

## Iodometric Method<sup>1</sup>

**Method 10100****50–150 g/L or 5–15% as Cl<sub>2</sub> (HR)****Digital Titrator**

**Scope and application:** For concentrated liquid bleach (sodium hypochlorite, soda bleach) used as a disinfectant in drinking water or wastewater treatment

<sup>1</sup> Adapted from ASTM method D2022.



## Test preparation

### Before starting

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

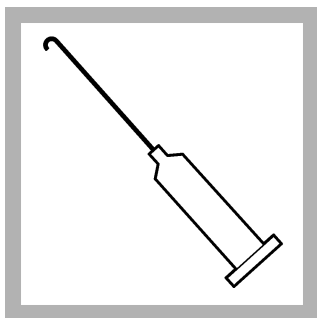
Description	Quantity
HR Hypochlorite (Bleach) Reagent Set, 5–15% as Cl <sub>2</sub>	1
Pipet, TenSette <sup>®</sup> , 0.1–1.0 mL	1
Pipet tips, for TenSette <sup>®</sup> Pipet, 0.1–1.0 mL	1
Digital Titrator	1
Delivery tube for Digital Titrator	1
Erlenmeyer flask, 125 mL	1
Water, deionized	varies

Refer to [Consumables and replacement items](#) on page 4 for order information.

### Sample collection

- Collect samples in clean glass bottles.
- Analyze the samples as soon as possible for best results.
- Prevent exposure of the sample to heat or light.
- If prompt analysis is not possible, keep the samples in a cool and dark location.

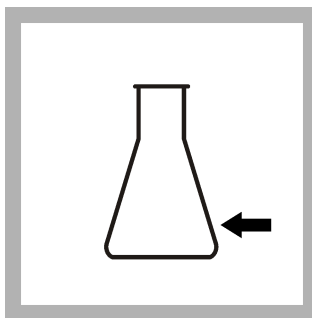
## Test procedure



1. Insert a clean delivery tube into the 2.26 N Sodium Thiosulfate Titrant Solution cartridge. Attach the cartridge to the Digital Titrator.

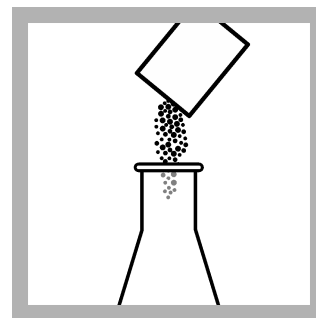


2. Hold the Digital Titrator with the cartridge tip up. Turn the delivery knob to eject air and a few drops of titrant. Reset the counter to zero and clean the tip.

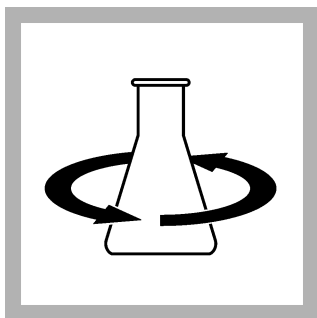


3. Fill a clean 125-mL Erlenmeyer flask to approximately the 75-mL mark with deionized water or tap water.

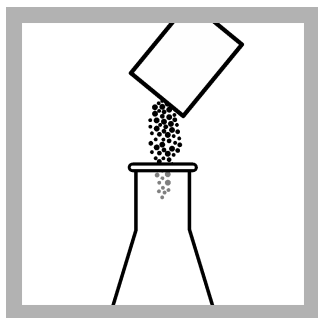
**Note:** The level of residual chlorine in tap water will not cause interference with the test.



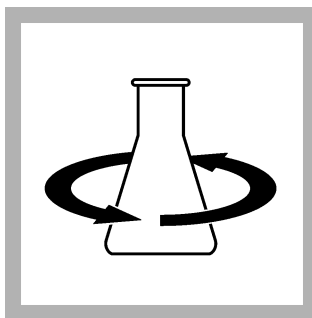
4. Add the contents of one Potassium Iodide Powder Pillow.



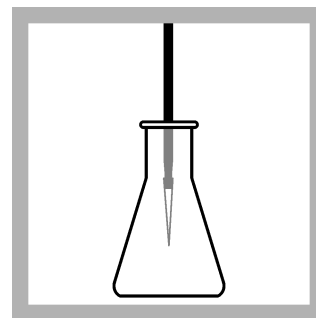
5. Swirl to mix.



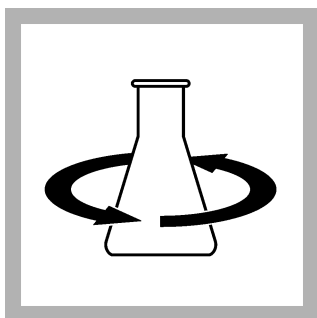
6. Add the contents of one Acid Reagent Powder Pillow.



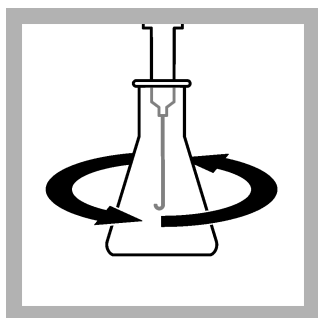
7. Swirl to mix.



8. Use a TenSette pipet with a new tip to add 0.2 mL of bleach sample to the flask. Make sure to add the sample below the solution level.



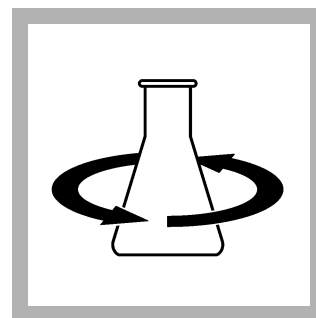
9. Swirl to mix. The color of the solution changes to dark brown.



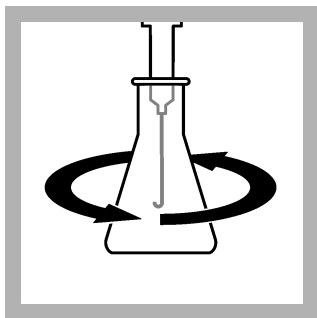
10. Put the end of the delivery tube fully into the solution. Swirl the flask. Turn the knob on the Digital Titrator to add titrant to the solution. Continue to swirl the flask. Add titrant until the color changes to pale yellow.



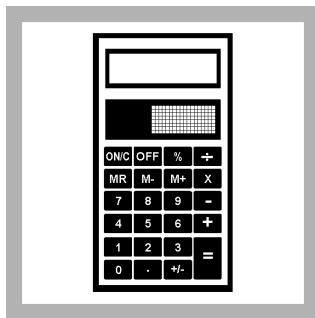
11. Add one dropperful of Starch Indicator Solution.



12. Swirl to mix. The color of the solution changes to dark blue or green.



13. 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 dark blue to colorless. Record the number of digits on the counter.



14. Calculate the concentration.  
 Digits used  $\times 0.5 = \text{g/L chlorine}$ .  
 $\text{g/L chlorine} \times 0.10 = \%$  chlorine by volume ("trade percent").

## Interferences

The test determines the hypochlorite ion ( $\text{ClO}^-$ ) and also the chlorite ion ( $\text{ClO}_2^-$ ). However, the chlorite level in commercial bleach is not important (typically less than 0.2%). Other interferences are unlikely.

Interfering substance	Interference level
Caustic agent	A high level of caustic can cause low results. To remove the interferences: <ol style="list-style-type: none"> <li>1. After the Acid Reagent Powder Pillow is added, examine the pH of the solution with pH Paper. The pH must be less than 3.</li> <li>2. If the pH is not less than 3, add more Acid Reagent, one pillow at a time, until the pH of the solution is below 3.</li> </ol>
Temperature	For most accurate results, the temperature of the dilution water must be less than 20 °C (68 °F).

## Accuracy check

### Standard solution method

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

**Note:** The strength of the Sodium Thiosulfate Standard Solution is validated with Potassium Iodide-Iodate Standard Solution. It is recommended to validate the reagent accuracy with each new lot of reagents.

Items to collect:

- Potassium Iodide-Iodate Standard Solution, 0.0125 N
  - Potassium Iodide Powder Pillows
  - Acid Reagent Powder Pillows
  - 125-mL Erlenmeyer flask
  - 50-mL volumetric pipet, Class A and pipet filler safety bulb
1. Use a Class A pipet to add 50.00 mL of the standard solution to a 125-mL Erlenmeyer flask.
  2. Add the contents of one Potassium Iodide Powder Pillow to the flask. Swirl to mix.
  3. Add the contents of three Acid Reagent Powder Pillows to the flask. Swirl until all of the powder is dissolved.

