

USEPA DPD Method¹
Method 8167
0.02 to 2.00 mg/L Cl₂
Powder Pillows or AccuVac[®] Ampuls

Scope and application: For testing residual chlorine and chloramines in water, wastewater, estuary water and seawater; USEPA-accepted for reporting for drinking and wastewater analyses.² This product has not been evaluated to test for chlorine and chloramines in medical applications in the United States.

¹ Adapted from Standard Methods for the Examination of Water and Wastewater.

² Procedure is equivalent to USEPA and Standard Method 4500-Cl G for drinking water and wastewater analysis.



Test preparation

Instrument-specific information

Table 1 shows sample cell and orientation requirements for reagent addition tests, such as powder pillow or bulk reagent tests. Table 2 shows sample cell and adapter requirements for AccuVac Ampul tests. The tables also show all of the instruments that have the program for this test.

To use the table, select an instrument, then read across to find the applicable information for this test.

Table 1 Instrument-specific information for reagent addition

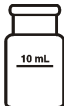



Instrument	Sample cell orientation	Sample cell
DR 6000 DR 3800 DR 2800 DR 2700 DR 1900	The fill line is to the right.	2495402 
DR 5000 DR 3900	The fill line is toward the user.	
DR 900	The orientation mark is toward the user.	2401906 

Table 2 Instrument-specific information for AccuVac Ampuls

Instrument	Adapter	Sample cell
DR 6000 DR 5000 DR 900	—	2427606 
DR 3900	LZV846 (A)	
DR 1900	9609900 or 9609800 (C)	
DR 3800 DR 2800 DR 2700	LZV584 (C)	2122800 

Before starting

Analyze the samples immediately. The samples cannot be preserved for later analysis.

Install the instrument cap on the DR 900 cell holder before ZERO or READ is pushed.

If the test result is over-range, or if the sample temporarily turns yellow after the reagent addition, dilute the sample with a known volume of high quality, chlorine demand-free water and do the test again. Some loss of chlorine may occur due to the dilution. Multiply the result by the dilution factor. Additional methods are available to measure chlorine without dilution.

For chloramination disinfection control, use one of the available Chloramine (Mono) methods.

For the best results, measure the reagent blank value for each new lot of reagent. Replace the sample with deionized water in the test procedure to determine the reagent blank value. Subtract the reagent blank value from the sample results automatically with the reagent blank adjust option.

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.

The SwifTest Dispenser for Total Chlorine can be used in place of the powder pillow in the test procedure. One dispensation is equal to one powder pillow for 10-mL samples.

An AccuVac Ampul for Blanks can be used to zero the instrument in the AccuVac test procedure.

Items to collect

Powder pillows

Description	Quantity
DPD Total Chlorine Reagent Powder Pillow, 10-mL	1
Sample cells. (For information about sample cells, adapters or light shields, refer to Instrument-specific information on page 1.)	2

Refer to [Consumables and replacement items](#) on page 6 for order information.

AccuVac Ampuls

Description	Quantity
DPD Total Chlorine Reagent AccuVac [®] Ampul	1
Beaker, 50-mL	1
Sample cells (For information about sample cells, adapters or light shields, refer to Instrument-specific information on page 1.)	1
Stopper for 18-mm tubes and AccuVac Ampuls	1

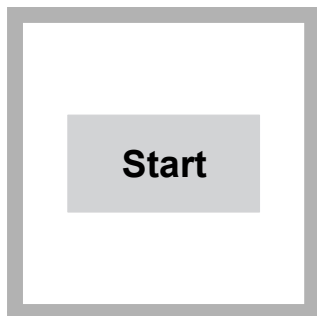
Refer to [Consumables and replacement items](#) on page 6 for order information.

Sample collection

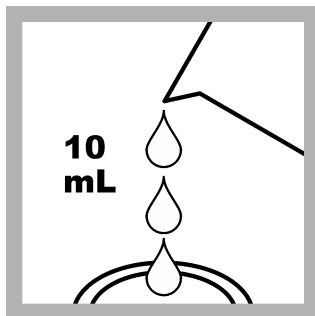
- Analyze the samples immediately. The samples cannot be preserved for later analysis.
- Chlorine is a strong oxidizing agent and is unstable in natural waters. Chlorine reacts quickly with various inorganic compounds and more slowly with organic compounds. Many factors, including reactant concentrations, 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.

