

## Iodometric Method Using Sodium Thiosulfate

Method 8209

1 to 400 mg/L or 20 to 70,000 as Cl<sub>2</sub>

Digital Titrator

Scope and application: For water, wastewater and seawater.



### Test preparation

#### Before starting

Percent (%) chlorine = mg/L ÷ 10,000

Use these test procedures to determine the iodine or bromine concentration in a sample if chlorine is not in the sample. Refer to [Conversions](#) on page 6.

For higher concentrations, refer to the hypochlorite procedure Method 10100.

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
Acetate Buffer Solution, pH 4 (for the 1–400 mg/L Cl <sub>2</sub> range)	2 mL
Dissolved Oxygen 3 Powder Pillow (for the 20–70,000 mg/L Cl <sub>2</sub> range)	1
Potassium Iodide Powder Pillow	1
Sodium Thiosulfate Titration Cartridge (refer to <a href="#">Sample volumes and digit multipliers</a> on page 5)	1
Starch Indicator Solution	1 dropper full
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, 125-mL	1
Water, deionized	varies

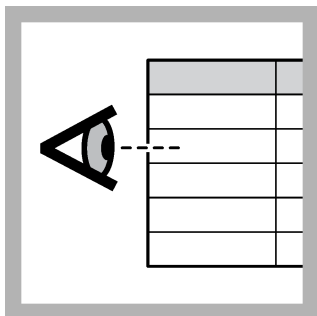
Refer to [Consumables and replacement items](#) on page 7 for order information.

#### Sample collection

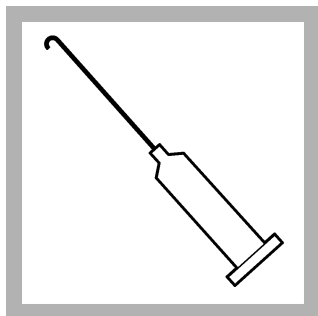
- Analyze the samples immediately. The samples cannot be preserved for later analysis.
- Chlorine is a strong oxidizing agent and is unstable in natural waters. Chlorine reacts quickly with various inorganic compounds and more slowly with organic compounds. Many factors, including reactant concentrations, sunlight, pH, temperature and salinity influence the decomposition of chlorine in water.
- Collect samples in clean glass bottles. Do not use plastic containers because these can have a large chlorine demand.

- Pretreat glass sample containers to remove chlorine demand. Soak the containers in a weak bleach solution (1 mL commercial bleach to 1 liter of deionized water) for at least 1 hour. Rinse fully with deionized or distilled water. If sample containers are rinsed fully with deionized or distilled water after use, only occasional pretreatment is necessary.
- Make sure to get a representative sample. If the sample is taken from a spigot or faucet, let the water flow for at least 5 minutes. Let the container overflow with the sample several times and then put the cap on the sample container so that there is no headspace (air) above the sample.

### Test procedure—1 to 400 mg/L chlorine



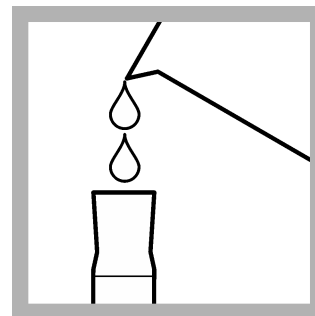
1. Select a sample volume and titration cartridge from [Table 1](#) on page 5.



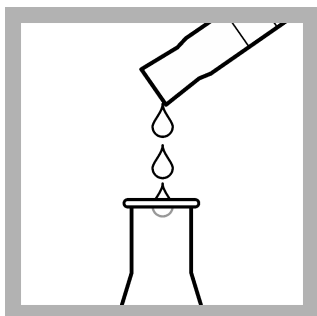
2. Insert a clean delivery tube into the digital titration cartridge. Attach the cartridge to the Digital Titrator.



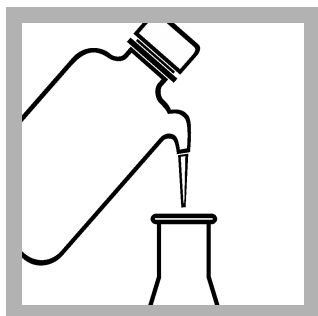
3. Hold the Digital Titrator with the cartridge tip up. Turn the delivery knob to eject air and a few drops of titrant. Reset the counter to zero and clean the tip.