4. Titrate the prepared standard solution to the endpoint color. The correct number of digits for this titration is 217–250 digits.
5. Compare the actual number of digits that were used in the titration to the correct number of digits. If much more or less titrant was used, there can be a problem with user technique, reagents or apparatus.

### Precision

When a commercial bleach sample of 91.2 g/L (9.12 %)  $\text{Cl}_2$  is tested, one analyst caused a standard deviation of  $\pm 1.5$  g/L ( $\pm 1.5$  %)  $\text{Cl}_2$ .

### Summary of method

In acidic conditions, hypochlorite reacts with iodide to form an equivalent quantity of triiodide ( $\text{I}_3^-$ ). The released  $\text{I}_3^-$  is titrated with sodium thiosulfate to a colorless end point. The quantity of sodium thiosulfate required is directly related to the hypochlorite concentration in the sample.

### Consumables and replacement items

#### Required reagents

Description	Quantity/Test	Unit	Item no.
HR Hypochlorite (Bleach) Reagent Set, 5–15% as $\text{Cl}_2$	—	each	2687000
Acid Reagent Powder Pillows	1 pillow	100/pkg	104299
Potassium Iodide Powder Pillows	1 pillow	50/pkg	2059996
Sodium Thiosulfate Titration Cartridge, 2.26 N	varies	each	2686901
Starch Indicator Solution	1 mL	100 mL MDB	34932

#### Required apparatus

Description	Quantity/test	Unit	Item no.
Clippers for plastic pillows	1	each	96800
Digital Titrator	1	each	1690001
Delivery tube for Digital Titrator, J-hook tip	1	5/pkg	1720500
Flask, Erlenmeyer, 125 mL	1	each	50543
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.
Potassium Iodide-Iodate Standard Solution, 0.0125 N	1 L	1400153

#### Optional reagents and apparatus

Description	Unit	Item no.
Paper, pH, 0–14 pH range	100/pkg	2601300
Bottle, sample, glass, 4 oz, with cap	3/pkg	2161303
Pipet, volumetric, Class A, 50 mL	each	1451541
Pipet filler, safety bulb	each	1465100
Stir bar, octagonal	each	2095352
TitraStir <sup>®</sup> Titration Stand, 115 VAC	each	1940000

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**Optional reagents and apparatus (continued)**

Description	Unit	Item no.
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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FAX: (970) 669-2932

## Titration Method with EDTA

10–4000 mg/L as CaCO<sub>3</sub>

Method 8204

Digital Titrator

**Scope and application:** For water, wastewater and seawater.



### 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 Powder Pillow, use a 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

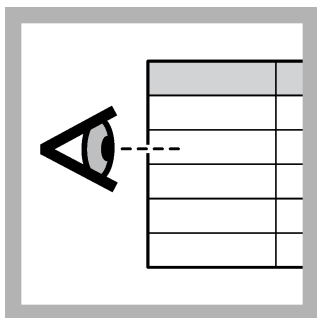
Description	Quantity
CalVer 2 Calcium Indicator Powder Pillow	1 pillow
Potassium Hydroxide Standard Solution, 8 N	1 or 2 mL
EDTA Titration Cartridge (refer to <a href="#">Sample volumes and digit multipliers</a> on page 3)	1
Digital Titrator	1
Delivery tube for Digital Titrator	1
Graduated cylinder (use 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 5 for order information.

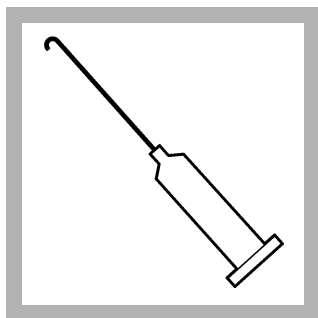
#### Sample collection

- 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



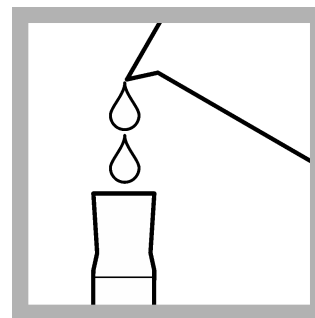
1. Select a sample volume and titration cartridge from [Table 1](#) on page 3.



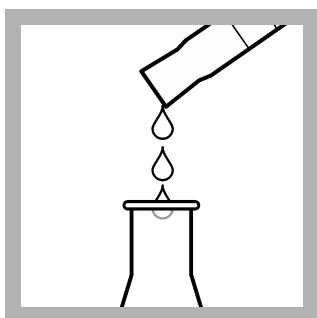
2. Insert a clean delivery tube into the digital titration cartridge. Attach the cartridge to the Digital Titrator.



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.



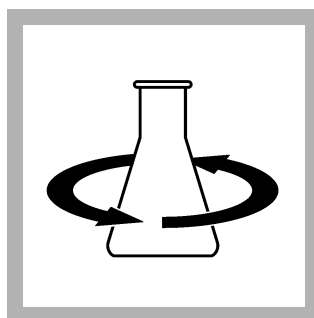
4. Use a graduated cylinder or a pipet<sup>1</sup> to measure the sample volume from [Table 1](#) on page 3.



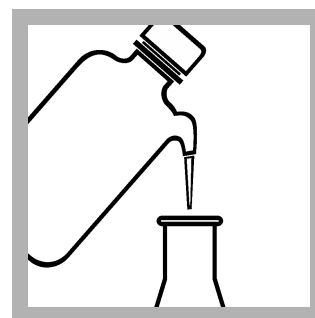
5. Pour the sample into a clean, 250-mL Erlenmeyer flask.



6. If the sample volume is 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.



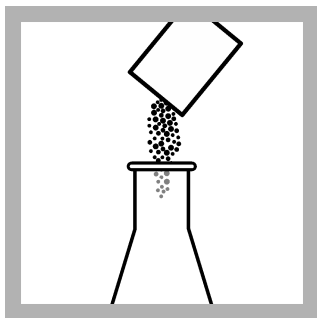
7. Swirl to mix.



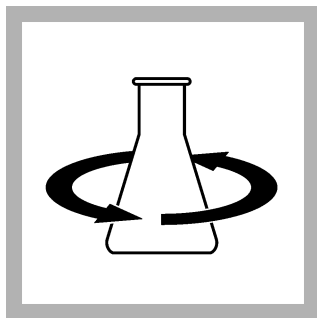
8. If the sample volume is less than 100 mL, dilute to approximately 100 mL with deionized water.

<sup>1</sup> 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.

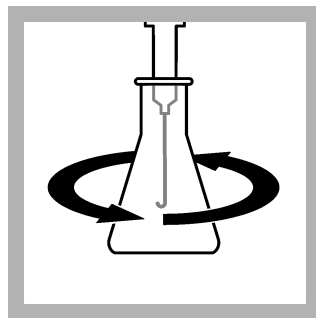




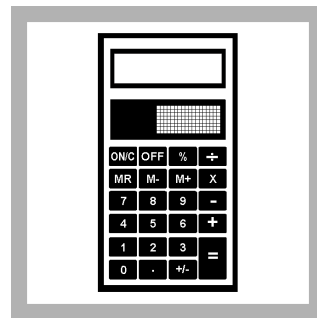
9. Add the contents of one CalVer 2 Calcium Indicator Powder Pillow.



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 1](#) on page 3 to calculate the concentration. Digits used  $\times$  digit multiplier = mg/L (or Gdh) Ca as  $\text{CaCO}_3$ .

### 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  $250 \text{ digits} \times 2.0 = 500 \text{ mg/L}$  as  $\text{CaCO}_3$  (or with the 0.714 M EDTA titration cartridge,  $250 \times 0.1 = 25 \text{ mg/L Gdh}$ ).

**Table 1 Sample volumes and digit multipliers—mg/L**

Range (mg/L as $\text{CaCO}_3$ )	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 $\text{CaCO}_3$ )	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 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 Potassium Hydroxide 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	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 Potassium Hydroxide 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 Potassium Hydroxide 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 Potassium Hydroxide 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.

**Table 4 Interferences (continued)**

Interfering substance	Interference level
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 Potassium Hydroxide 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:

- 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 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.