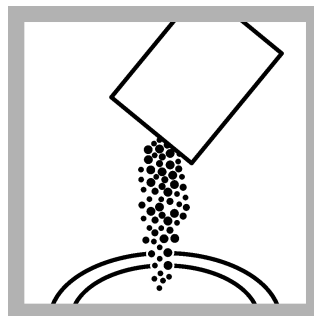
Powder pillow procedure



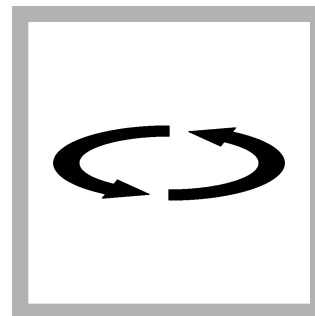
1. Start program **80 Chlorine F&T PP**. For information about sample cells, adapters or light shields, refer to [Instrument-specific information](#) on page 1.



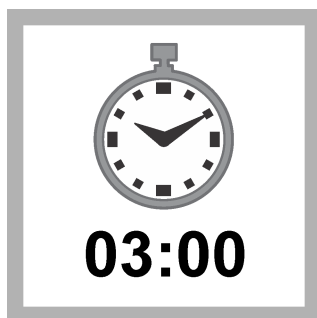
2. Fill a sample cell with 10 mL of sample.



3. **Prepare the sample:** Add the contents of one powder pillow to the sample cell.

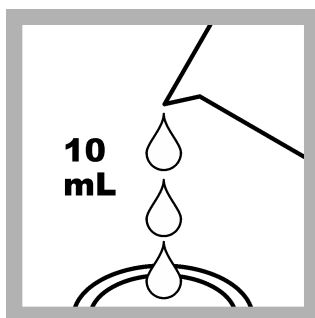


4. Swirl the sample cell for 20 seconds to mix. A pink color shows if chlorine is present in the sample.

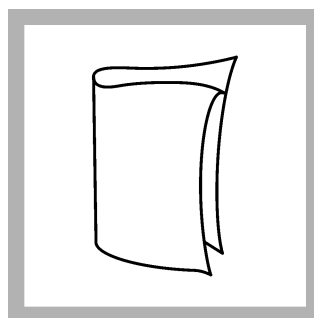


5. Start the instrument timer. A 3-minute reaction time starts.

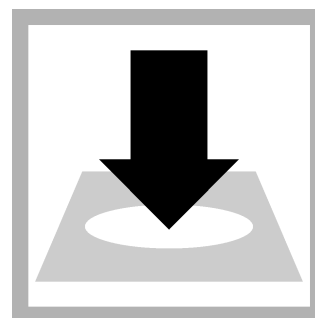
Prepare the sample blank and set the instrument to zero during the reaction time.



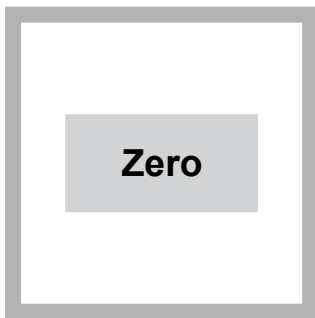
6. **Prepare the blank:** Fill a second sample cell with 10 mL of sample.



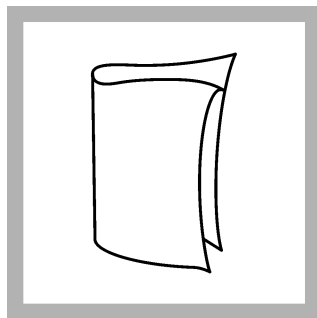
7. Clean the blank sample cell.



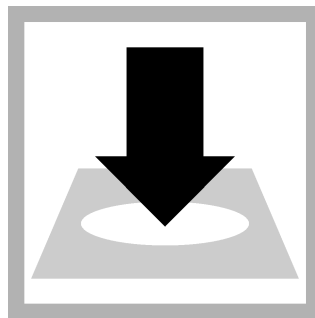
8. Insert the blank into the cell holder.



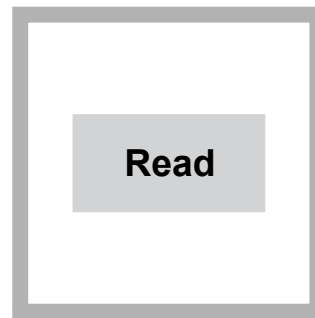
9. Push **ZERO**. The display shows 0.00 mg/L Cl₂.



