

Chlorine, Free and Total

DOC316.53.01172

DPD-FEAS Method

Method 8210

0 to 3.00 mg/L as Cl₂

Digital Titrator

Scope and application: For water, wastewater and seawater. This product has not been evaluated to test for chlorine and chloramines in medical applications in the United States.



Test preparation

Before starting

For the best results, use Erlenmeyer flasks that are only used for free chlorine or total chlorine determinations to prevent cross-contamination from iodide in the DPD Total Chlorine Reagent.

mg/L combined chlorine = mg/L total chlorine – mg/L free chlorine

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
DPD Free Chlorine Powder Pillow	1
DPD Total Chlorine Powder Pillow	1
Ferrous Ethylenediammonium Sulfate (FEAS) Titration Cartridge, 0.00564 N	1
Digital Titrator	1
Delivery tube for Digital Titrator	1
Pipet, volumetric, Class A, 25-mL	1
Erlenmeyer flask, 50-mL	1

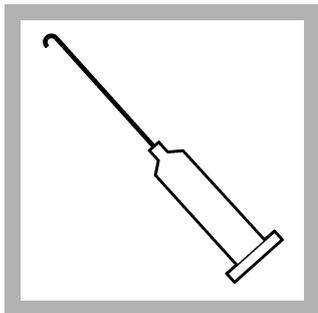
Refer to [Consumables and replacement items](#) on page 5 for order information.

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—Free Chlorine



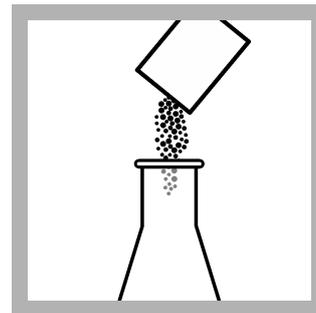
1. Insert a clean delivery tube into the digital titration cartridge. Attach the cartridge to the Digital Titrator.



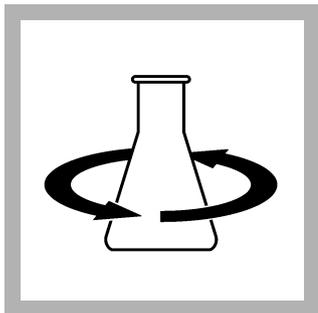
2. Hold the Digital Titrator with the cartridge tip up. Turn the delivery knob to eject air and a few drops of titrant. Reset the counter to zero and clean the tip.



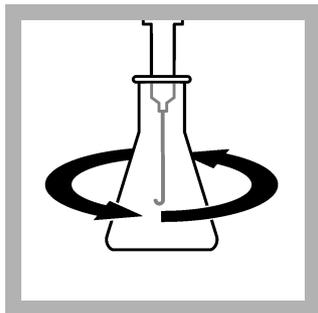
3. Use a pipet to add 25 mL of sample to a clean, 50-mL Erlenmeyer flask.



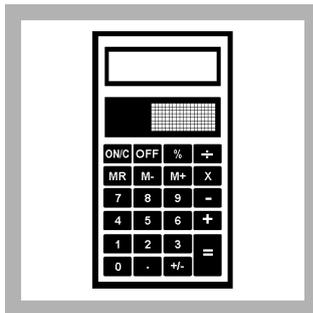
4. Add the contents of one DPD Free Chlorine Powder Pillow.



5. Swirl to mix. A small amount of undissolved powder will not have an effect on the results. A pink color forms if free chlorine is in the sample.



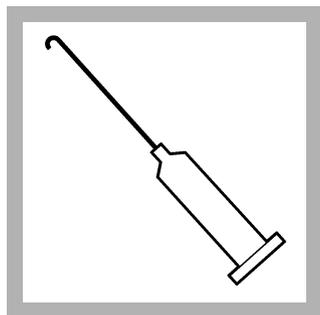
6. Put the end of the delivery tube fully into the solution. Swirl the flask. Turn the knob on the Digital Titrator to add titrant to the solution. Continue to swirl the flask. Add titrant until the color changes to colorless. Record the number of digits on the counter.