## 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.
Reagent set, 10–160 mg/L range (approximately 100 tests):	—	each	2447200
CalVer 2 Calcium Indicator Powder Pillows	1 pillow	100/pkg	85299
Potassium Hydroxide Standard Solution, 8 N	1–2 mL	100 mL MDB	28232H
EDTA Titration Cartridge, 0.0800 M	varies	each	1436401
Reagent set, 100–4000 mg/L range (approximately 100 tests):	—	each	2447500
CalVer 2 Calcium Indicator Powder Pillows	1 pillow	100/pkg	85299
Potassium Hydroxide Standard Solution, 8 N	1–2 mL	100 mL MDB	28232H

## Consumables and replacement items (continued)

Description	Quantity/Test	Unit	Item no.
EDTA Titration Cartridge, 0.800 M	varies	each	1439901
Reagent set, 1–16 G.d.h. range (approximately 100 tests):	—	each	2447300
CalVer 2 Calcium Indicator Powder Pillows	1 pillow	100/pkg	85299
Potassium Hydroxide Standard Solution, 8 N	1–2 mL	100 mL MDB	28232H
EDTA Titration Cartridge, 0.1428 M	varies	each	1496001
Reagent set, 10–100 G.d.h. range (approximately 100 tests):	—	each	2447400
CalVer 2 Calcium Indicator Powder Pillows	1 pillow	100/pkg	85299
Potassium Hydroxide Standard Solution, 8 N	1–2 mL	100 mL MDB	28232H
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 <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
Hardness Quality Control Standard, low range	500 mL	2833449

## 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
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

**Optional reagents and apparatus (continued)**

<b>Description</b>	<b>Unit</b>	<b>Item no.</b>
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
Bottle, sampling, 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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FAX: (970) 669-2932

## Titration Method with EDTA

10–4000 mg/L as CaCO<sub>3</sub>

Method 8213

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

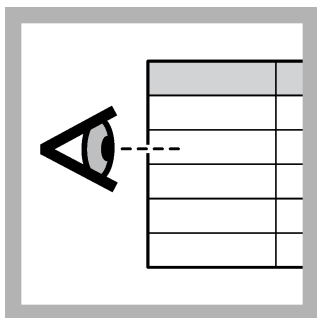
Description	Quantity
ManVer 2 Hardness Indicator Powder Pillow	1
Hardness 1 Buffer Solution	2 mL
EDTA Titration Cartridge (refer to <a href="#">Sample volumes and digit multipliers</a> on page 3)	1
Digital Titrator	1
Delivery tube for Digital Titrator	1
Graduated cylinder (use a size that is applicable 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.

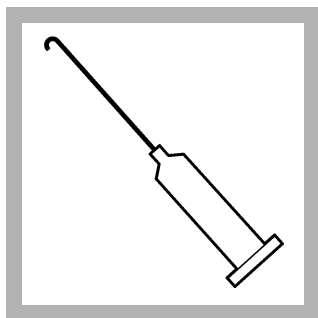
#### Sample collection and storage

- 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



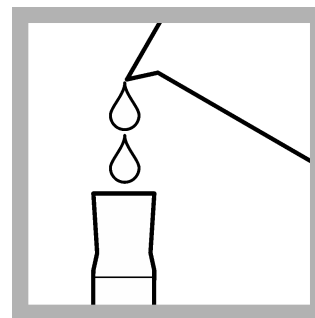
1. Select a sample volume and titration cartridge from [Table 1](#) on page 3.



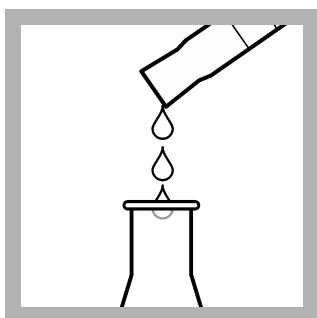
2. Insert a clean delivery tube into the digital titration cartridge. Attach the cartridge to the Digital Titrator.



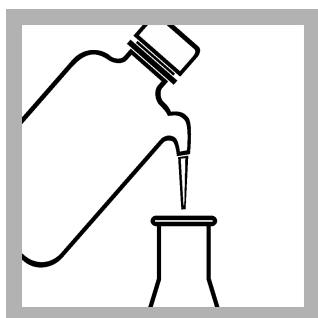
3. Hold the Digital Titrator with the cartridge tip up. Turn the delivery knob to eject air and a few drops of titrant. Reset the counter to zero and clean the tip.



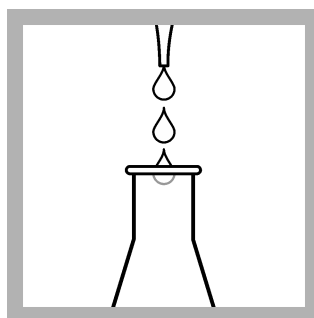
4. Use a graduated cylinder or a pipet<sup>1</sup> to measure the sample volume from [Table 1](#) on page 3.



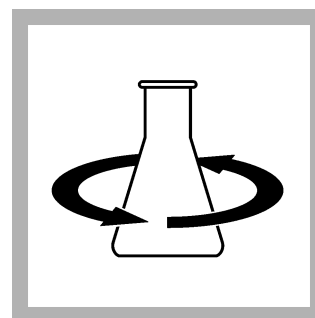
5. Pour the sample into a clean, 250-mL Erlenmeyer flask.



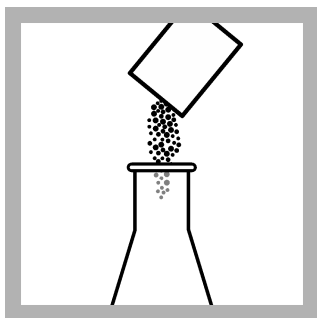
6. If the sample volume is less than 100 mL, dilute to approximately 100 mL with deionized water.



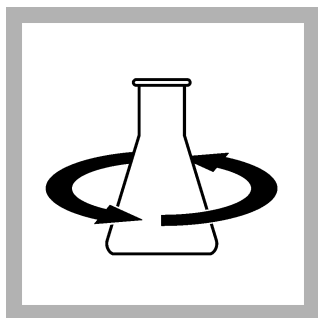
7. Add 2 mL of Hardness 1 Buffer Solution.



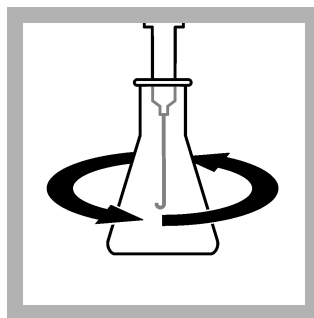
8. Swirl to mix.



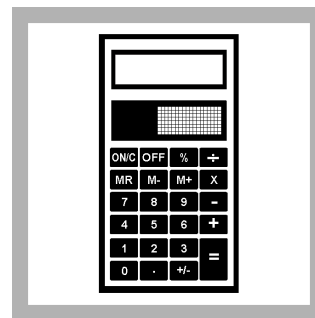
9. Add the contents of one ManVer 2 Hardness Indicator Powder Pillow.



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  $\times$  digit multiplier = mg/L (or Gdh) total hardness as CaCO<sub>3</sub>.

<sup>1</sup> 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  $\times$  2.0 = 500 mg/L as CaCO<sub>3</sub> (or with the 0.714 M EDTA titration cartridge, 250  $\times$  0.1 = 25 mg/L Gdh).

**Table 1 Sample volumes and digit multipliers—mg/L**

Range (mg/L as CaCO <sub>3</sub> )	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 <sub>3</sub> )	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 <sub>3</sub> to...	multiply by...	Example
mg/L Total Hardness as Ca	0.40	1000 mg/L as CaCO <sub>3</sub> $\times$ 0.40 = 400 mg/L Ca
German degrees hardness (Gdh)	0.056	1000 mg/L as CaCO <sub>3</sub> $\times$ 0.056 = 56 Gdh
Grains per gallon (gpg)	0.058	1000 mg/L as CaCO <sub>3</sub> $\times$ 0.058 = 58 gpg
mg/L Total Hardness as Mg	0.243	1000 mg/L as CaCO <sub>3</sub> $\times$ 0.243 = 243 mg/L Mg

## Hardness relationships

- mg/L Mg Hardness as CaCO<sub>3</sub> = mg/L Total Hardness as CaCO<sub>3</sub> – mg/L Ca Hardness as CaCO<sub>3</sub>
- mg/L MgCO<sub>3</sub> = mg/L Mg Hardness as CaCO<sub>3</sub>  $\times$  0.842
- mg/L Mg = mg/L MgCO<sub>3</sub>  $\times$  0.29

## Interferences

<b>⚠ WARNING</b>	
	<p>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.</p>

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	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 <a href="#">Use CDTA to remove metal interferences</a> 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 <a href="#">Use CDTA to remove metal interferences</a> 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 <a href="#">Use CDTA to remove metal interferences</a> 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 <a href="#">Use CDTA to remove metal interferences</a> 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 <a href="#">Use CDTA to remove metal interferences</a> 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<sub>3</sub>)**

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<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 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<sub>3</sub>
  - 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<sub>3</sub>.
  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 <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 Chloride Standard Solution, 1000-mg/L as CaCO <sub>3</sub>	1 L	12153
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
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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# Hardness, Total, Sequential

DOC316.53.01230

**Titration Method with EDTA****Method 8329****10–4000 mg/L as CaCO<sub>3</sub>****Digital Titrator****Scope and application:** For water, wastewater and seawater.

