Hardness, Total

DOC316.53.01317

EDTA Titration Method

Method 10247

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

Digital Titrator

Scope and application: For oil and gas field waters.

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.
As an alternative to stirring by hand, use the TitraStir Titration Stand to 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
ManVer 2 Hardness Indicator Powder Pillow	1
Hardness 1 Buffer Solution	2 mL
0.800 M EDTA titration cartridge	1
Digital Titrator	1
Delivery tube for Digital Titrator	1
Graduated cylinder (size varies with 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 5 N sodium 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.

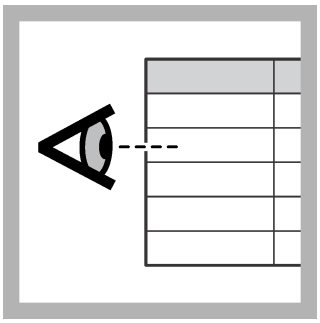
1. Add approximately 75–100 mL of deionized water to a clean titration flask.
2. Use a TenSette pipet to add 0.2 mL of the sample to the titration flask. Swirl to mix.

3. Add 1 mL of Hardness 1 Buffer Solution. Swirl to mix.
4. Add the contents of one ManVer 2 Hardness 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.

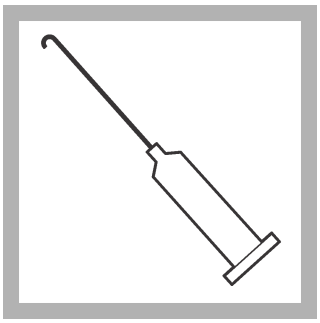
Table 1 Determine the sample volume

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

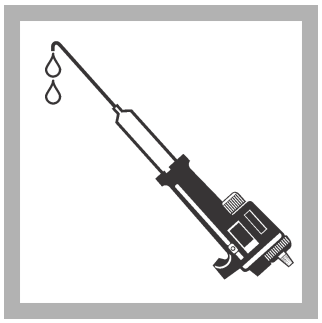
Test procedure



1. Select a sample volume and titration cartridge from Table 2 on page 3. Refer to Determine the sample volume on page 1.

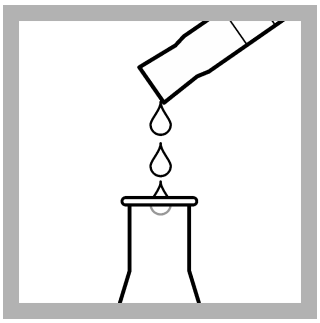


2. Insert a clean delivery tube into the 0.800 M EDTA Titration Cartridge. Attach the cartridge to the Digital Titrator.

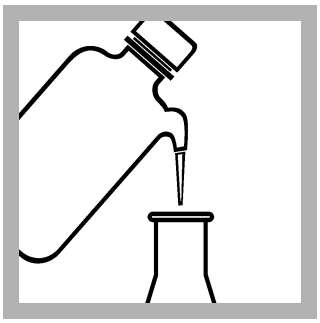


3. Hold the Digital Titrator vertically with the cartridge tip up. Turn the delivery knob to eject air and a few drops of titrant. Reset the counter to zero and clean the tip.

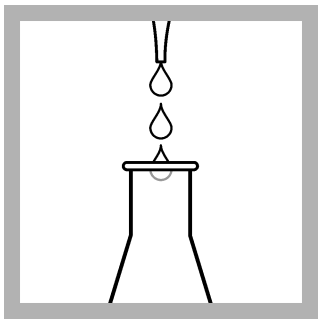
4. Use a graduated cylinder to measure the sample volume from Table 2 on page 3.



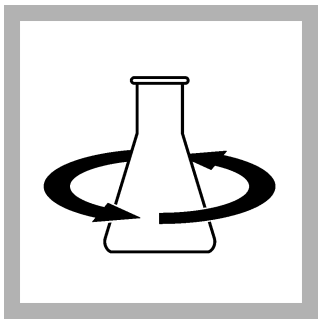
5. Pour the sample into a clean, 250-mL Erlenmeyer flask.