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



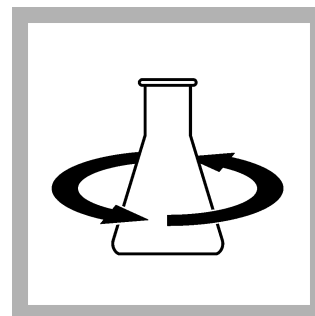
5. Pour the sample into a clean, 125-mL Erlenmeyer flask.



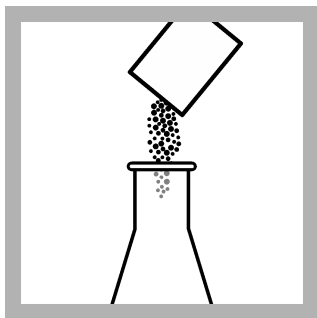
6. If the sample volume is less than 100 mL, dilute to approximately 100 mL with deionized water.



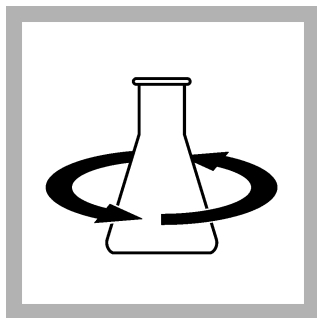
7. Add 2 mL of Acetate Buffer Solution, pH 4.



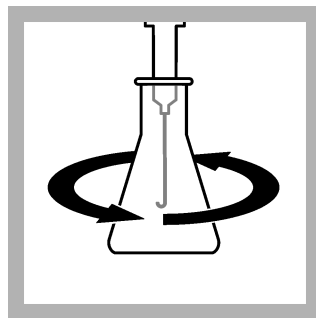
8. Swirl to mix.



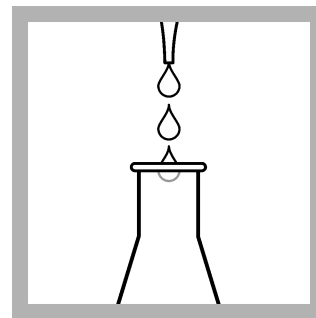
**9.** Add the contents of one Potassium Iodide Powder Pillow.



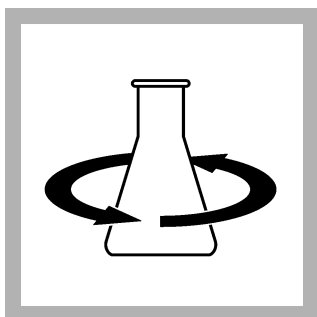
**10.** Swirl to mix.



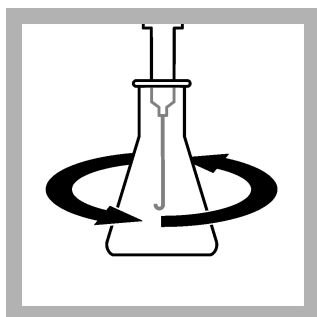
**11.** Put the end of the delivery tube fully into the solution. Swirl the flask. Turn the knob on the Digital Titrator to add titrant to the solution. Continue to swirl the flask. Add titrant until the color changes to pale yellow.



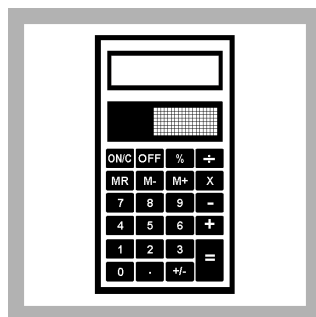
**12.** Add 1 full dropper of Starch Indicator Solution.



**13.** Swirl to mix. The color of the solution changes to dark blue.

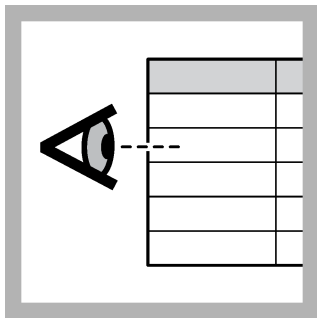


**14.** Put the end of the delivery tube fully into the solution. Swirl the flask. Turn the knob on the Digital Titrator to add titrant to the solution. Continue to swirl the flask. Add titrant until the color changes from dark blue to colorless. Record the number of digits on the counter.