## Test preparation

### Before starting

The first titration gives the results for calcium hardness and the second titration gives total hardness. The difference between the values is the magnesium hardness level. All the concentration results are in mg/L as CaCO<sub>3</sub>. Refer to [Conversions units](#) on page 5 for conversions to other units.

As an alternative to the CalVer 2 Calcium Indicator Powder Pillow, use a 0.1-g scoop of CalVer 2 Calcium Indicator Powder.

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
CalVer 2 Calcium Indicator Powder Pillow	1
Potassium Hydroxide Standard Solution, 8 N	1 mL
Hardness 1 Buffer Solution	1 mL
ManVer 2 Hardness Indicator Powder Pillow	1
Sulfuric Acid Standard Solution, 5.25 N	1 mL
EDTA Titration Cartridge (refer to <a href="#">Sample volumes and digit multipliers</a> on page 4)	1
Digital Titrator	1
Delivery tube for Digital Titrator	1
Graduated cylinder or pipet (use a size that is applicable to the selected sample volume)	1
Erlenmeyer flask, 250-mL	1
Water, deionized	varies

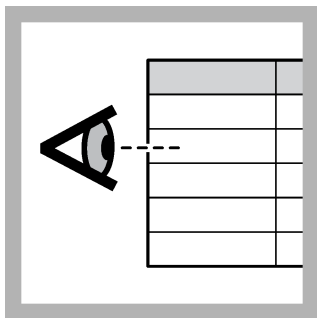
Refer to [Consumables and replacement items](#) on page 7 for order information.

### Sample collection and storage

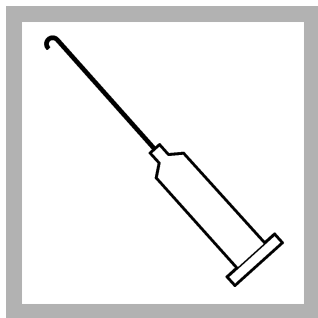
- Collect samples in clean glass or plastic bottles that have been cleaned with a detergent and rinsed with 1:1 nitric acid and deionized water.
- To preserve samples for later analysis, adjust the sample pH to 2 or less with concentrated nitric acid (about 2 mL per liter). No acid addition is necessary if the sample is tested immediately.
- Keep the preserved samples at or below 6 °C (43 °F) for a maximum of 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.

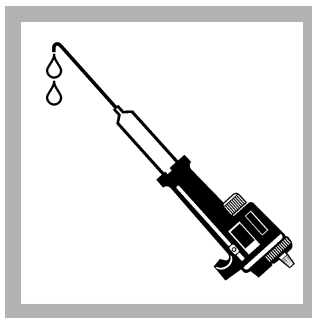
## Test procedure



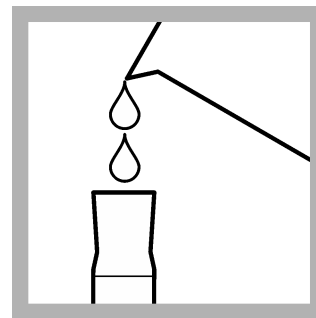
1. Select a sample volume and titration cartridge from [Table 1](#) on page 4.



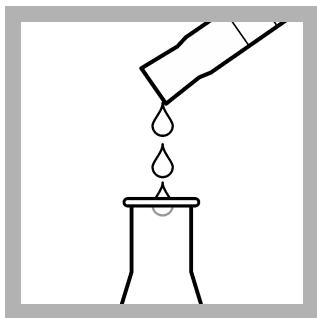
2. Insert a clean delivery tube into the digital titration cartridge. Attach the cartridge to the Digital Titrator.



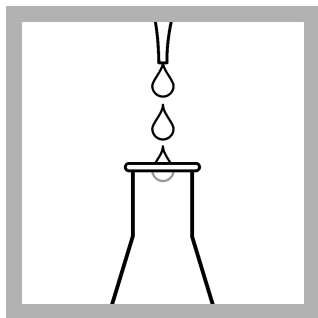
3. Hold the Digital Titrator with the cartridge tip up. Turn the delivery knob to eject air and a few drops of titrant. Reset the counter to zero and clean the tip.



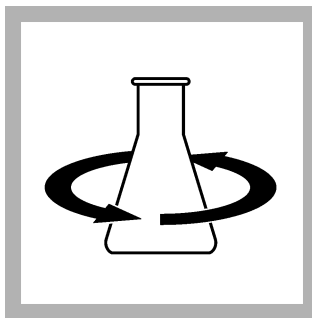
4. Use a graduated cylinder or a pipet<sup>1</sup> to measure the sample volume from [Table 1](#) on page 4.



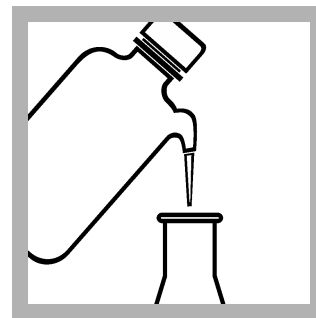
5. Pour the sample into a clean, 250-mL Erlenmeyer flask.



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.



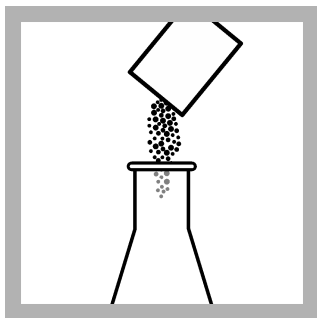
7. Swirl to mix.



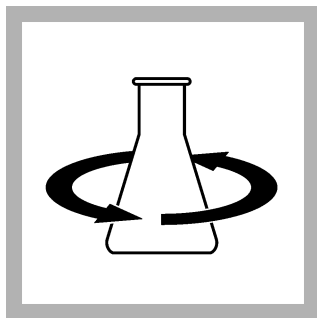
8. If the sample volume is less than 100 mL, dilute to approximately 100 mL with deionized water.

<sup>1</sup> 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.

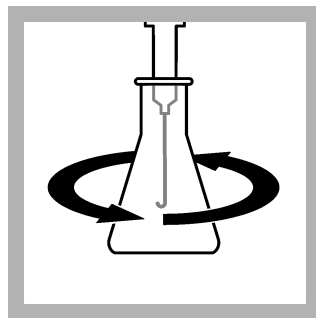




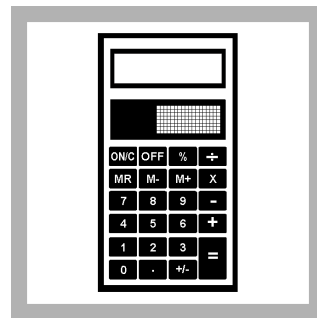
**9.** Add the contents of one CalVer 2 Calcium Indicator Powder Pillow.



**10.** Swirl to mix.



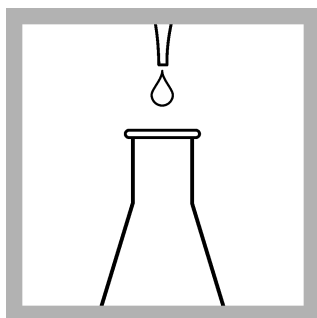
**11.** Put the end of the delivery tube fully into the solution. Swirl the flask. Turn the knob on the Digital Titrator to add titrant to the solution. Continue to swirl the flask. Add titrant until the color changes from red to pure blue. Record the number of digits on the counter.



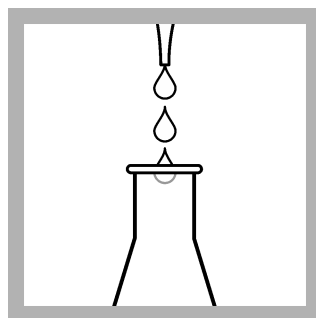
**12.** Use the multiplier in [Table 1](#) on page 4 to calculate the concentration. Digits used  $\times$  digit multiplier = mg/L (or Gdh) Calcium as  $\text{CaCO}_3$ .



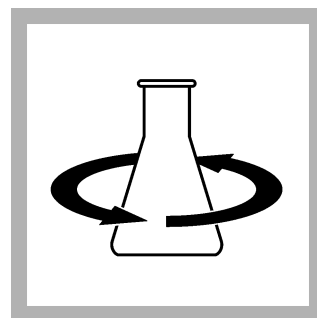
**13.** Add 1 mL of 5.25 Sulfuric Acid Standard Solution.