7. Calculate the concentration. Digits used $\times 0.01 =$ mg/L free chlorine as Cl_2 .

Example: A 25-mL sample was titrated with the digital cartridge and the counter showed 250 digits at the endpoint. The concentration is $250 \times 0.01 = 2.50$ mg/L free chlorine as Cl_2 .

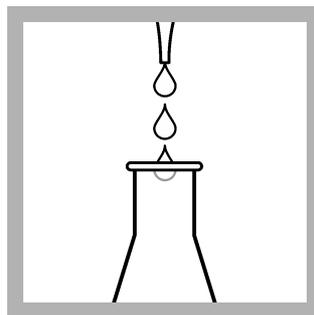
Test procedure—Total Chlorine



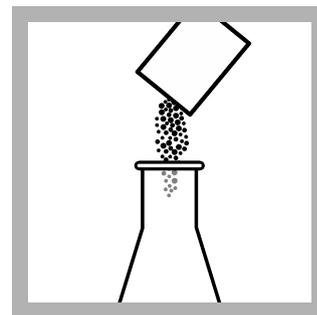
1. Insert a clean delivery tube into the digital titration cartridge. Attach the cartridge to the Digital Titrator.



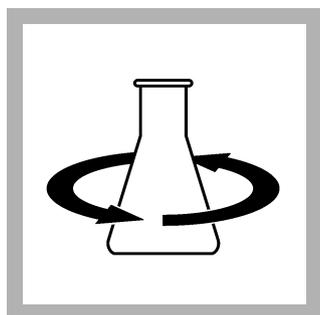
2. Hold the Digital Titrator with the cartridge tip up. Turn the delivery knob to eject air and a few drops of titrant. Reset the counter to zero and clean the tip.



3. Use a pipet to add 25 mL of sample to a clean, 50-mL Erlenmeyer flask.



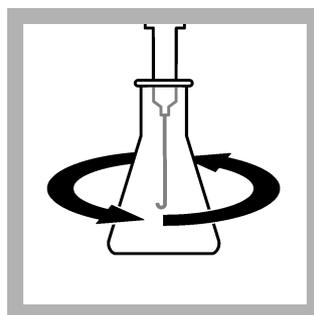
4. Add the contents of one DPD Total Chlorine Powder Pillow.



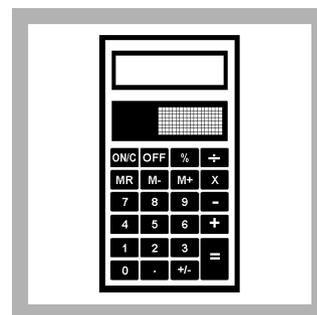
5. Swirl to mix. A small amount of undissolved powder will not have an effect on the results. After 3 minutes, a pink color forms if total chlorine is in the sample.



6. Set and start a timer for 3 minutes. A 3-minute reaction time starts.



7. 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 colorless. Record the number of digits on the counter.



8. Calculate the concentration. Digits used \times 0.01 = mg/L total chlorine as Cl_2 .
Example: A 25-mL sample was titrated with the digital cartridge and the counter showed 250 digits at the endpoint. The concentration is $250 \times 0.01 = 2.50$ mg/L total chlorine as Cl_2 .

Interferences

Interfering substance	Interference level
Acidity	More than 150 mg/L CaCO_3 . The full color may not develop or the color may fade instantly. Adjust to pH 6–7 with 1 N Sodium Hydroxide. Measure the amount to add on a separate sample aliquot, then add the same amount to the sample that is tested. Correct the test result for the dilution from the volume addition.
Alkalinity	More than 250 mg/L CaCO_3 . The full color may not develop or the color may fade instantly. Adjust to pH 6–7 with 1 N Sulfuric Acid. Measure the amount to add on a separate sample aliquot, then add the same amount to the sample that is tested. Correct the test result for the dilution from the volume addition.
Bromine, Br_2	Positive interference at all levels
Chlorine Dioxide, ClO_2	Positive interference at all levels
Inorganic chloramines	Included in the total chlorine result
Chloramines, organic	Can cause interference

