

## USEPA DPD Method<sup>1</sup>

## Method 8021

0.02 to 2.00 mg/L Cl<sub>2</sub>

Powder Pillows or AccuVac<sup>®</sup> Ampuls

**Scope and application:** For testing free chlorine (hypochlorous acid and hypochlorite ion) in water, treated waters, estuary and seawater. USEPA accepted for reporting for drinking water analyses.<sup>2</sup> This product has not been evaluated to test for chlorine and chloramines in medical applications in the United States.

<sup>1</sup> Adapted from Standard Methods for the Examination of Water and Wastewater.

<sup>2</sup> Procedure is equivalent to USEPA and Standard Method 4500-Cl G for drinking water.



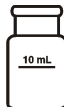
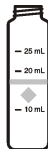
## Test preparation

## Instrument-specific information



The tables in this section show all of the instruments that have the program for this test. [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.

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

**Table 1 Instrument-specific information for powder pillows**

Instrument	Sample cell orientation	Sample cell
DR 6000 DR 3800 DR 2800 DR 2700	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 3800 DR 2800 DR 2700	LZV584 (C)	2122800 

## Before starting

Samples must be analyzed immediately after collection and cannot be preserved for later analysis.

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

Do not use the same sample cells for free and total chlorine. If trace iodide from the total chlorine reagent is carried over into the free chlorine determination, monochloramine will interfere. It is best to use separate, dedicated sample cells for free and total chlorine measurements.

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

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

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

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

The SwiftTest Dispenser for Free Chlorine can be used in place of the powder pillow in the test procedure.

## Items to collect

### Powder pillows

Description	Quantity
DPD Free Chlorine Reagent Powder Pillows, 10-mL	1
Sample cells. (For information about sample cells, adapters or light shields, refer to <a href="#">Instrument-specific information</a> on page 1.)	2

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

### AccuVac Ampuls

Description	Quantity
DPD Free Chlorine Reagent AccuVac Ampuls	1
Beaker, 50-mL	1
Sample cells (For information about sample cells, adapters or light shields, refer to <a href="#">Instrument-specific information</a> on page 1.)	1
Stopper for 18-mm tubes and AccuVac Ampuls	1

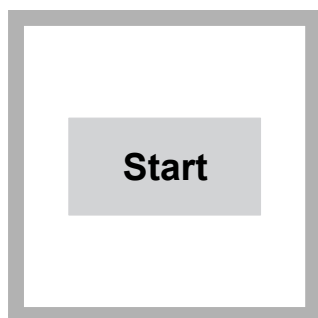
Refer to [Consumables and replacement items](#) on page 6 for reorder information.

## Sample collection

- Samples must be analyzed immediately and cannot be preserved for later analysis.
- Chlorine is a strong oxidizing agent and it is unstable in natural waters. It 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. Avoid plastic containers since these may have a large chlorine demand.

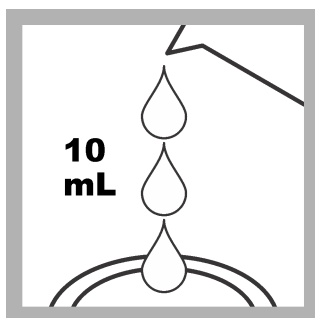
- Pre-treat glass sample containers to remove any chlorine demand. Soak the containers in a dilute bleach solution (1 mL commercial bleach to 1 liter of deionized water) for at least 1 hour. Rinse thoroughly with deionized or distilled water. If sample containers are rinsed thoroughly with deionized or distilled water after use, only occasional pre-treatment is necessary.
- Be 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. Then 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. If a sample cell is used, rinse the cell several times with the sample, then carefully fill to the 10-mL mark.