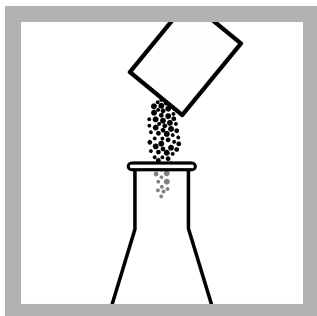
**14.** Add more acid, 1 drop at a time until the color changes from pure blue to purple, and then to red. Swirl the flask to make sure that all the precipitated magnesium hydroxide has dissolved.



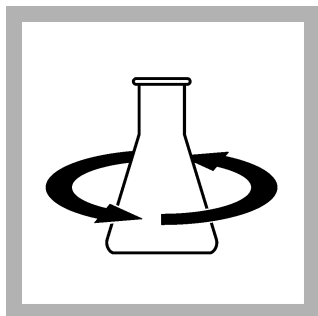
**15.** Add 2 mL of Hardness 1 Buffer Solution.



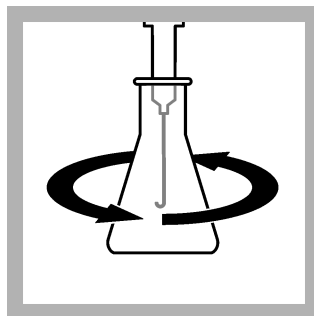
**16.** Swirl to mix.



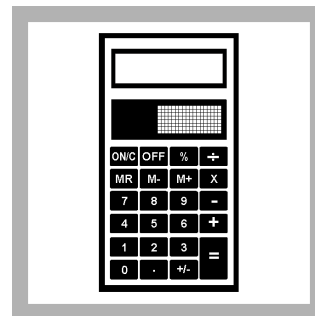
17. Add the contents of one ManVer 2 Hardness Indicator Powder Pillow.



18. Swirl to mix.



19. 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.



20. Use the multiplier in [Table 1](#) on page 4 to calculate the concentration. Digits used  $\times$  digit multiplier = mg/L (or Gdh) total hardness<sup>2</sup> as CaCO<sub>3</sub>.

### 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  $\times$  2.0 = 500 mg/L as CaCO<sub>3</sub> (or with the 0.714 M EDTA titration cartridge, 250  $\times$  0.1 = 25 mg/L Gdh).

**Table 1 Sample volumes and digit multipliers—mg/L**

Range (mg/L as CaCO <sub>3</sub> )	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 <sub>3</sub> )	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

<sup>2</sup> Total digits = digits from step 11 + digits from step 19.

## 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 <sub>3</sub> to...	multiply by...	Example
mg/L Total Hardness 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
mg/L Total Hardness as Mg	0.243	1000 mg/L as CaCO <sub>3</sub> x 0.243 = 243 mg/L Mg

## Hardness relationships

- $\text{mg/L Mg Hardness as CaCO}_3 = \text{mg/L Total Hardness as CaCO}_3 - \text{mg/L Ca Hardness as CaCO}_3$
- $\text{mg/L MgCO}_3 = \text{mg/L Mg Hardness as CaCO}_3 \times 0.842$
- $\text{mg/L Mg} = \text{mg/L MgCO}_3 \times 0.29$

## Interferences

<b>⚠ WARNING</b>	
	Chemical hazard. Do not use potassium cyanide to remove interferences because it will form deadly hydrogen cyanide gas when the sulfuric acid solution is added.

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	Interferes at all levels. Add a DTA powder pillow to remove the interference. Refer to <a href="#">Use CDTA to remove metal interferences</a> on page 6.
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 at all levels. Add a DTA powder pillow to remove the interference. Refer to <a href="#">Use CDTA to remove metal interferences</a> on page 6.
Copper	Interferes when the sample contains 0.10 and 0.20 mg/L copper.
Heavy metals	Some transition and heavy metals have an effect in the indicator and prevent the color change at the end point.
Iron	Iron does not interfere until 15 mg/L. More than this level will cause a red-orange to green endpoint, which is sharp and usable with a maximum of 30 mg/L iron. Change a 0.0800 M CDTA or 0.800 M CDTA titration cartridge for the 0.0800 M EDTA or 0.800 M EDTA titration cartridges, respectively, if iron interference is possible. For results in Gdh, divide the mg/L result by 17.9.
Manganese	Interferes when the sample contains more than 20 mg/L manganese. Add a 0.1-gram scoop of hydroxylamine hydrochloride to increase this level to 200 mg/L manganese.
Nickel	Interferes at all levels. Add a DTA powder pillow to remove the interference. Refer to <a href="#">Use CDTA to remove metal interferences</a> on page 6.

**Table 4 Interferences (continued)**

Interfering substance	Interference level
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.
Zinc	Interferes at all levels. Add a DTA powder pillow to remove the interference. Refer to <a href="#">Use CDTA to remove metal interferences</a> on page 6.

**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<sub>3</sub>)**

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

## Summary of method

This test procedure is a combination of the calcium and total hardness procedures. Refer to each method for more information.

## Consumables and replacement items

### Required reagents

Description	Quantity/Test	Unit	Item no.
Calcium and Total Hardness Reagent Set (approximately 100 tests):	—	each	2272100
Buffer Solution, Hardness 1	1 mL	100 mL MDB	42432
CalVer 2 Calcium Indicator Powder Pillows	1	100/pkg	94799
ManVer 2 Hardness Indicator Powder Pillows	1	100/pkg	85199
(x2) Potassium Hydroxide Standard Solution, 8 N	1 mL	100 mL MDB	28232H
EDTA Titration Cartridge, 0.0800 M	varies	each	1436401
EDTA Titration Cartridge, 0.800 M	varies	each	1439901
EDTA Titration Cartridge, 0.1428 M	varies	each	1496001
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 <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 Chloride Standard Solution, 1000-mg/L as CaCO <sub>3</sub>	1 L	12153
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
Hardness Quality Control Standard, low range	500 mL	2833449

### Optional reagents and apparatus- DT hardness total sequential

Description	Unit	Item no.
Ampule Breaker, 10-mL Voluette <sup>®</sup> Ampules	each	2196800
CDTA Magnesium Salt Powder Pillow	100/pkg	1408099

**Optional reagents and apparatus- DT hardness total sequential (continued)**

<b>Description</b>	<b>Unit</b>	<b>Item no.</b>
CDTA cartridge for Digital Titrator, 0.08 M	each	1440201
CDTA cartridge for Digital Titrator, 0.80 M	each	1440301
Delivery tube for Digital Titrator, 90-degree bend for use with TitraStir Titration Stand	5/pkg	4157800
Hydroxylamine Hydrochloride	113 g	24614
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
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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## TitraVer Titration Method

**Method 8214**
**10–1000 mg/L as Fe**
**Digital Titrator**

**Scope and application:** For water, wastewater and seawater.



### Test preparation

#### Before starting

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

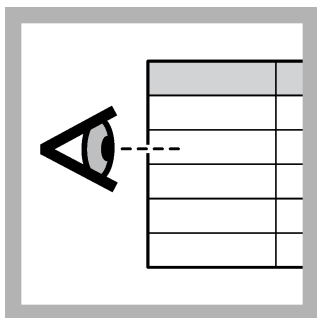
Description	Quantity
Citrate Buffer Powder Pillow	1
Sodium Periodate Powder Pillow	1
Sulfosalicylic Acid Powder Pillow	1
TitraVer Standard Solution Titration Cartridge (refer to <a href="#">Sample volumes and digit multipliers</a> on page 3)	1
Digital Titrator	1
Delivery tube for Digital Titrator	1
Graduated cylinder (use a size that is applicable to the selected sample volume)	1
Erlenmeyer flask, 125 mL	1
Water, deionized	varies

Refer to [Consumables and replacement items](#) on page 4 for order information.

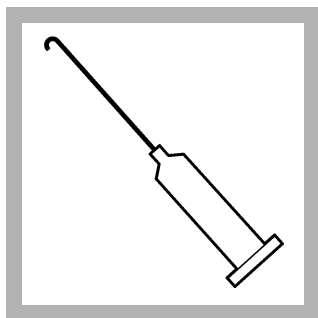
#### Sample collection

- Collect samples in clean glass or plastic bottles.

## Test procedure



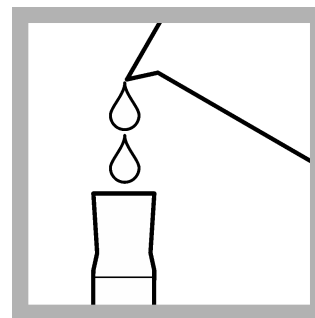
1. Select a sample volume and titration cartridge from [Table 1](#) on page 3.



