

## Silver Nitrate Method

Method 10246

100 to 200,000 mg/L as Cl<sup>-</sup>

Digital Titrator

**Scope and application:** For oil and gas field waters.



### Test preparation

#### Before starting

As an alternative to stirring by hand, use the TitraStir Titration Stand to hold the Digital Titrator and stir the sample.

Review the Safety Data Sheets (MSDS/SDS) for the chemicals that are used. Use the recommended personal protective equipment.

Dispose of reacted solutions according to local, state and federal regulations. Refer to the Safety Data Sheets for disposal information for unused reagents. Refer to the environmental, health and safety staff for your facility and/or local regulatory agencies for further disposal information.

#### Items to collect

Description	Quantity
Chloride 2 Indicator Powder Pillows	1
Silver Nitrate Titration Cartridge, 1.128 N	1
Digital Titrator	1
Delivery tube for Digital Titrator	1
Graduated cylinder (size varies with selected sample volume), or TenSette pipet with tips	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.
- The sample can be kept for a maximum of 7 days before analysis.

#### Determine the sample volume

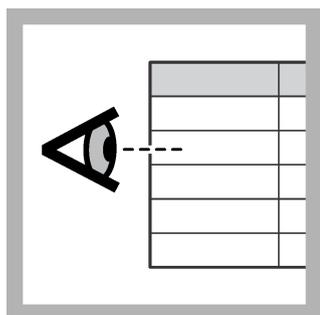
Use the steps that follow to make an estimate of the sample volume to use in the test procedure.

1. Add approximately 75–100 mL of deionized water to a clean titration flask.
2. Use a TenSette pipet to add 0.1 mL of the sample to the titration flask. Swirl to mix.
3. Add the contents of one Chloride 2 Indicator Powder Pillow to the flask. Swirl to mix. The sample color becomes yellow.
4. Titrate the solution quickly with the Silver Nitrate Titration Cartridge until the color changes from yellow to red-brown. Refer to [Technique tips](#) on page 3. Record the number of digits on the counter.
5. Find the sample volume to use in the test procedure from [Table 1](#).
6. Rinse the flask fully with deionized water.

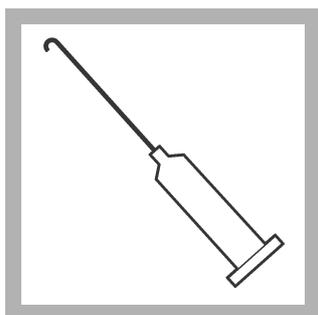
**Table 1 Determine the sample volume**

Number of digits	Sample volume (mL)
250	0.1
125	0.2
50	0.5
25	1.0
10	2.0
5	5.0
2	20
1	50

**Test procedure**



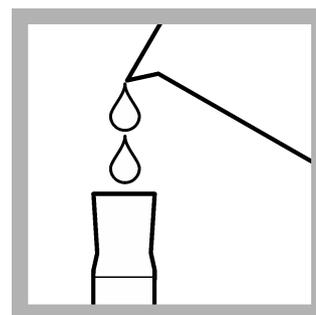
**1.** Select a sample volume and titration cartridge from [Table 2](#) on page 3. Refer to [Determine the sample volume](#) on page 1.



**2.** Insert a clean delivery tube into the Silver Nitrate Titration Cartridge. Attach the cartridge to the Digital Titrator. Keep the silver nitrate cartridge in a dark area when not in use.



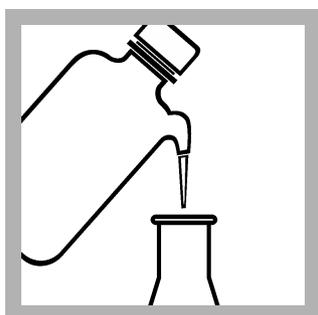
**3.** Hold the Digital Titrator vertically with the cartridge tip up. Turn the delivery knob to eject air and a few drops of titrant. Reset the counter to zero and clean the tip.



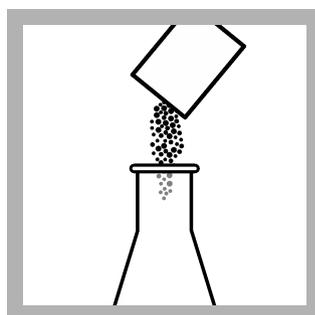
**4.** Use a graduated cylinder or TenSette pipet to measure the sample volume from [Table 2](#) on page 3.