## Powder pillow procedure

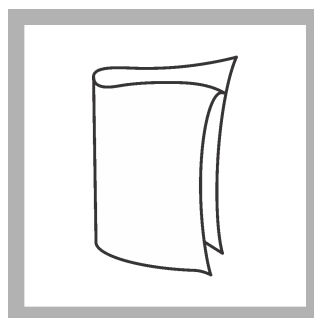


1. Start program **80 Chlorine F&T PP**. For information about sample cells, adapters or light shields, refer to [Instrument-specific information](#) on page 1.

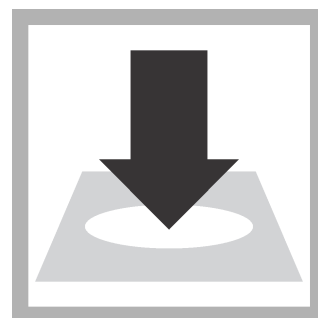
**Note:** Although the program name may vary between instruments, the program number does not change.



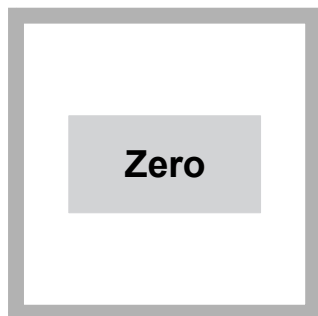
2. **Prepare the blank:** Fill the sample cell with 10 mL of sample.



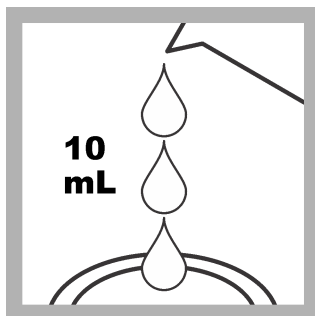
3. Clean the prepared sample.



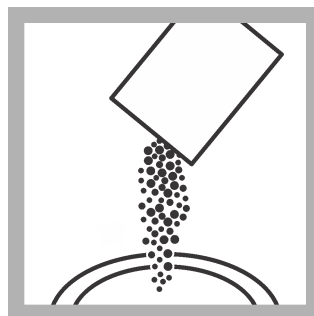
4. Insert the blank into the cell holder.



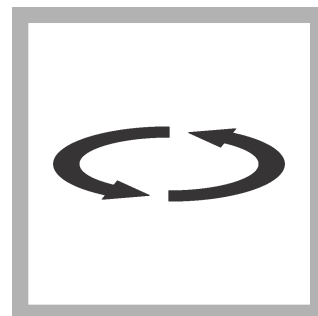
5. Push **ZERO**. The display shows 0.00 mg/L.



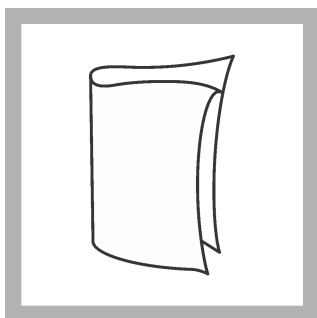
6. **Prepare the sample:** Fill a second sample cell with 10 mL of sample.



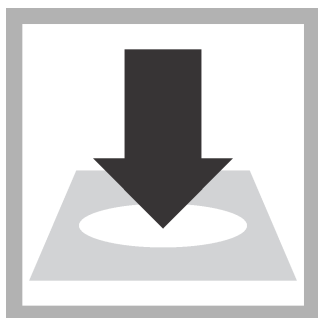
7. Add the contents of one powder pillow to the sample cell.



8. Swirl the sample cell for 20 seconds to mix. A pink color will develop if chlorine is present. Proceed to the next step immediately.