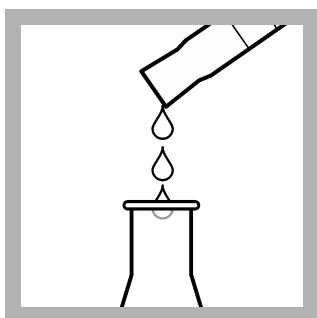
2. Insert a clean delivery tube into the digital titration cartridge. Attach the cartridge to the Digital Titrator.



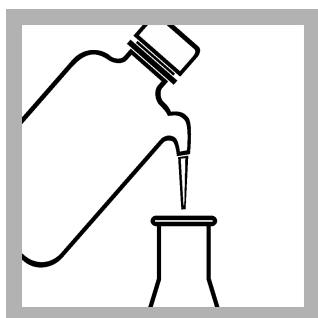
3. Hold the Digital Titrator with the cartridge tip up. Turn the delivery knob to eject air and a few drops of titrant. Reset the counter to zero and clean the tip.



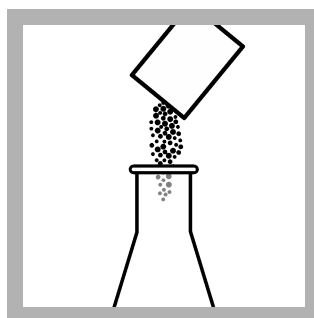
4. Use a graduated cylinder or a pipet<sup>1</sup> to measure the sample volume from [Table 1](#) on page 3.



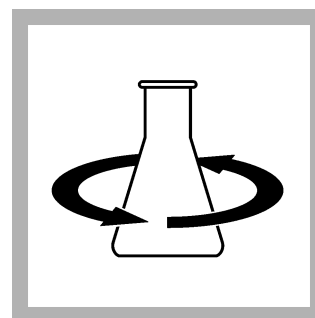
5. Pour the sample into a clean, 125-mL Erlenmeyer flask.



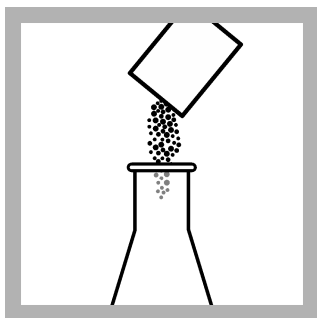
6. If the sample volume is less than 50 mL, dilute to approximately 50 mL with deionized water.



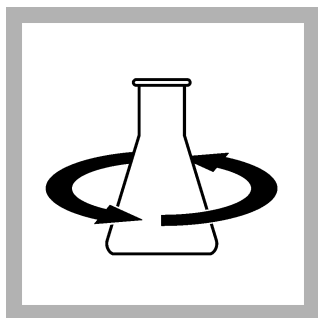
7. Add the contents of one Citrate Buffer Powder Pillow.



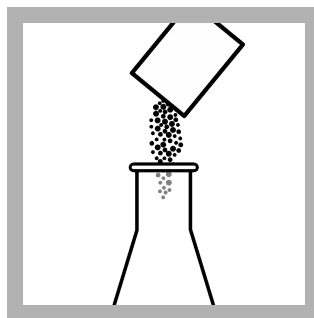
8. Swirl to mix.



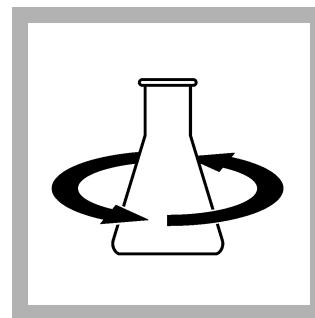
9. Add the contents of one Sodium Periodate Powder Pillow.



10. Swirl to mix. The color of the solution changes to yellow if iron is in the sample.



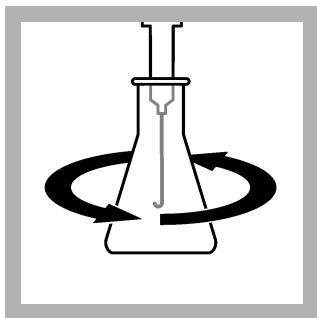
11. Add the contents of one Sulfosalicylic Acid Powder Pillow.



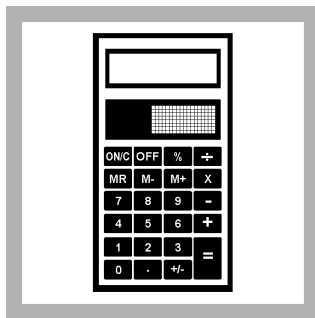
12. Swirl to mix. The color of the solution changes to red if iron is in the sample.

<sup>1</sup> 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.





13. 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 yellow. Record the number of digits on the counter.



14. Use the multiplier in [Table 1](#) on page 3 to calculate the concentration.  $\text{Digits used} \times \text{digit multiplier} = \text{mg/L Fe.}$

### Sample volumes and digit multipliers

Select a range in [Table 1](#), 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 0.0716 M TitraVer Standard Solution Titration Cartridge and the counter showed 250 digits at the endpoint. The concentration is  $250 \text{ digits} \times 0.1 = 25 \text{ mg/L Fe.}$

**Table 1 Sample volumes and digit multipliers**

Range (mg/L as Fe)	Sample volume (mL)	Titration cartridge	Digit multiplier
10–40	50	0.0716	0.1
25–100	20	0.0716	0.25
100–400	50	0.716	1.0
250–1000	20	0.716	2.5

### 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:

- Iron Standard Solution, 1000 mg/L as Fe
- 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 0.5 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 0.5-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 0.5-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 0.0716 M TitraVer Standard Solution Titration Cartridge (100 digits of the

0.0716 M titration cartridge) for each 0.5-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

Ferrous iron  $\text{Fe}^{2+}$  is oxidized by sodium periodate to ferric ion  $\text{Fe}^{3+}$ . The ferric ion develops a red complex with sulfosalicylic acid. The red complex is removed by titration with EDTA. Citric acid is used to buffer the solution and to make the ferric ion stable in the solution.

## Consumables and replacement items

### Required reagents

Description	Quantity/Test	Unit	Item no.
Reagent set, 10–100 mg/L range (approximately 100 tests):	—	each	2449200
Citrate Buffer Powder Pillows	1 pillow	100/pkg	2081599
Sodium Periodate Powder Pillows	1 pillow	100/pkg	98499
Sulfosalicylic Acid Powder Pillows	1 pillow	100/pkg	2081669
TitraVer Standard Solution Titration Cartridge, 0.0716 M	varies	each	2081701
Reagent set, 100–1000 mg/L range (approximately 100 tests):	—	each	2449300
Citrate Buffer Powder Pillows	1 pillow	100/pkg	2081599
Sodium Periodate Powder Pillows	1 pillow	100/pkg	98499
Sulfosalicylic Acid Powder Pillows	1 pillow	100/pkg	2081669
TitraVer Standard Solution Titration Cartridge, 0.716 M	varies	each	2081801

### Required apparatus

Description	Quantity/test	Unit	Item no.
Graduated cylinders—Select one or more for the sample volume:			
Cylinder, graduated, 25 mL	1	each	50840
Cylinder, graduated, 50 mL	1	each	50841
Digital Titrator	1	each	1690001
Delivery tube for Digital Titrator, J-hook tip	1	5/pkg	1720500
Pipet filler, safety bulb	1	each	1465100
Pipet, volumetric, Class A, 20 mL	1	each	1451520
Flask, Erlenmeyer, 125 mL	1	each	50543

### Recommended standards

Description	Unit	Item no.
Iron Standard Solution, 1000 mg/L as Fe	100 mL	227142
Iron Standard Solution, 10 mg/L as Fe	500 mL	14049
Iron Standard Solution, 25 mg/L as Fe	10 mL/16	1425310
Iron Standard Solution, 50 mg/L as Fe	10 mL/16	1425410
Iron Standard Solution, 100 mg/L as Fe	100 mL	1417542

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**Optional apparatus**

<b>Description</b>	<b>Unit</b>	<b>Item no.</b>
Ampule Breaker, 10-mL Voluette® Ampules	each	2196800
Pipet, TenSette®, 1.0–10.0 mL	each	1970010
Pipet tips for TenSette® Pipet, 1.0–10.0 mL	50/pkg	2199796
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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## Ceric Acid Titration Method

100–2500 mg/L as NaNO<sub>2</sub>

Method 8351

Digital Titrator

**Scope and application:** For cooling tower waters.



### Test preparation

#### Before starting

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

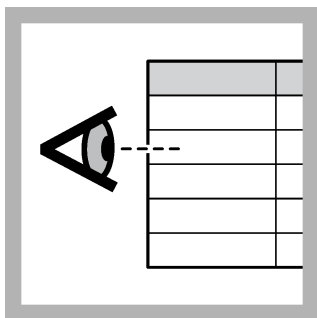
Description	Quantity
Ferriin Indicator Solution	1
Sulfuric Acid Standard Solution, 5.25 N	1
Ceric Standard Solution Titration Cartridge, 0.5 N	1
Digital Titrator	1
Delivery tube for Digital Titrator	1
Graduated cylinder (use a size that is applicable to the selected sample volume)	1
Erlenmeyer flask, 125 mL	1
Water, deionized	varies

Refer to [Consumables and replacement items](#) on page 4 for order information.