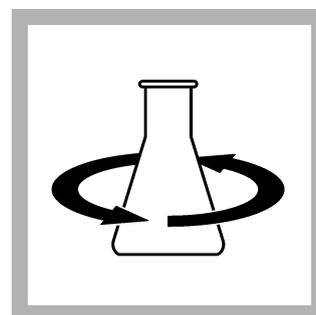
**5.** Pour the sample into a clean, 250-mL Erlenmeyer flask.



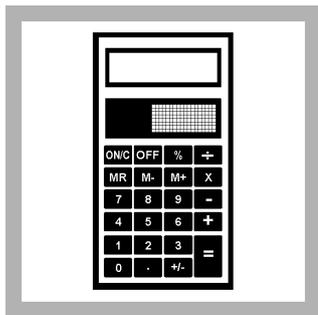
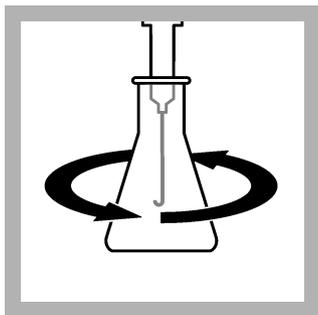
**6.** If the sample volume is less than 100 mL, dilute to approximately 100 mL with deionized water.



**7.** Add the contents of one Chloride 2 Indicator Powder Pillow.



**8.** Swirl to mix. A small amount of undissolved powder will not have an effect on the results.



9. Put the delivery tube point fully into the solution and swirl the flask. Turn the knob on the Digital Titrator to add titrant to the solution. Continue to swirl the flask and add titrant until the color changes from yellow to red-brown. Refer to [Technique tips](#) on page 3. Record the number of digits on the counter.

10. Use the multiplier in [Table 2](#) on page 3 to calculate the concentration.  
 Digits used × digit multiplier  
 = mg/L Cl<sup>-</sup>

### Sample volumes and digit multipliers

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

**Note:** Refer to [Determine the sample volume](#) on page 1 to find a sample volume for this test.

**Example:** A 50-mL sample was titrated and the counter showed 250 digits at the endpoint. The concentration is: 250 digits x 1 = 250 mg/L Cl<sup>-</sup>.

**Table 2 Sample volumes and digit multipliers**

Range (mg/L as Cl <sup>-</sup> )	Sample volume (mL)	Digit multiplier
100–400	50	1
250–1000	20	2.5
1000–4000	5	10
2500–10,000	2	25
5000–20,000	1	50
10,000–40,000	0.5	100
25,000–100,000	0.2	250
50,000–200,000	0.1	500

### Technique tips

- As an alternative to the deionized water, use demineralized water or other sources of chloride-free water.
- Use the TitraStir Titration Stand to reproducibly stir the sample at a steady rate.
- If the precipitate is red or orange but the solution is yellow, the test result will be low. Do the test again and increase the stir rate during the titration. Complete the steps that follow to prevent the red or orange precipitate formation:

1. Do not add one Chloride 2 Indicator Powder Pillow in step 7 of the test procedure and go directly to step 8.
2. Titrate a fresh sample with the Silver Nitrate Titration Cartridge to approximately 50–75% of the expected endpoint. The solution will have a milky-white precipitate.
3. Add one Chloride 2 Indicator Powder Pillow and swirl to dissolve. The solution becomes yellow. Continue to titrate with the Silver Nitrate Titration Cartridge to the red-brown endpoint.  
If the sample becomes red-brown after the addition of one Chloride 2 Indicator Powder Pillow, too much titrant was added. Repeat the procedure with less titrant.

## Conversions

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 chloride (Cl <sup>-</sup> ) to...	multiply by...	Example
mg/L sodium chloride (NaCl)	1.65	1000 mg/L chloride x 1.65 = 1650 mg/L NaCl
meq/L chloride (Cl <sup>-</sup> )	0.02821	1000 mg/L chloride x 0.02821 = 28.21 meq/L Cl <sup>-</sup>

## Interferences

[Table 4](#) shows the substances that can interfere with this test.

