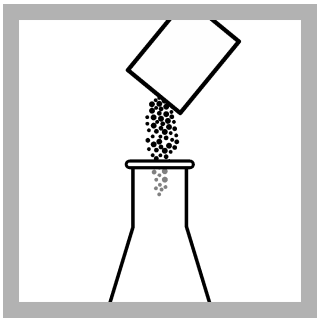
6. If the sample volume is 100 mL, add 2 mL of 8 N Potassium Hydroxide Standard Solution. If the sample volume is 50 mL or less, add 1 mL of 8 N Potassium Hydroxide Standard Solution.



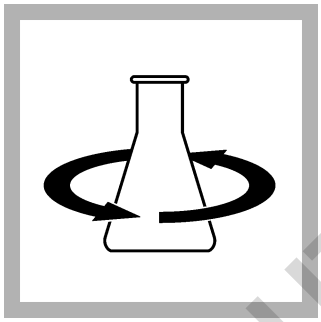
7. Swirl to mix.



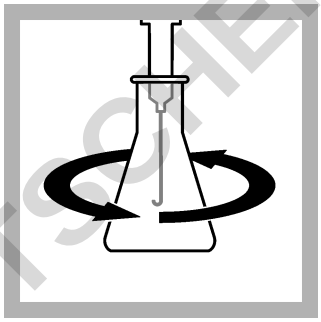
8. If the sample volume is less than 100 mL, dilute to approximately 100 mL with deionized water.



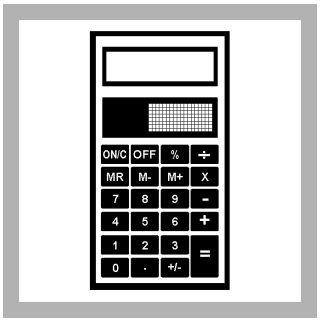
9. Add the contents of one CalVer 2 Calcium Indicator Powder Pillow.



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 × digit multiplier = mg/L Ca as $CaCO_3$.

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 x 2 = 500 mg/L Ca as $CaCO_3$.

Table 2 Sample volumes and digit multipliers

Range (mg/L as $CaCO_3$)	Sample volume (mL)	Digit multiplier
100–400	100	1
200–800	50	2
500–2000	20	5
1000–4000	10	10

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Table 2 Sample volumes and digit multipliers (continued)

Range (mg/L as $CaCO_3$)	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 $CaCO_3$ 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 4 shows the substances that can interfere with this test.

Table 4 Interferences

Interfering substance	Interference level
Acidity	10,000 mg/L acidity as $CaCO_3$ 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	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 $CaCO_3$, then subtract this number from the calcium as $CaCO_3$ 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.

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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 $CaCO_3$, then subtract this number from the calcium as $CaCO_3$ 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 $CaCO_3$
- 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.

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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®, 0.1–1.0 mL	1	each	1970001
Pipet tips, for TenSette® 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 $CaCO_3$, 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® Ampules	each	2196800
CalVer® 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

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Optional reagents and apparatus (continued)

Description	Unit	Item no.
Magnesium Standard Solution, 10 g/L as $CaCO_3$	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® Titration Stand, 115 VAC	each	1940000
TitraStir® Titration Stand, 230 VAC	each	1940010

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