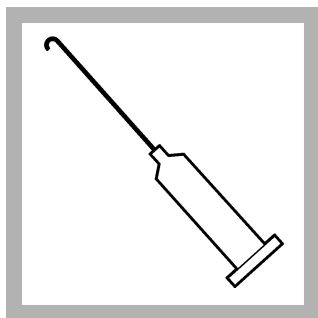
#### Sample collection and storage

- Collect samples in clean glass or plastic bottles.
- Analyze the samples as soon as possible for best results.
- If immediate analysis is not possible, keep the samples at or below 6 °C (43 °F) for a maximum of 24 hours.
- Let the sample temperature increase to room temperature before analysis.

## Test procedure



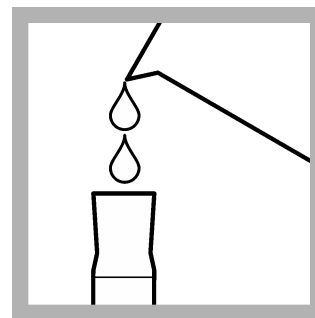
1. Select a sample volume from [Table 1](#) on page 3.



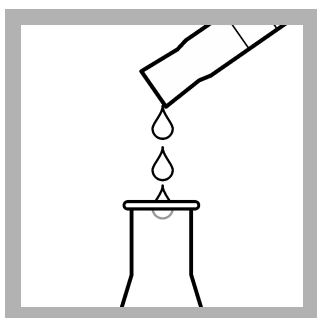
2. Insert a clean delivery tube into the digital titration cartridge. Attach the cartridge to the Digital Titrator.



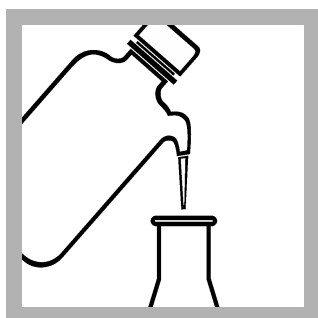
3. Hold the Digital Titrator with the cartridge tip up. Turn the delivery knob to eject air and a few drops of titrant. Reset the counter to zero and clean the tip.



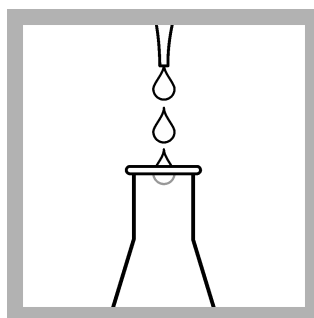
4. Use a graduated cylinder or a pipet<sup>1</sup> to measure the sample volume from [Table 1](#) on page 3.



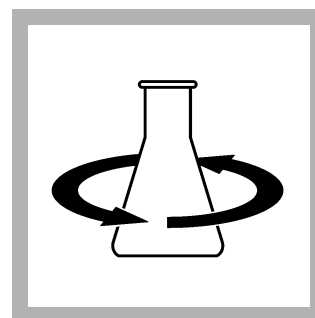
5. Pour the sample into a clean, 125-mL Erlenmeyer flask.



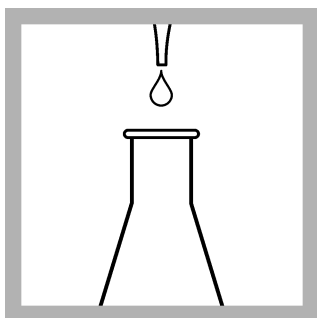
6. Dilute to approximately 75 mL with deionized water.



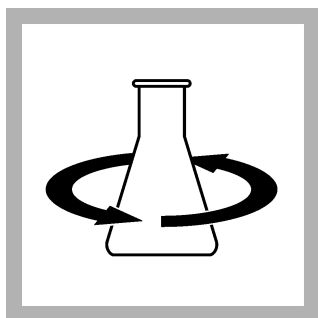
7. Add 5 drops of 5.25 N Sulfuric Acid Standard Solution.



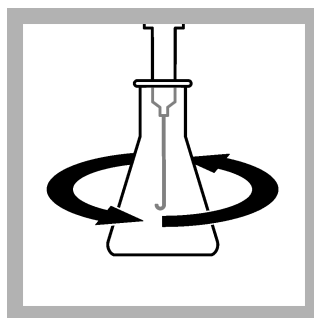
8. Swirl to mix.



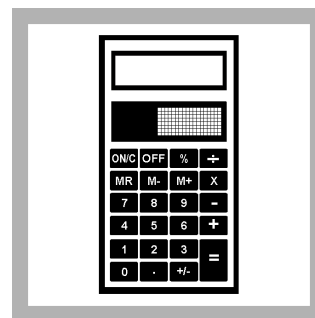
9. Add one drop of Ferroin Indicator Solution.



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 orange to pale 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  $\times$  digit multiplier = mg/L sodium nitrite as  $\text{NaNO}_2$ .

<sup>1</sup> A pipet is recommended for sample volumes less than 10 mL.

## Sample volumes and digit multipliers

Select a range in [Table 1](#), 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 25-mL sample was titrated with 0.5 N Ceric Standard Solution Titration Cartridge and the counter showed 250 digits at the endpoint. The concentration is  $250 \text{ digits} \times 0.86 = 215 \text{ mg/L}$  sodium nitrite as  $\text{NaNO}_2$ .

**Table 1 Sample volumes and digit multipliers**

Range (mg/L as $\text{NaNO}_2$ )	Sample volume (mL)	Digit multiplier
100–400	25	0.86
400–800	10	2.15
800–1500	5	4.31
1500–2500	2	10.78

## Accuracy check

### Standard solution method

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

Items to collect:

- Sodium Nitrite, ACS
- 1000-mL volumetric flask, Class A
- 5-mL volumetric pipet, Class A and pipet filler safety bulb
- Deionized water

1. Prepare a 1000-mg/L sodium nitrite standard solution as follows:
  - a. Add 1.000 gram of sodium nitrite to the volumetric flask.
  - b. Dilute to the mark with deionized water. Mix well.
2. Use the test procedure to measure the concentration of the prepared standard solution. Use 5.0 mL of the prepared standard solution.
3. Compare the actual result to the correct result. The correct result for this titration is approximately 1000 mg/L as  $\text{NaNO}_2$ .

### Standardization of the ceric standard solution

The normality of the ceric standard solution can decrease over time. Before use, examine the normality with the standardization procedure. It is recommended to do the standardization procedure monthly.

Items to collect:

- Sodium Thiosulfate Titration Cartridge, 0.200 N
  - 125-mL Erlenmeyer flask
  - Deionized water
1. Use a graduated cylinder to measure 50 mL of deionized water into a 125-mL Erlenmeyer flask.
  2. Use a pipet to add 5 mL of 19.2 N Sulfuric Acid Standard Solution. Swirl to mix.
  3. Insert a clean delivery tube into the Ceric Standard Titration Cartridge. Attach the cartridge to the titrator.
  4. Hold the Digital Titrator with the cartridge tip pointing up. Turn the delivery knob to eject a few drops of titrant. Reset the counter to zero and wipe the tip.
  5. Put the delivery tube into the solution and swirl the flask. Turn the knob on the titrator to add 200 digits of titrant to the solution.

6. Insert a clean delivery tube into a 0.200 N Sodium Thiosulfate Titration Cartridge. Attach the cartridge to the titrator.
7. Hold the Digital Titrator with the cartridge tip pointed up. Turn the delivery knob to eject a few drops of titrant. Reset the counter to zero and clean the tip.
8. Titrate the solution until the color changes from intense yellow to faint yellow. Record the number of digits on the counter. The correct number of digits for this step is 400–450 digits.
9. Add 1 drop of Ferroin Indicator Solution to the flask. Swirl to mix. The color of the solution changes to faint blue.
10. Continue the titration with Sodium Thiosulfate until the color changes to orange. Record the number of digits on the counter.
11. Divide the number of digits by 500 to calculate the correction factor.
12. Multiply the mg/L sodium nitrite from the titration procedure by the correction factor to get the correct sodium nitrite concentration.