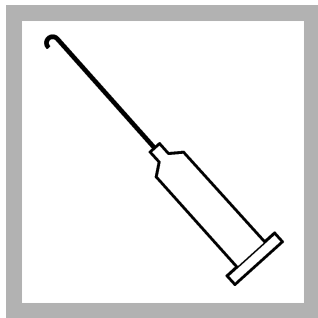


**15.** Use the multiplier in [Table 1](#) on page 5 to calculate the concentration. Digits used  $\times$  digit multiplier = mg/L total chlorine as  $\text{Cl}_2$ .

## Test procedure—20 to 70,000 mg/L chlorine



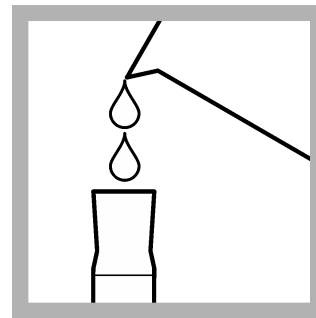
1. Select a sample volume and titration cartridge from [Table 2](#) on page 5.



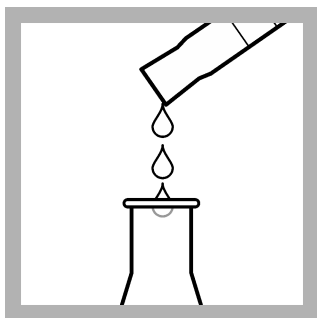
2. Insert a clean delivery tube into the digital titration cartridge. Attach the cartridge to the Digital Titrator.



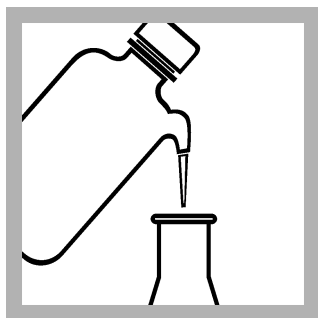
3. Hold the Digital Titrator with the cartridge tip up. Turn the delivery knob to eject air and a few drops of titrant. Reset the counter to zero and clean the tip.



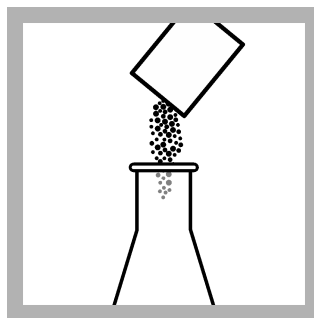
4. Use graduated cylinder (or pipet) to measure the sample volume from [Table 2](#) on page 5.



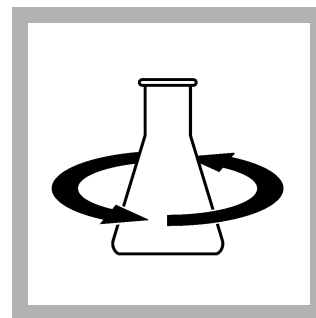
5. Pour the sample into a clean, 125-mL Erlenmeyer flask.



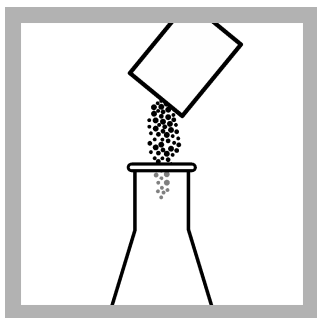
6. If the sample volume is less than 50 mL, dilute to approximately 50 mL with deionized water.



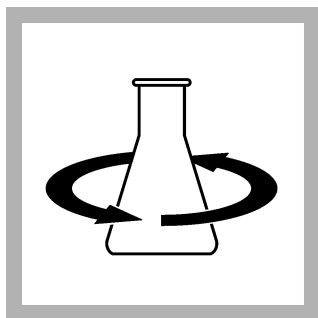
7. Add the contents of one Dissolved Oxygen 3 Powder Pillow.



