

## Silver Nitrate Method<sup>1, 2</sup>

Method 8225

0 to 25,000 mg/L as Cl<sup>-</sup>

Buret Titration

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

<sup>1</sup> USEPA accepted for NPDES reporting when 0.0141 N silver nitrate standard solution is used.

<sup>2</sup> Adapted from *Standard Methods for the Examination of Water and Wastewater*, Standard Method 4500 Cl- B.



### Test preparation

#### Before starting

The optional TitraStir Titration Stand can hold the buret 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

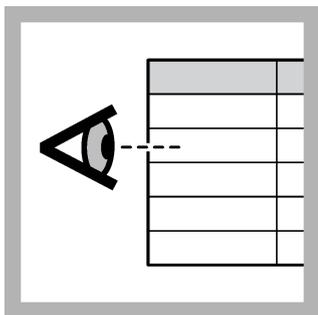
Description	Quantity
Chloride 2 Indicator Powder Pillow	1
Silver Nitrate Standard Solution (use a concentration that is applicable to the selected sample volume)	varies
Buret, Class A, 25 mL	1
Graduated cylinder (use a size that is applicable to the selected sample volume), or TenSette pipet with tips	1
Erlenmeyer flask, 250 mL	1
Funnel, micro	1
Support stand with buret clamp	1
Water, deionized	varies

Refer to [Consumables and replacement items](#) on page 5 for order information.

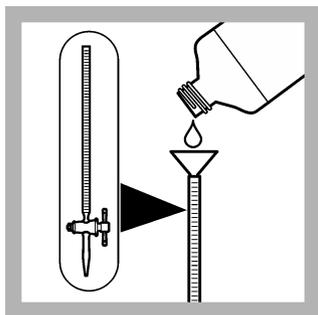
#### Sample collection

- Collect samples in clean glass or plastic bottles.
- If prompt analysis is not possible, keep the sample for a maximum of 7 days.

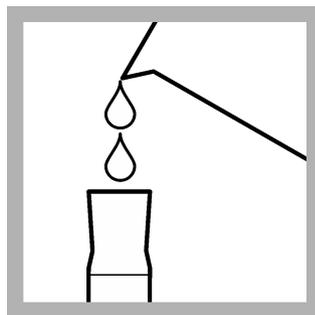
## Test procedure



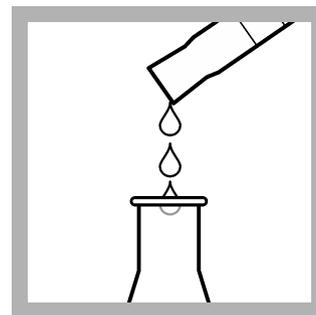
1. Select a sample volume and titrant from [Table 1](#) on page 3.



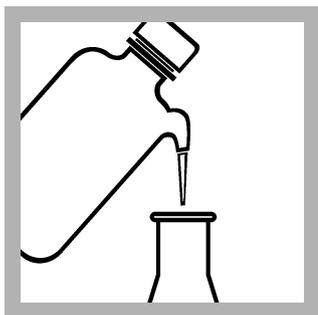
2. Fill a 25-mL buret to the zero mark with the titrant.



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



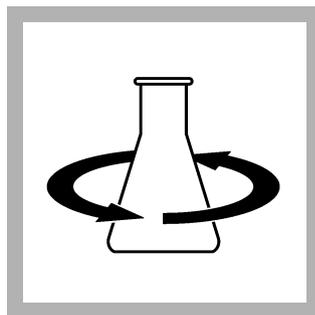
4. Pour the sample into a clean, 250-mL Erlenmeyer flask.



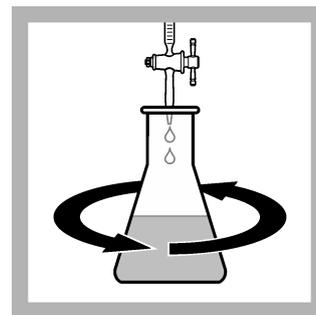
5. If the sample volume is less than 100 mL, dilute to approximately 100 mL with deionized water.



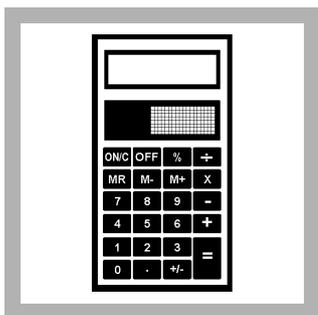
6. Add the contents of one Chloride 2 Indicator Powder Pillow.