Interfering substance	Interference level
Iodine, I ₂	Positive interference at all levels
Manganese, Oxidized (Mn ⁴⁺ , Mn ⁷⁺) or Chromium, Oxidized (Cr ⁶⁺)	Pre-treat the sample as follows: <ol style="list-style-type: none"> 1. Adjust the sample pH to 6–7. 2. Add 3 drops of Potassium Iodide (30-g/L) to 10 mL of sample. 3. Mix and wait 1 minute. 4. Add 3 drops of Sodium Arsenite¹ (5-g/L) and mix. 5. Use the test procedure to measure the concentration of the treated sample. 6. Subtract this result from the result without the treatment to obtain the correct chlorine concentration.
Ozone	Positive interference at all levels
Peroxides	Can cause interference
Highly buffered samples or extreme sample pH	Can prevent the correct pH adjustment (of the sample) by the reagents. Sample pretreatment may be necessary. Sample pre-treatment may be necessary. Adjust to pH 6–7 with acid (Sulfuric Acid, 1.000 N) or base (Sodium Hydroxide, 1.00 N).
Temperature	Positive interference at higher room temperatures because of the chloramine reaction. May not develop full color or color may fade instantly.

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:

- Chlorine Standard Solution², PourRite Ampule, 50–75 mg/L Cl₂
- 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 20–30 digits of the Ferrous Ethylenediammonium Sulfate (FEAS) 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. To identify the correct number of digits for each 0.1-mL addition, multiply the actual concentration by 4 and by the spike volume. For example, 50 mg/L × 4 × 0.1 mL = 20 digits

Summary of method

The DPD-FEAS method is a titrimetric procedure used to determine free available chlorine in the sample. In addition, the DPD-FEAS method gives an estimation of free and combined chlorine fractions that are in the sample together. The magenta species that is a result of the oxidation of DPD by chlorine is quantitatively removed by titration with

¹ Samples that are treated with sodium arsenite will contain arsenic and may require special disposal consideration. Refer to the current MSDS/SDS for safe handling and disposal instructions.

² Refer to the certification supplied with the ampule for the actual concentration.

ferrous ethylenediammonium sulfate. The volume of titrant that is necessary to get to a colorless endpoint is proportional to the chlorine concentration. In addition, total residual chlorine can be determined with this test.

Consumables and replacement items

Required reagents

Description	Quantity/Test	Unit	Item no.
Free and Total Chlorine Reagent Set (approximately 100 tests)	—	each	2445300
DPD Free Chlorine Powder Pillows	1 pillow	100/pkg	1407099
DPD Total Chlorine Powder Pillows	1 pillow	100/pkg	1406499
FEAS Titration Cartridge, 0.00564 N	varies	each	2292301

Required apparatus

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, 50-mL	1	each	50541
Pipet, volumetric, Class A, 25-mL	1	each	1451540
Pipet filler, safety bulb	1	each	1465100
PourRite® Ampule breaker	1	each	2484600

Recommended standards

Description	Unit	Item no.
Chlorine Standard Solution, PourRite™ Ampule, 50–75 mg/L Cl ₂ , 2 mL	20/pkg	1426820

Optional reagents and apparatus

Description	Unit	Item no.
Potassium Iodide, 30-g/L	100 mL	34332
Sodium Arsenite, 5-g/L	100 mL	104732
Sodium Hydroxide Standard Solution, 1.0 N	100 mL MDB	104532
Sulfuric Acid Standard Solution, 1 N	100 mL MDB	127032
Chlorine Standard Solution, 10-mL Voluette® Ampule, 50–75 mg/L	16/pkg	1426810
Chlorine Standard Solution, 2-mL PourRite® Ampule, 25-30 mg/L	20/pkg	2630020
Ampule Breaker, 10-mL Voluette® Ampules	each	2196800
Bottle, sampling, with cap, low density polyethylene, 250-mL	12/pkg	2087076
Clippers	each	96800
Water, deionized	500 mL	27249
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

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



FOR TECHNICAL ASSISTANCE, PRICE INFORMATION AND ORDERING:
In the U.S.A. – Call toll-free 800-227-4224
Outside the U.S.A. – Contact the HACH office or distributor serving you.
On the Worldwide Web – www.hach.com; E-mail – techhelp@hach.com

HACH COMPANY
WORLD HEADQUARTERS
Telephone: (970) 669-3050
FAX: (970) 669-2932