Hardness, Total

DOC316.53.01176

Titration Method with EDTA **Method 8213**

10–4000 mg/L as $CaCO_3$ **Digital Titrator**

Scope and application: For water, wastewater and seawater.

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.
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

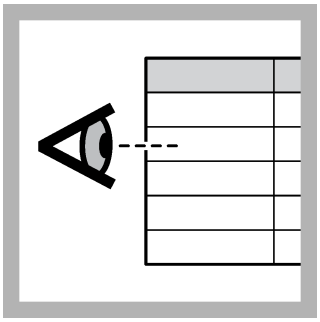
Description	Quantity
ManVer 2 Hardness Indicator Powder Pillow	1
Hardness 1 Buffer Solution	2 mL
EDTA Titration Cartridge (refer to Sample volumes and digit multipliers on page 3)	1
Digital Titrator	1
Delivery tube for Digital Titrator	1
Graduated cylinder (use a size that is applicable to the selected sample volume)	1
Erlenmeyer flask, 250 mL	1
Water, deionized	varies

Refer to Consumables and replacement items on page 6 for order information.

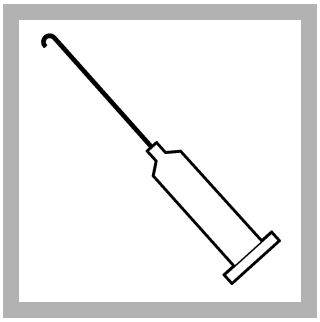
Sample collection and storage

- Collect samples in clean glass or plastic bottles that have been cleaned with 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 7 days.
- Before analysis, adjust the pH to 7 with sodium hydroxide solution.
- Correct the test result for the dilution caused by the volume additions.

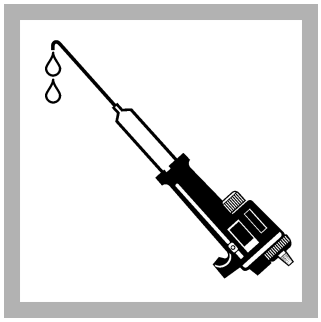
Test procedure



1. Select a sample volume and titration cartridge from Table 1 on page 3.

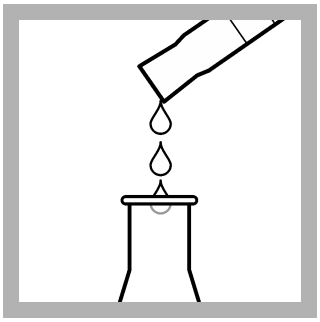


2. Insert a clean delivery tube into the digital titration cartridge. Attach the cartridge to the Digital Titrator.

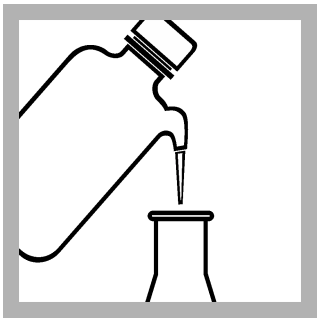


3. Hold the Digital Titrator with the cartridge tip up. Turn the delivery knob to eject air and a few drops of titrant. Reset the counter to zero and clean the tip.

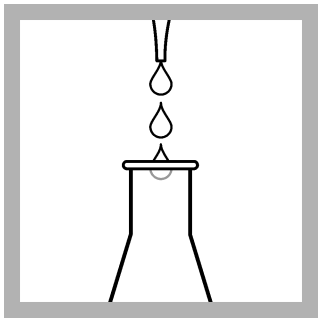
4. Use a graduated cylinder or a pipet[1] to measure the sample volume from Table 1 on page 3.



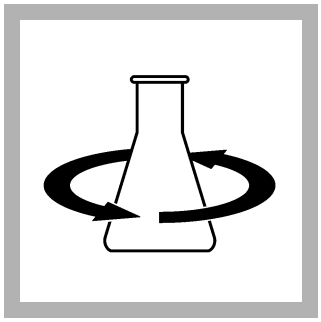
5. Pour the sample into a clean, 250-mL Erlenmeyer flask.



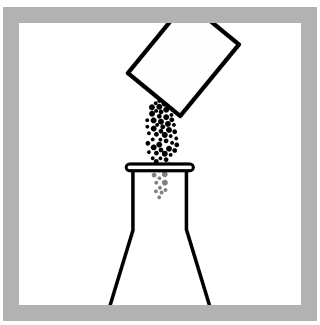
6. If the sample volume is less than 100 mL, dilute to approximately 100 mL with deionized water.



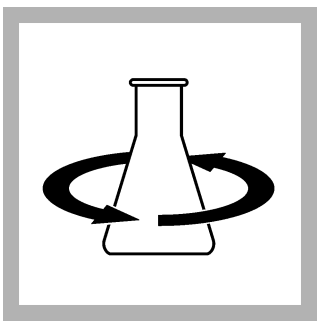
7. Add 2 mL of Hardness 1 Buffer Solution.



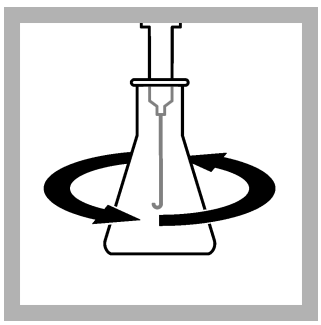
8. Swirl to mix.