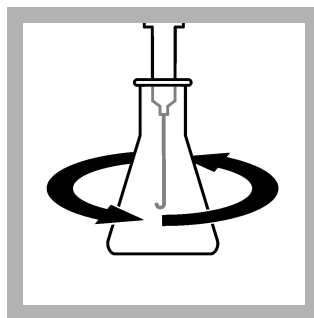
8. Swirl to mix.



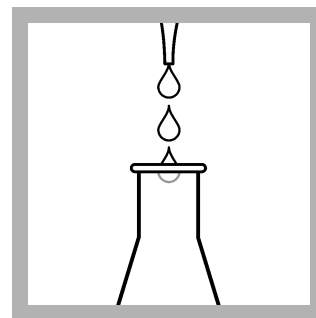
9. Add the contents of one Potassium Iodide Powder Pillow.



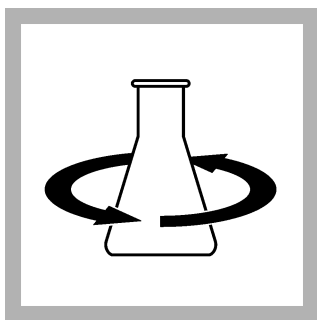
10. Swirl to mix.



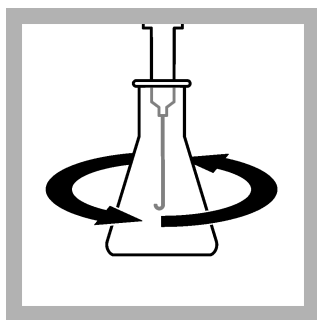
11. Put the end of the delivery tube fully into the solution. Swirl the flask. Turn the knob on the Digital Titrator to add titrant to the solution. Continue to swirl the flask. Add titrant until the color changes to pale yellow.



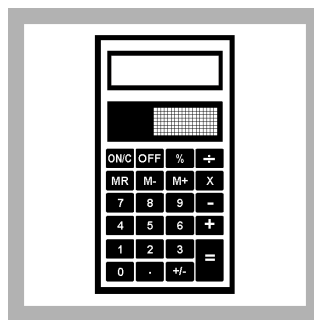
12. Add 1 full dropper of Starch Indicator Solution.



**13.** Swirl to mix. The color of the solution changes to dark blue.



**14.** 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.



**15.** Use the multiplier in [Table 2](#) on page 5 to calculate the concentration. Digits used  $\times$  digit multiplier = mg/L total chlorine as  $\text{Cl}_2$ .

### 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 100-mL sample was titrated with 0.02256 N Sodium Thiosulfate Titration Cartridge and the counter showed 250 digits at the endpoint. The concentration is  $250 \text{ digits} \times 0.01 = 2.5 \text{ mg/L as } \text{Cl}_2$ .

**Table 1 Sample volumes and digit multipliers—1 to 400 mg/L**

Range (mg/L as $\text{Cl}_2$ )	Sample volume (mL)	Titration cartridge	Digit multiplier
1–4	100	0.02256 N	0.01
2–8	50	0.02256 N	0.02
5–20	20	0.02256 N	0.05
100–400	1	0.02256 N	1.0

**Table 2 Sample volumes and digit multipliers—20 to 70,000 mg/L**

Range (mg/L as $\text{Cl}_2$ )	Sample volume (mL)	Titration cartridge	Digit multiplier
20–80	25	0.113 N	0.2
50–200	10	0.113 N	0.5
100–400	5	0.113 N	1.0
250–1000	2	0.113 N	2.5
500–2000	1	0.113 N	5
2000–9000 (0.2–0.9%)	4	2.00 N	22.2
5000–18,000 (0.5–1.8%)	2	2.00 N	44.3
10,000–35,000 (1.0–3.5%)	1	2.00 N	88.7
20,000–70,000 (2.0–7.0%)	0.5	2.00 N	177

## 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 chlorine (Cl <sub>2</sub> ) to...	multiply results by...	Example
mg/L iodine	3.58	mg/L chlorine × 3.58 = mg/L iodine
mg/L bromine	2.25	mg/L chlorine × 2.25 = mg/L bromine