9. Clean the prepared sample.

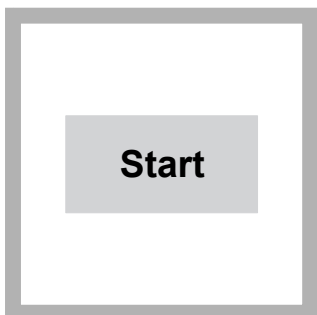


10. Within 60 seconds of adding the reagent, insert the prepared sample into the cell holder.



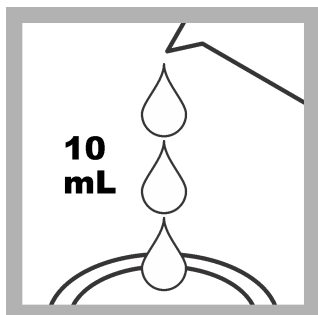
11. Push **READ**. Results show in mg/L  $\text{Cl}_2$ .

## AccuVac Ampul procedure

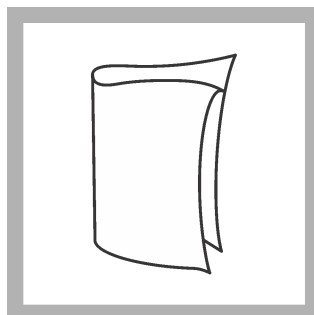


1. Start program **85 Chlorine F&T AV**. For information about sample cells, adapters or light shields, refer to [Instrument-specific information](#) on page 1.

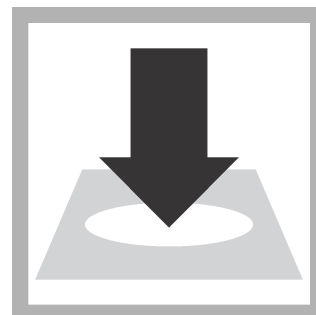
**Note:** Although the program name may vary between instruments, the program number does not change.



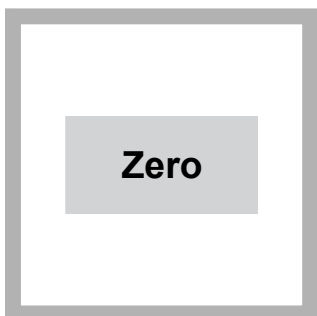
2. **Prepare the blank:** Fill the sample cell with 10 mL of sample.



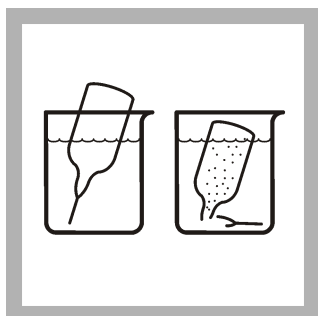
3. Clean the blank.



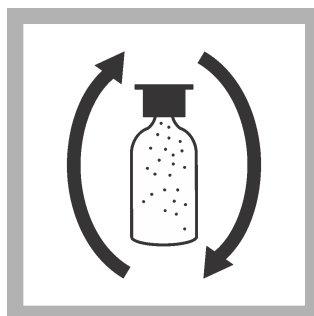
4. Insert the blank into the cell holder.



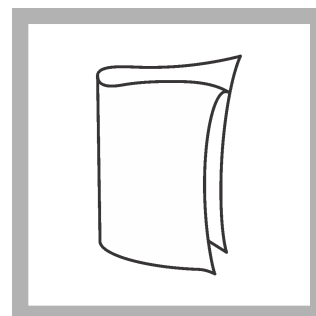
5. Push **ZERO**. The display shows 0.00 mg/L.



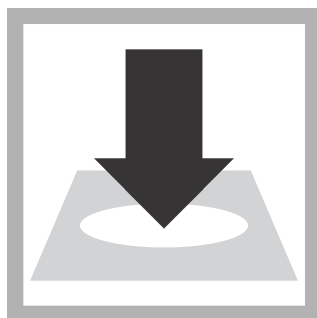
6. **Prepare the sample:** Collect at least 40 mL of sample in a 50-mL beaker. Fill the AccuVac Ampul with sample. Keep the tip immersed while the Ampul fills completely.