## Summary of method

Ferroin indicator and acid is added to the sample. The sample is titrated with tetravalent cerium ion, which is a strong oxidant. After the cerium oxidizes the nitrite, the indicator is oxidized and causes a color change from orange to pale blue. The quantity of titrant used changes in relation to the concentration of sodium nitrite in the sample.

## Consumables and replacement items

### Required reagents

Description	Quantity/Test	Unit	Item no.
Ceric Standard Solution Titration Cartridge, 0.5 N	1	each	2270701
Ferroin Indicator Solution	1	29 mL DB	181233
Sulfuric Acid Standard Solution, 5.25 N	1	100 mL MDB	244932

### Required apparatus

Description	Quantity/test	Unit	Item no.
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, 125 mL	1	each	50543
Pipet filler, safety bulb	1	each	1465100
Pipet, volumetric, Class A, 2.00 mL	1	each	1451536
Pipet, volumetric, Class A, 5.00 mL	1	each	1451537
Pipet, volumetric, Class A, 10.0 mL	1	each	1451538
Pipet, volumetric, Class A, 20.0 mL	1	each	1451520

### Recommended standards

Description	Unit	Item no.
Sodium Nitrite, ACS	454 g	245201
Sodium Thiosulfate Titration Cartridge, 0.200 N	each	2267501
Sulfuric Acid Standard Solution, 19.2 N	100 mL	203832



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**Optional apparatus**

<b>Description</b>	<b>Unit</b>	<b>Item no.</b>
Ampule Breaker, 10-mL Voluette <sup>®</sup> Ampules	each	2196800
Pipet, TenSette <sup>®</sup> , 1.0–10.0 mL	each	1970010
Pipet tips for TenSette <sup>®</sup> Pipet, 1.0–10.0 mL	50/pkg	2199796
Stir bar, octagonal	each	2095352
TitraStir <sup>®</sup> Titration Stand, 115 VAC	each	1940000
TitraStir <sup>®</sup> 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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## Sodium Hydroxide Method

100–2400 mg/L CH<sub>3</sub>COOH

Method 8218

Digital Titrator

Scope and application: For wastewater.



### Test preparation

#### Before starting

Refer to the *Volatile Acids Procedure, Sample Distillation* in the distillation apparatus documentation to distill the sample. As an alternative, refer to the distillation procedure in *Standard Methods for the Examination of Water and Wastewater*.

The final result is adjusted to give the correct answer based on a 70% correction factor. For higher recoveries, use the esterification method.

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

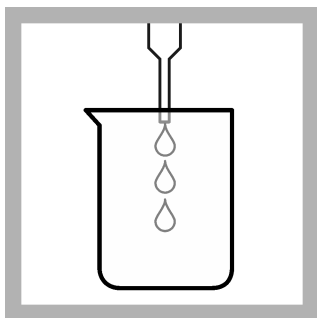
Description	Quantity
Phenolphthalein Indicator Powder Pillows	1
Sodium Hydroxide Titration Cartridge, 0.9274 N	1
Digital Titrator	1
Delivery tube for Digital Titrator	1
Graduated cylinder (use a size that is applicable to the selected sample volume)	1
Erlenmeyer flask, 250-mL	1
Water, deionized	varies

Refer to [Consumables and replacement items](#) on page 3 for order information.

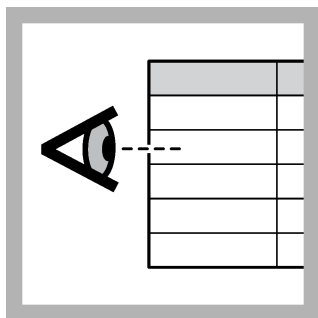
#### Sample collection

- Collect samples in clean glass or plastic bottles.

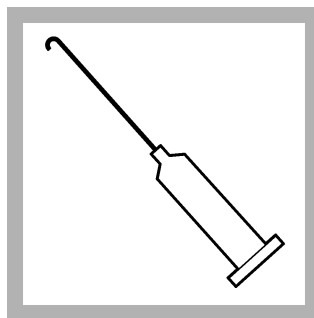
## Test procedure



1. Collect 125 mL of distillate.



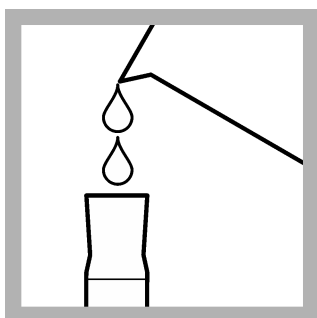
2. Select a sample volume and titration cartridge from [Table 1](#) on page 3.



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



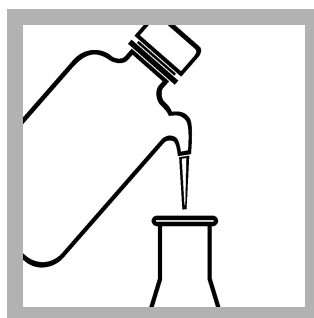
4. Hold the Digital Titrator with the cartridge tip up. Turn the delivery knob to eject air and a few drops of titrant. Reset the counter to zero and clean the tip.



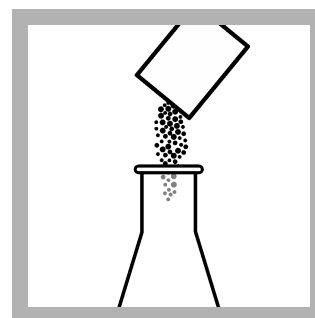
5. Use a graduated cylinder or a pipet to measure the sample volume from [Table 1](#) on page 3.



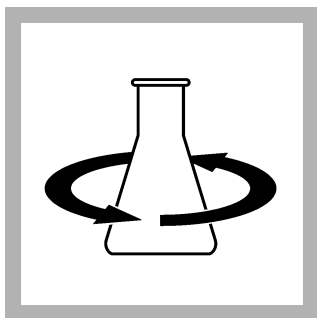
6. Pour the sample into a clean, 250-mL Erlenmeyer flask.



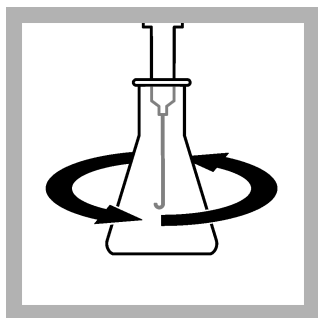
7. If the sample volume is less than 150 mL, dilute to approximately 150 mL with deionized water.



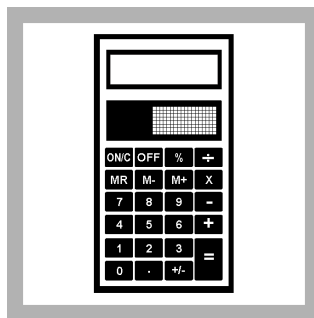
8. Add the contents of one Phenolphthalein Indicator Powder Pillow.



9. Swirl to mix.



10. 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 to light pink. Record the number of digits on the counter.



11. Use the multiplier in [Table 1](#) on page 3 to calculate the concentration. Digits used  $\times$  digit multiplier = mg/L Volatile Acids (as acetic acid,  $\text{CH}_3\text{COOH}$ ).

## Sample volumes and digit multipliers

Select a range in [Table 1](#), 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 150-mL sample was titrated with 0.9274 N Sodium Hydroxide Titration Cartridge and the counter showed 250 digits at the endpoint. The concentration is  $250 \text{ digits} \times 1 = 250 \text{ mg/L Volatile Acids (as acetic acid, CH}_3\text{COOH)}$ .

**Table 1 Sample volumes and digit multipliers**

Range (mg/L as CH <sub>3</sub> COOH)	Sample volume (mL)	Digit multiplier
100–400	150	1
200–800	75	2
600–2400	25	6

## Summary of method

The sample is acidified with sulfuric acid and distilled with deionized water. The distillate is titrated to the phenolphthalein endpoint with sodium hydroxide standard.

## Consumables and replacement items

### Required reagents

Description	Quantity/Test	Unit	Item no.
Volatile Acid Reagent set (approximately 100 tests):	—	each	2460200
Phenolphthalein Indicator Powder Pillows	1 pillow	100/pkg	94299
Sodium Hydroxide Titration Cartridge, 0.9274 N	varies	each	1484201
Water, deionized	varies	100 mL	27242

### 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

### Recommended standards

Description	Unit	Item no.
Volatile Acids Standard Solution, 1000 mg/L as Acetic Acid	100 mL	1420542

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**Optional apparatus**

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