10. Clean the prepared sample cell.

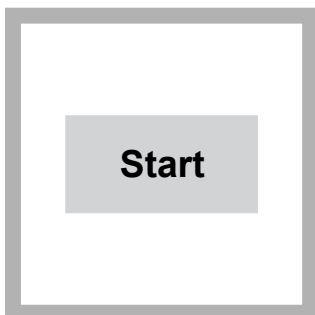


11. Within 3 minutes after the timer expires, insert the prepared sample into the cell holder.

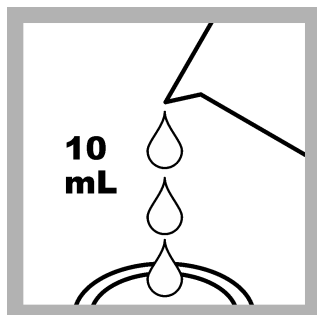


12. Push **READ**. Results show in mg/L Cl₂.

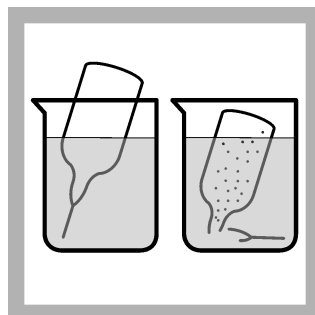
AccuVac Ampul procedure



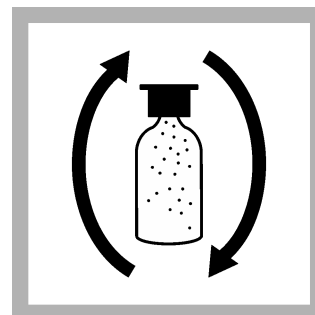
1. Start program **85 Chlorine F&T AV**. For information about sample cells, adapters or light shields, refer to [Instrument-specific information](#) on page 1.



2. **Prepare the blank:** Fill the sample cell with 10 mL of sample.



3. **Prepare the sample:** Collect at least 40 mL of sample in a 50-mL beaker. Fill the AccuVac Ampul with sample. Keep the tip immersed while the AccuVac Ampul fills completely.

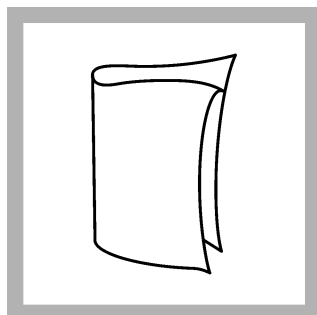


4. Quickly invert the AccuVac Ampul several times to mix.

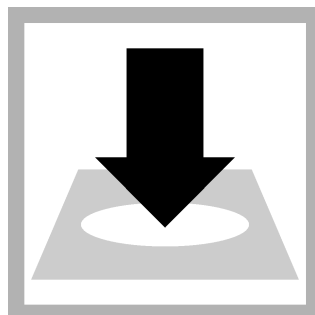


5. Start the instrument timer. A 3-minute reaction time starts.

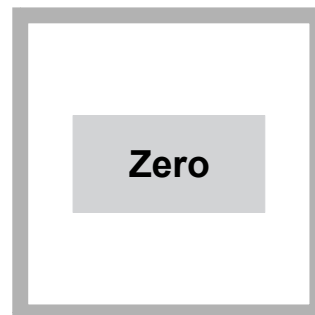
Prepare the sample blank and set the instrument to zero during the reaction time.



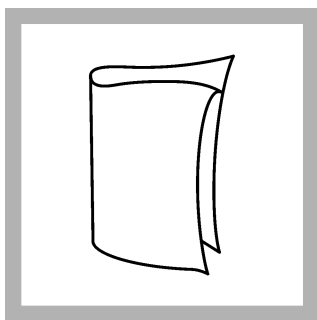
6. Clean the blank sample cell.



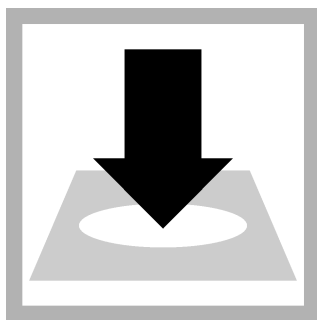
7. Insert the blank into the cell holder.



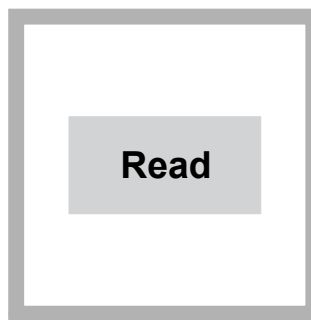
8. Push **ZERO**. The display shows 0.00 mg/L Cl₂.



9. Clean the AccuVac Ampul.



10. Within 3 minutes after the timer expires, insert the prepared sample AccuVac Ampul into the cell holder.



11. Push **READ**. Results show in mg/L Cl₂.

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	Positive interference at all levels
Chloramines, organic	May interfere in the result for total chlorine analysis
Hardness	No effect at less than 1000 mg/L as CaCO ₃
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 Arsenite (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	May interfere
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 to pH 6–7 with acid (Sulfuric Acid, 1.000 N) or base (Sodium Hydroxide, 1.00 N).

Accuracy check

Standard additions method (sample spike)

Use the standard additions method (for applicable instruments) to validate the test procedure, reagents and instrument and to find if there is an interference in the sample.