7. Quickly invert the Ampul several times to mix.



8. Clean the AccuVac Ampul.



**9.** Within 60 seconds of adding the reagent, insert the prepared sample AccuVac Ampul into the cell holder.



**10.** Push **READ**. Results show in mg/L  $\text{Cl}_2$ .

## Interferences

Interfering substance	Interference level
Acidity	More than 150 mg/L $\text{CaCO}_3$ . 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 be added 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 $\text{CaCO}_3$ . 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, $\text{Br}_2$	Interferes at all levels
Chlorine Dioxide, $\text{ClO}_2$	Interferes at all levels
Chloramines, organic	May interfere
Hardness	No effect at less than 1000 mg/L as $\text{CaCO}_3$
Iodine, $\text{I}_2$	Interferes at all levels
Manganese, Oxidized ( $\text{Mn}^{4+}$ , $\text{Mn}^{7+}$ ) or Chromium, Oxidized ( $\text{Cr}^{6+}$ )	Pre-treat the sample as follows: <ol style="list-style-type: none"> <li>1. Adjust the sample pH to 6–7.</li> <li>2. Add 3 drops of Potassium Iodide (30-g/L) to 10 mL of sample.</li> <li>3. Mix and wait 1 minute.</li> <li>4. Add 3 drops of Sodium Arsenite (5-g/L) and mix.</li> <li>5. Use the test procedure to measure the concentration of the treated sample.</li> <li>6. Subtract this result from the result without the treatment to obtain the correct chlorine concentration.</li> </ol>
Monochloramine	Causes a gradual drift to higher readings. When read within 1 minute after reagent addition, 3 mg/L monochloramine causes less than a 0.1 mg/L increase in the reading.
Ozone	Interferes 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).

## Pollution prevention and waste management

If sodium arsenite was added to the sample for manganese or chromium interferences, the reacted samples will contain arsenic and must be disposed of as a hazardous waste. Dispose of reacted solutions according to local, state and federal regulations.

## 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 may 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 <sub>2</sub>	1.23–1.27 mg/L Cl <sub>2</sub>	0.02 mg/L Cl <sub>2</sub>
85	1.25 mg/L Cl <sub>2</sub>	1.21–1.29 mg/L Cl <sub>2</sub>	0.02 mg/L Cl <sub>2</sub>

## Summary of method

Chlorine in the sample as hypochlorous acid or hypochlorite ion (free chlorine or free available chlorine) immediately reacts with DPD (N,N-diethyl-p-phenylenediamine) indicator to form a pink color, the intensity of which is proportional to the 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 Free Chlorine Reagent Powder Pillow, 10-mL	1	100/pkg	2105569
OR			
DPD Free Chlorine Reagent AccuVac® Ampul	1	25/pkg	2502025

## 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, 2-mL PourRite® Ampules, 25–30 mg/L	20/pkg	2630020

## Optional reagents and apparatus

Description	Unit	Item no.
AccuVac® vials for sample blanks	25/pkg	2677925
Ampule Breaker, PourRite® ampules	each	2484600
Ampule Breaker, Voluette® ampules	each	2196800
Water, Chlorine-demand Free	500 mL	2641549
Cylinder, mixing, 25-mL	each	2088640
Cylinder, mixing, 50-mL	each	189641
Chlorine Standard Solution, 2-mL PourRite® Ampules, 50–75 mg/L	20/pkg	1426820
Chlorine Standard Solution, 10-mL Voluette® Ampule, 50–75 mg/L	16/pkg	1426810
DPD Free Chlorine Reagent Powder Pillows, 10-mL	1000/pkg	2105528
DPD Free Chlorine Reagent Powder Pillows, 10-mL	300/pkg	2105503
DPD Free Chlorine Reagent, 10 mL, SwifTest™ Dispenser refill vial	250 tests	2105560
Paper, pH, 0–14 pH range	100/pkg	2601300
Pipet, TenSette®, 0.1–1.0 mL	each	1970001
Pipet tips for TenSette Pipet 1970001	50/pkg	2185696
Pipet tips for TenSette Pipet 1970001	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



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