7. Swirl to mix.



8. Put the flask under the buret. Swirl the flask. Add titrant until the color changes from yellow to red-brown.



9. Use the multiplier in [Table 1](#) on page 3 to calculate the concentration.  
 $\text{mL of titrant} \times \text{multiplier} = \text{mg/L as Cl}^-$

## Sample volumes and multipliers

Select a range in [Table 1](#), then read across the table row to find the applicable information for this test. Use the multiplier to calculate the concentration in the test procedure.

<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.

**Example:** A 100-mL sample was titrated with 0.0141 N titrant and 12 mL of titrant was used at the endpoint. The concentration is  $12 \text{ mL} \times 5 = 60 \text{ mg/L}$  as  $\text{Cl}^-$ .

**Table 1 Sample volumes and multipliers**

Range (mg/L)	Sample volume (mL)	Titrant—silver nitrate	Multiplier
0–125	100	0.0141 N	5
100–250	50	0.0141 N	10
200–500	25	0.0141 N	20
500–1250	100	0.141 N	50
1000–2500	50	0.141 N	100
2500–10,000	25	0.141 N	200
5000–25,000	10	0.141 N	500

## Conversions

To change the units or chemical form of the test result, multiply the test result by the factor in [Table 2](#).

**Table 2 Conversions**

mg/L chloride ( $\text{Cl}^-$ ) to...	multiply by...	Example
mg/L sodium chloride (NaCl)	1.65	$1000 \text{ mg/L chloride} \times 1.65 = 1650 \text{ mg/L NaCl}$
meq/L chloride ( $\text{Cl}^-$ )	0.02821	$1000 \text{ mg/L chloride} \times 0.02821 = 28.21 \text{ meq/L Cl}^-$

## 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 20 mg/L prevent the color change at the endpoint.
Orthophosphate	Concentrations that are more than 25 mg/L cause a precipitate to form.
Highly buffered samples or extreme sample pH	Can prevent the correct pH adjustment (of the sample) by the reagents. Sample pretreatment may be necessary. Adjust strongly alkaline or acidic samples to a pH of 7 to 9 with 5.25 N sulfuric acid or 5.0 N sodium hydroxide. Do not use a pH meter directly for the pH adjustment because the pH electrode will contaminate the sample. Collect a separate sample to find the correct quantity of acid or base to add. Then, add the same quantity of acid or base to the sample that is used in the test procedure. As an alternative, use pH paper to measure the pH.
Sulfide	Remove sulfide interference as follows: <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 in a funnel.</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 remove sulfite interference, add 3 drops of 30% Hydrogen Peroxide to the sample, then start the test.

## Accuracy check

### Standard additions method (sample spike)—0.0141 N titrant

Use the standard additions method to validate the test procedure, reagents, apparatus, technique and to find if there is an interference in the sample.

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Items to collect:

- Chloride Voluette Ampule Standard Solution, 12,500-mg/L  $\text{Cl}^-$
  - Ampule Breaker
  - Pipet, TenSette, 0.1–1.0 mL and pipet tips
1. Use the test procedure to measure the concentration of the standard solution. Use the 0.0141 N titrant.
  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 mL of titrant added.
  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 mL of titrant added.
  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 mL of titrant added.
  8. Compare the actual result to the correct result. The correct result for this titration is 2.5 mL of 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 additions method (sample spike)—0.141 N titrant**

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  $\text{Cl}^-$
  - Ampule Breaker
  - Pipet, TenSette, 0.1–1.0 mL and pipet tips
1. Use the test procedure to measure the concentration of the standard solution. Use the 0.141 N titrant.
  2. Use a TenSette pipet to add 1.0 mL of the standard solution to the titrated sample.
  3. Titrate the spiked sample to the endpoint. Record the mL of titrant added.
  4. Add one more 1.0-mL addition of the standard solution to the titrated sample.
  5. Titrate the spiked sample to the endpoint. Record the mL of titrant added.
  6. Add one more 1.0-mL addition of the standard solution to the titrated sample.
  7. Titrate the spiked sample to the endpoint. Record the mL of titrant added.
  8. Compare the actual result to the correct result. The correct result for this titration is 2.5 mL of titrant for each 1.0-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.

#### **Titrant test—0.0141 N titrant**

Examine the strength of the Silver Nitrite Standard Solution each month. The strength of Sodium Hydroxide Standard Solution slowly decreases in light.