## Accuracy check

### Standard additions method (sample spike)—0.02256 N cartridge

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:

- Chlorine Standard Solution<sup>1</sup>, PourRite Ampule, 50–75 mg/L Cl<sub>2</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 0.2 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 0.2-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 0.2-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 10–15 digits of the 0.02256 N Sodium Thiosulfate Titration Cartridge for each 0.2-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. To identify the correct number of digits for each 0.2-mL addition, multiply the actual standard concentration by the spike volume. For example, 50 mg/L × 0.2 mL = 10 digits

### Standard additions method (sample spike)—0.113 N cartridge

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:

- Chlorine Standard Solution<sup>2</sup>, Voluette Ampule, 50–75 mg/L Cl<sub>2</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 1.0 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 1.0-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 1.0-mL addition of the standard solution to the titrated sample.

<sup>1</sup> Refer to the certificate supplied with the ampule for the actual concentration.

<sup>2</sup> Refer to the certificate supplied with the ampule for the actual concentration.

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 10–15 digits of the 0.113 N Sodium Thiosulfate Titration Cartridge 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. To identify the correct number of digits for each 1.0-mL addition, multiply the actual standard concentration by the spike volume and divide by 5. For example,  $50 \text{ mg/L} \times 1.0 \text{ mL} \div 5 = 10$  digits

## Summary of method

Total chlorine concentration is equal to the concentration of the free and the combined forms of chlorine. Free chlorine reacts with ammonia to form combined chlorine such as monochloramines. When potassium iodide is added to a sample that has chlorine at an acidic pH, free iodine is released in direct proportion to the amount of total chlorine in the sample. Then, the iodine is titrated with sodium thiosulfate to a colorless endpoint.

## Consumables and replacement items

### Required reagents

Description	Quantity/Test	Unit	Item no.
<b>1–400 mg/L range:</b>			
Acetate Buffer Solution, pH 4	2 mL	100 mL MDB	1490932
Potassium Iodide Powder Pillows	1 pillow	100/pkg	107799
Sodium Thiosulfate Titration Cartridge, 0.02256 N	varies	each	2409101
Starch Indicator Solution	1 mL	100 mL MDB	34932
<b>20–2000 mg/L range:</b>			
Total Chlorine Reagent Set (approximately 100 tests)	—	each	2272500
Dissolved Oxygen 3 Powder Pillows	1 pillow	100/pkg	98799
Potassium Iodide Powder Pillows	1 pillow	100/pkg	107799
Sodium Thiosulfate Titration Cartridge, 0.113 N	varies	each	2267301
Starch Indicator Solution	1 mL	100 mL MDB	34932
<b>2000–70,000 mg/L range:</b>			
Total Chlorine Reagent Set (approximately 100 tests)	—	each	2444800
Dissolved Oxygen 3 Powder Pillows	1 pillow	100/pkg	98799
Potassium Iodide Powder Pillows (2x)	1 pillow	50/pkg	2059996
Sodium Thiosulfate Titration Cartridge, 2.00 N (2x)	varies	each	1440101
Starch Indicator Solution	1 mL	100 mL MDB	34932

### 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

**Required apparatus (continued)**

Description	Quantity/test	Unit	Item no.
Digital Titrator	1	each	1690001
Delivery tube for Digital Titrator, J-hook tip	1	5/pkg	1720500
Flask, Erlenmeyer, 125 mL	1	each	50543

**Recommended standards**

Description	Unit	Item no.
Chlorine Standard PourRite <sup>®</sup> Ampule, 50–75 mg/L, 2 mL	20/pkg	1426820
Chlorine Standard Voluette <sup>®</sup> Ampule, 50–75 mg/L, 10 mL	16/pkg	1426810

**Optional reagents and apparatus**

Description	Unit	Item no.
Clippers	each	96800
Water, deionized	500 mL	27249
Pipet, TenSette <sup>®</sup> , 0.1–1.0 mL	each	1970001
Pipet tips for TenSette <sup>®</sup> Pipet, 0.1–1.0 mL	50/pkg	2185696
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
Ampule Breaker, 10-mL Voluette <sup>®</sup> Ampules	each	2196800



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