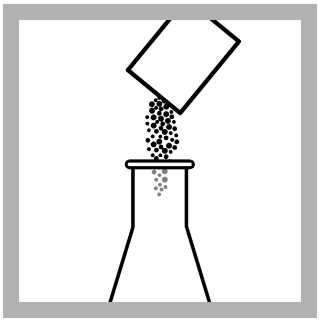
6. If the sample volume is less than 100 mL, dilute to approximately 100 mL with deionized water.



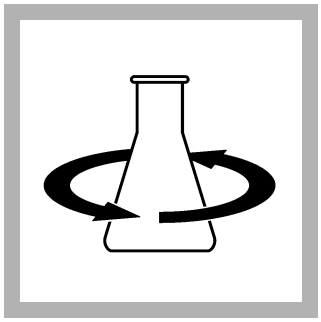
7. Add 2 mL of Hardness 1 Buffer Solution.



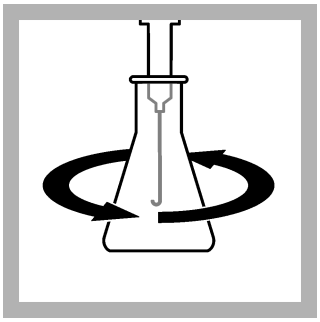
8. Swirl to mix.



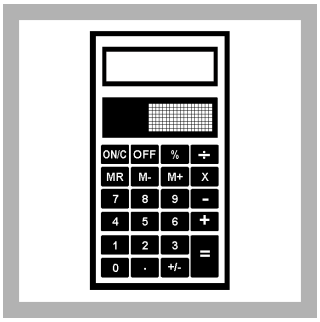
9. Add the contents of one ManVer 2 Hardness Indicator Powder Pillow.



10. Swirl to mix.



11. Put the delivery tube point fully into the solution and swirl the flask. Turn the knob on the Digital Titrator to add titrant to the solution. Continue to swirl the flask and 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 total hardness as $CaCO_3$

Sample volumes and digit multipliers

Select a range in Table 2, then read across to find the applicable information for this test. Use the digit multiplier to calculate the concentration in the test procedure.

Example: A 50-mL sample was titrated and the counter showed 250 digits at the endpoint. The concentration is: 250 digits x 2 = 500 mg/L total hardness 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
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

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. Refer to Use CDTA to remove metal interferences on page 5.
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 hardness 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 total hardness 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 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. Refer to Use CDTA to remove metal interferences on page 5.
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. Refer to Use CDTA to remove metal interferences on page 5.
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. Refer to Use CDTA to remove metal interferences on page 5.
Manganese	Interferes when the sample contains more than 5 mg/L manganese. As an alternative, add a CDTA powder pillow to remove the interference. Refer to Use CDTA to remove metal interferences on page 5.
Nickel	Interferes when the sample contains 0.5 mg/L nickel. 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. 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	Interfere directly and are included in the test result.
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	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 hardness 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 total hardness as $CaCO_3$ test result.

Table 3 Interferences (continued)

Interfering substance	Interference level
Zinc	Interferes at 5 mg/L zinc. 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. Refer to Use CDTA to remove metal interferences on page 5.
Highly buffered samples or extreme sample pH	Can prevent the correct pH adjustment of the sample by the reagents. Sample pre-treatment may be necessary.

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)

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:

- 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.

Standard solution method

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 $CaCO_3$

1. Use the test procedure to measure the concentration of the standard solution. Use 20-mL of the prepared standard solution.
2. Compare the actual result to the correct result. If much more or less titrant was used, there can be a problem with user technique, reagents or apparatus.

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, magnesium, barium and strontium 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.
Total Hardness Reagent Set, HR	—	each	2448100
ManVer 2 Hardness Indicator Powder Pillows	1	100/pkg	85199
Buffer Solution, Hardness 1	2 mL	100 mL MDB	42432
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 based on 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 Chloride Standard Solution, 1000-mg/L as $CaCO_3$	1 L	12153
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
Hardness 2 Indicator Solution	100 mL	42532
ManVer 2 Hardness Indicator Powder	113 g	28014
CDTA Magnesium Salt Powder Pillow	100/pkg	1408099
Nitric Acid, concentrated	500 mL	15249
Nitric Acid Solution, 1:1	500 mL	254049
Potassium Cyanide, ACS	100 g	76714
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
Delivery tube for Digital Titrator, 90-degree bend for use with TitraStir Titration Stand	5/pkg	4157800

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12/2014, Edition 2