Items to collect:

- Sodium Chloride Standard Solution, 1000 mg/L as  $\text{Cl}^-$
  - 100-mL Class A volumetric flask
  - 250-mL Erlenmeyer flask
1. Add 10.0 mL of Sodium Chloride Standard Solution (as 1000-mg/L as  $\text{Cl}^-$ ) to a 100-mL Class A volumetric flask.
  2. Dilute the standard solution to approximately 100 mL with deionized water.
  3. Add 100.0 mL of the diluted standard solution (100-mg/L as  $\text{Cl}^-$ ) to a 250-mL Erlenmeyer flask.

4. Add one Chloride 2 Indicator Powder Pillow to the flask.
5. Titrate the solution to the endpoint with the 0.0141 N titrant. Record the mL of titrant added.
6. If more than 21 mL of titrant was added (test result = 105 mg/L chloride), discard the titrant. Get new titrant.

#### Titrant test—0.141 N titrant

Examine the strength of the 0.141 N Silver Nitrite Standard Solution each month. The strength of Sodium Hydroxide Standard Solution slowly decreases in light.

Items to collect:

- Sodium Chloride Standard Solution, 1000 mg/L as Cl<sup>-</sup>
  - 250-mL Erlenmeyer flask
1. Add 100.0 mL of Sodium Chloride Standard Solution (as 1000-mg/L as Cl<sup>-</sup>) to a 250-mL Erlenmeyer flask.
  2. Add one Chloride 2 Indicator Powder Pillow to the flask.
  3. Titrate the solution to the endpoint with the 0.141 N titrant. Record the mL of titrant added.
  4. If more than 21 mL of titrant was added (test result = 1050 mg/L chloride), discard the titrant. Get new titrant.

#### Summary of Method

Silver nitrate is used as the titrant and potassium chromate as the indicator. Silver nitrate first reacts selectively with the chloride in the sample to make insoluble white silver chloride. After all the chloride has precipitated, the silver nitrate reacts with the chromate to form an orange or red-brown silver chromate precipitate.

#### Consumables and replacement items

##### Required reagents

Description	Quantity/Test	Unit	Item no.
Chloride 2 Indicator Powder Pillows	1 pillow	50/pkg	105766
Silver Nitrate Standard Solution, 0.0141 N	varies	1 L	31653
Silver Nitrate Standard Solution, 0.141 N	varies	500 mL	1255149
Water, deionized	varies	4 L	27256

##### Required apparatus

Description	Quantity/test	Unit	Item no.
Buret clamp, double	1	each	32800
Buret, Class A, 25 mL	1	each	2636540
Support stand	1	each	56300
Funnel, micro	1	each	2584335
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

**Required apparatus (continued)**

Description	Quantity/test	Unit	Item no.
Tensette <sup>®</sup> pipets and pipet tips—Select one or more for the sample volume:			
Pipet, TenSette <sup>®</sup> , 0.1–1.0 mL	1	each	1970001
Pipet tips, TenSette <sup>®</sup> Pipet, 0.1–1.0 mL	varies	50/pkg	2185696
Pipet, TenSette <sup>®</sup> , 1.0–10.0 mL	1	each	1970010
Pipet tips, TenSette <sup>®</sup> Pipet, 1.0–10.0 mL	varies	50/pkg	2199796
Flask, Erlenmeyer, 250 mL	1	each	50546

**Recommended standards**

Description	Unit	Item no.
Chloride Standard Solution, 12,500 mg/L as Cl <sup>-</sup> , 10-mL Voluette ampules	16/pkg	1425010
Sodium Chloride Standard Solution, 1000-mg/L as Cl <sup>-</sup>	500 mL	18349

**Optional reagents and apparatus**

Description	Unit	Item no.
Ampule Breaker, 10-mL Voluette <sup>®</sup> Ampules	each	2196800
Bottle, sampling, with cap, low density polyethylene, 250 mL	12/pkg	2087076
Clippers	each	96800
Dropper, LDPE, 0.5 –1.0 mL	20/pkg	2124720
Filter paper, folded, 3–5-micron, 12.5-cm	100/pkg	69257
Flask, volumetric, Class A, 100-mL	each	1457442
Funnel, poly, 65 mm	each	108367
Hydrogen Peroxide Solution, 30%, ACS	473 mL	14411
Paper, pH, 0–14 pH range	100/pkg	2601300
Sodium Hydroxide Standard Solution, 5.0 N	100 mL MDB	245032
Sulfide Inhibitor Reagent Powder Pillows	100/pkg	241899
Sulfuric Acid Standard Solution, 5.25 N	100 mL	244932
Stir bar, octagonal	each	2095352
TitraStir <sup>®</sup> Titration Stand, 115 VAC	each	1940000
TitraStir <sup>®</sup> Titration Stand, 230 VAC	each	1940010



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