**Table 4 Interferences**

Interfering substance	Interference level
Bromide	Interferes directly and is included in the test result.
Cyanide	Interferes directly and is included in the test result.
Iodide	Interferes directly and is included in the test result.
Iron	Concentrations that are more than 10 mg/L prevent the color change at the endpoint.
Orthophosphate	Concentrations that are more than 25 mg/L will form a precipitate with the silver from the titrant.
Highly buffered samples or extreme sample pH	Can prevent the correct pH adjustment of the sample by the reagents. Sample pre-treatment may be necessary. Neutralize strongly alkaline or acidic samples to a pH of 2 to 7 with 5.25 N sulfuric acid or 5.0 N sodium hydroxide. If a pH meter is used in the pH adjustment, use a separate sample to find the correct amount of acid or base to use. Then add the same amount of acid or base to the sample to be tested. pH electrodes will contaminate the sample.
Sulfide	Complete the steps that follow to remove sulfide interference: <ol style="list-style-type: none"> <li>1. Add the contents of one Sulfide Inhibitor Reagent Powder Pillow to approximately 125 mL of sample.</li> <li>2. Mix for 1 minute.</li> <li>3. Pour the solution through folded filter paper.</li> <li>4. Use the filtered sample in the chloride test procedure.</li> </ol>
Sulfite	Concentrations that are more than 10 mg/L interfere with this method. To eliminate sulfite interference, add 3 drops of Hydrogen Peroxide, 30%, to the sample before the test is started.

## 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:

- Chloride Voluette Ampule Standard Solution, 12,500-mg/L Cl<sup>-</sup>

- 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 25 digits of the Silver Nitrate Titration Cartridge for each 0.1 mL addition of the standard solution. If much more or less titrant was used, there can be a problem with user technique, reagents, apparatus or an interference.

### Standard solution method

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

Items to collect:

- Chloride Voluette Ampule Standard Solution, 12,500-mg/L Cl<sup>-</sup>
  - Ampule Breaker
  - Pipet, TenSette, 0.1–1.0 mL and pipet tips
1. Use a TenSette pipet to add 1.0 mL of the standard solution to a 250-mL Erlenmeyer flask.
  2. Dilute to approximately 100 mL with deionized water.
  3. Add one Chloride 2 Indicator Powder Pillow. Swirl to mix.
  4. Titrate the prepared standard solution until the color changes from yellow to red-brown. Refer to [Technique tips](#) on page 3. The correct number of digits for this titration is 250 (± 25) 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.

### Summary of Method

Silver ions in the titrant react with chloride in the sample to form a silver chloride precipitate. After all of the chloride is in the form of silver chloride, the silver ions react with chromate (from the Chloride 2 Indicator Powder Pillow) to form a silver chromate precipitate. The silver chromate precipitate has an orange or a red-brown color, which shows the endpoint of the titration.

### Consumables and replacement items

#### Required reagents

Description	Quantity/Test	Unit	Item no.
Chloride Reagent Set (approximately 100 tests)	—	each	2288000
Chloride 2 Indicator Powder Pillows (2x)	1	50/pkg	105766
Silver Nitrate Titration Cartridge, 1.128 N	varies	each	1439701
Water, deionized	varies	4 L	27256

## Required apparatus

Description	Quantity/test	Unit	Item no.
Graduated cylinders—select one or more based on the sample volume:			
Cylinder, graduated, 5-mL	1	each	50837
Cylinder, graduated, 10-mL	1	each	50838
Cylinder, graduated, 25-mL	1	each	50840
Cylinder, graduated, 50-mL	1	each	50841
Cylinder, graduated, 100-mL	1	each	50842
Digital Titrator	1	each	1690001
Delivery tube for Digital Titrator, J-hook tip	1	5/pkg	1720500
Flask, Erlenmeyer, 250-mL	1	each	50546
Pipet, TenSette <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.
Chloride Standard Solution, 12,500 mg/L as Cl <sup>-</sup> , 10-mL Voluette ampules	16/pkg	1425010

## Optional reagents and apparatus

Description	Unit	Item no.
Ampule Breaker, 10-mL Voluette <sup>®</sup> Ampules	each	2196800
Filter paper, folded, 3–5-micron, 12.5-cm	100/pkg	69257
Funnel, poly, 65-mm	each	108367
Hydrogen Peroxide Solution, 30%, ACS	473 mL	14411
Sodium Hydroxide Standard Solution, 5.0 N	100 mL MDB	245032
Stir bar, octagonal	each	2095352
Sulfide Inhibitor Reagent Powder Pillows	100/pkg	241899
Sulfuric Acid Standard Solution, 5.25 N	100 mL	244932
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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