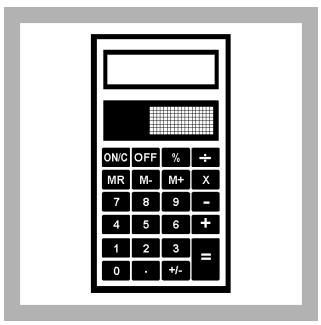
9. Add the contents of one ManVer 2 Hardness Indicator Powder Pillow.



10. Swirl to mix.



11. Put the 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 1 on page 3 to calculate the concentration. Digits used × digit multiplier = mg/L (or Gdh) total hardness as $CaCO_3$.

[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.

Sample volumes and digit multipliers

Select a range in Table 1 or Table 2 as applicable, 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.

Example: A 50-mL sample was titrated with 0.800 M EDTA titration cartridge and the counter showed 250 digits at the endpoint. The concentration is 250 digits × 2.0 = 500 mg/L as $CaCO_3$ (or with the 0.714 M EDTA titration cartridge, 250 x 0.1 = 25 mg/L Gdh).

Table 1 Sample volumes and digit multipliers—mg/L

Range (mg/L as $CaCO_3$)	Sample volume (mL)	Titration cartridge	Digit multiplier
10–40	100	0.0800	0.1
40–160	25	0.0800	0.4
100–400	100	0.800	1.0
200–800	50	0.800	2.0
500–2000	20	0.800	5.0
1000–4000	10	0.800	10.0

Table 2 Sample volumes and digit multipliers—Gdh

Range (Gdh as $CaCO_3$)	Sample volume (mL)	Titration cartridge	Digit multiplier
1–4	100	0.1428	0.01
4–16	25	0.1428	0.04
10–40	50	0.714	0.1
25–100	20	0.714	0.25
> 100	10	0.714	0.5

Conversions 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 Total Hardness as $CaCO_3$ to...	multiply by...	Example
mg/L Total Hardness 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
mg/L Total Hardness as Mg	0.243	1000 mg/L as $CaCO_3$ x 0.243 = 243 mg/L Mg

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. 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 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	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	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 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.
Manganese	Interferes when the sample contains more than 5 mg/L manganese.
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	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.

Table 4 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 pretreatment may be necessary. Before analysis, adjust the pH to 7.

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 5. If more than one metal is in the sample at or more than the concentration in Table 5, 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 6.

Metal hardness = (mg/L of metal in the sample) x (hardness equivalence factor)

Calcium and magnesium hardness = (total hardness) – (metal hardness)

Table 5 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 6 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 0.800 M titration cartridge or 100 digits of 0.0800 titration cartridge (11 digits of 0.714 M or 56 digits of 0.1428 M 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 solution method

Use the standard solution method to validate the test procedure, reagents, apparatus and technique.

- Calcium Chloride Standard Solution, 1000-mg/L as $CaCO_3$
- Hardness 1 Buffer Solution
- ManVer 2 Hardness Indicator Powder Pillow
- 20-mL volumetric pipet, Class A and pipet filler safety bulb
- 250-mL Erlenmeyer flask
- Deionized water

1. Use a pipet to add 20.0 mL of the calcium chloride standard solution to a 250-mL Erlenmeyer flask.
2. Dilute the standard solution to approximately 100 mL with deionized water.
3. Add one Hardness 1 Buffer Solution and one ManVer 2 Hardness Indicator Powder Pillow. Swirl to mix.
4. Titrate the prepared standard solution to the endpoint. Calculate the concentration of the standard solution. The correct result is 1000 mg/L or 55.9 Gdh as $CaCO_3$.
5. 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 and magnesium 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.
Reagent set, 10–160 mg/L range (approximately 100 tests):	—	each	2448000
ManVer 2 Hardness Indicator Powder Pillows	1 pillow	100/pkg	85199

Consumables and replacement items (continued)

Description	Quantity/Test	Unit	Item no.
Buffer Solution, Hardness 1	1 mL	100 mL MDB	42432
EDTA Titration Cartridge, 0.0800 M	varies	each	1436401
Reagent set, 100–4000 mg/L range (approximately 100 tests):	—	each	2448100
ManVer 2 Hardness Indicator Powder Pillows	1 pillow	100/pkg	85199
Buffer Solution, Hardness 1	1 mL	100 mL MDB	42432
EDTA Titration Cartridge, 0.800 M	varies	each	1439901
Reagent set, 1–16 G.d.h. range (approximately 100 tests):	—	each	2447800
ManVer 2 Hardness Indicator Powder Pillows	1 pillow	100/pkg	85199
Buffer Solution, Hardness 1	1 mL	100 mL MDB	42432
EDTA Titration Cartridge, 0.1428 M	varies	each	1496001
Reagent set, 10–100+ G.d.h. range (approximately 100 tests):	—	each	2447900
ManVer 2 Hardness Indicator Powder Pillows	1 pillow	100/pkg	85199
Buffer Solution, Hardness 1	1 mL	100 mL MDB	42432
EDTA Titration Cartridge, 0.714 M	varies	each	1495901

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 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
Hardness Quality Control Standard, high range	500 mL	2833349
Hardness Quality Control Standard, low range	500 mL	2833449

Optional reagents and apparatus

Description	Unit	Item no.
Ampule Breaker, 10-mL Voluette® Ampules	each	2196800
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
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
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
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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