Items to collect:

- Chlorine Standard Solution, 2-mL PourRite® Ampule, 25–30 mg/L (use mg/L on label)
- Breaker, PourRite Ampules
- Pipet, TenSette®, 0.1–1.0 mL and tips

1. Use the test procedure to measure the concentration of the sample, then keep the (unspiked) sample in the instrument.
2. Go to the Standard Additions option in the instrument menu.
3. Select the values for standard concentration, sample volume and spike volumes.
4. Open the standard solution.
5. Prepare three spiked samples: use the TenSette pipet to add 0.1 mL, 0.2 mL and 0.3 mL of the standard solution, respectively, to three 10-mL portions of fresh sample. Mix well.

Note: For AccuVac® Ampuls, add 0.4 mL, 0.8 mL and 1.2 mL of the standard solution to three 50-mL portions of fresh sample.

6. Use the test procedure to measure the concentration of each of the spiked samples. Start with the smallest sample spike. Measure each of the spiked samples in the instrument.
7. Select **Graph** to compare the expected results to the actual results.

Note: If the actual results are significantly different from the expected results, make sure that the sample volumes and sample spikes are measured accurately. The sample volumes and sample spikes that are used should agree with the selections in the standard additions menu. If the results are not within acceptable limits, the sample may contain an interference.

Method performance

The method performance data that follows was derived from laboratory tests that were measured on a spectrophotometer during ideal test conditions. Users can get different results under different test conditions.

Program	Standard	Precision (95% Confidence Interval)	Sensitivity Concentration change per 0.010 Abs change
80	1.25 mg/L Cl ₂	1.23–1.27 mg/L Cl ₂	0.02 mg/L Cl ₂
85	1.25 mg/L Cl ₂	1.21–1.29 mg/L Cl ₂	0.02 mg/L Cl ₂

Summary of method

Chlorine can be present in water as free chlorine and as combined chlorine. Both forms can exist in the same water and be determined together as total chlorine. Free chlorine is present as hypochlorous acid and/or hypochlorite ion. Combined chlorine exists as monochloramine, dichloramine, nitrogen trichloride and other chloro derivatives. The combined chlorine oxidizes iodide in the reagent to iodine. The iodine and free chlorine react with DPD (N,N-diethyl-p-phenylenediamine) to form a pink color which is proportional to the total chlorine concentration.

To find the concentration of combined chlorine, run a free chlorine test and a total chlorine test. Subtract the results of the free chlorine test from the total chlorine test to obtain the combined chlorine concentration. The measurement wavelength is 530 nm for spectrophotometers or 520 nm for colorimeters.

Consumables and replacement items

Required reagents

Description	Quantity/Test	Unit	Item no.
DPD Total Chlorine Reagent Powder Pillow, 10 mL	1	100/pkg	2105669
OR			
DPD Total Chlorine Reagent AccuVac® Ampul	1	25/pkg	2503025

Required apparatus

Description	Quantity/Test	Unit	Item no.
AccuVac Snapper	1	each	2405200
Beaker, 50 mL	1	each	50041H
Stoppers for 18-mm tubes and AccuVac Ampuls	2	6/pkg	173106

Recommended standards

Description	Unit	Item no.
Chlorine Standard Solution, 10-mL Voluette [®] Ampule, 50–75 mg/L	16/pkg	1426810
Chlorine Standard Solution, 2-mL PourRite [®] Ampules, 50–75 mg/L	20/pkg	1426820
Chlorine Standard Solution, 2-mL PourRite [®] Ampules, 25–30 mg/L	20/pkg	2630020

Optional reagents and apparatus

Description	Unit	Item no.
AccuVac [®] Ampul vials for sample blanks	25/pkg	2677925
Ampule Breaker, 2-mL PourRite [®] Ampules	each	2484600
Ampule Breaker, 10-mL Voluette [®] Ampules	each	2196800
Water, Chlorine-demand Free	500 mL	2641549
Mixing cylinder, graduated, 25-mL	each	2088640
Mixing cylinder, graduated, 50 mL	each	189641
DPD Total Chlorine Reagent Powder Pillows, 10 mL	1000/pkg	2105628
DPD Total Chlorine Reagent Powder Pillows, 10 mL	300/pkg	2105603
DPD Total Chlorine Reagent, 10-mL, SwifTest [™] Dispenser refill vial	250 tests	2105660
Paper, pH, 0–14 pH range	100/pkg	2601300
Pipet, TenSette [®] , 0.1–1.0 mL	each	1970001
Pipet tips for TenSette [®] Pipet, 0.1–1.0 mL	50/pkg	2185696
Pipet tips for TenSette [®] Pipet, 0.1–1.0 mL	1000/pkg	2185628
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
SpecCheck [™] Secondary Standard Kit, Chlorine DPD, 0–2.0 mg/L Set	each	2635300
Sulfuric Acid Standard Solution, 1 N	100 mL MDB	127032
Water, deionized	4 L	27256



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