

**USEPA DPD Method<sup>2</sup>**
**Method 10245<sup>1</sup>**
**0.05 to 4.00 mg/L Cl<sub>2</sub> (MR)**
**Powder Pillows**

**Scope and application:** For free chlorine (hypochlorous acid and hypochlorite ion) measurements in water, treated waters, estuary and seawater. This product has not been evaluated to test for chlorine and chloramines in medical applications in the United States.

<sup>1</sup> USEPA accepted for reporting wastewater and drinking water analyses.

<sup>2</sup> Procedure is equivalent to USEPA method 330.5 for wastewater and Standard Method 4500-Cl G for drinking water.





## Test preparation

### Instrument-specific information

Table 1 shows all of the instruments that have the program for this test. The table also shows sample cell and adapter requirements 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**

Instrument	Adapter	Sample cell
DR6000	—	2427606 
DR5000	A23618	
DR3900	LZV846 (A)	
DR3800	LZV584 (C)	
DR2800 DR2700		
DR1900	9609900 or 9609800 (C)	2401906 
DR900	—	

### Before starting

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

Install the instrument cap on the DR900 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 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 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.

Cold waters can cause condensation on the sample cells during color development. Examine the sample cells for condensation before measurements.

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

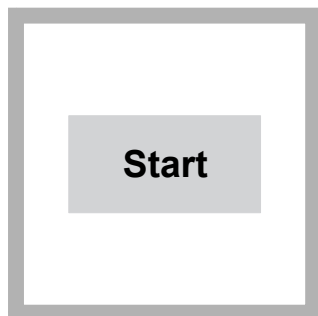
Description	Quantity
DPD Free Chlorine Reagent Powder Pillows, 25-mL	1
Sample cells (For information about sample cells, adapters or light shields, refer to <a href="#">Instrument-specific information</a> on page 1.)	2

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

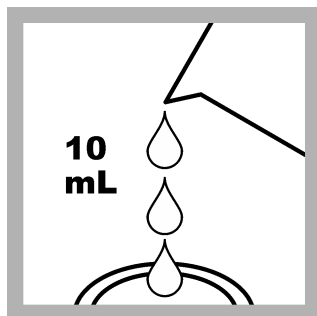
## Sample collection

- 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.

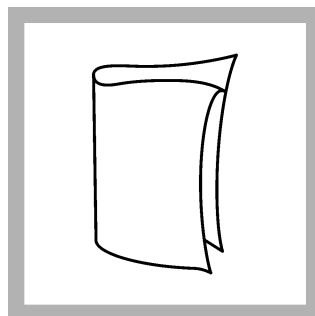
## Powder pillow procedure



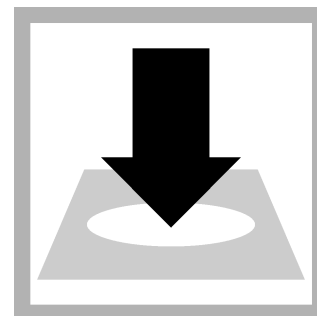
1. Start program **87 Chlorine, F&T PP MR**. For information about sample cells, adapters or light shields, refer to [Instrument-specific information](#) on page 1.



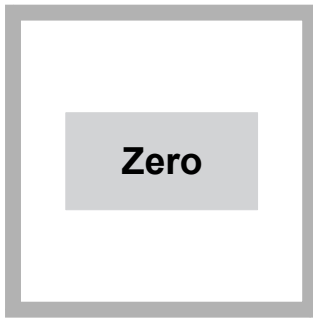
2. **Prepare the blank:** Fill the sample cell with 10 mL of sample.



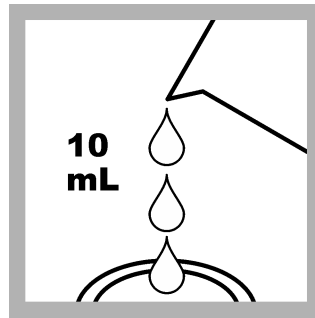
3. Clean the blank sample cell.



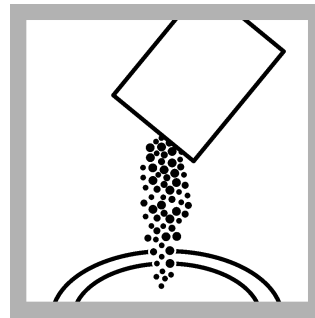
4. Insert the blank into the cell holder.



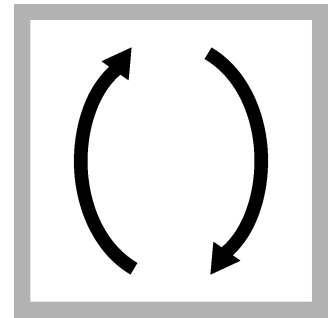
5. Push **ZERO**. The display shows 0.00 mg/L Cl<sub>2</sub>.



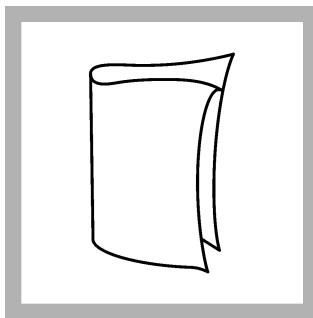
6. **Prepare the sample:** Fill a second sample cell with 10 mL of sample.



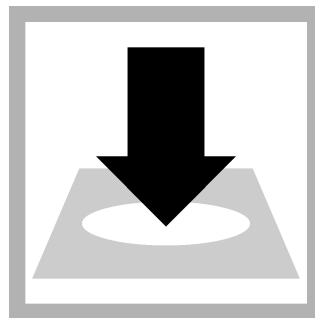
7. Add the contents of one DPD Free Chlorine Powder Pillow for 25-mL sample to the prepared sample cell.



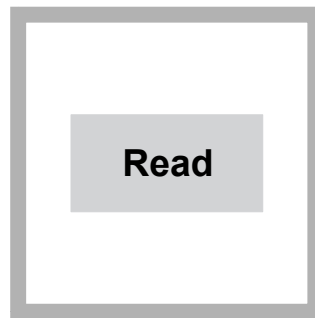
8. Put the stopper on the prepared sample cell. Invert the sample cell several times to mix. A pink color shows if chlorine is present. Go to the next step immediately.



9. Clean the prepared sample cell.



10. Within one minute of the reagent addition, insert the prepared sample into the cell holder.



11. Push **READ**. Results show in mg/L Cl<sub>2</sub>.

## Interferences

Interfering substance	Interference level
Acidity	More than 150 mg/L CaCO <sub>3</sub> . 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 <sub>3</sub> . 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 <sub>2</sub>	Positive interference at all levels
Chlorine Dioxide, ClO <sub>2</sub>	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 <sub>3</sub>

Interfering substance	Interference level
Manganese, Oxidized (Mn <sup>4+</sup> , Mn <sup>7+</sup> ) or Chromium, Oxidized (Cr <sup>6+</sup> )	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>
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).

### Monochloramine interference

For conventional free chlorine disinfection (beyond the breakpoint), typical monochloramine concentrations are very low. If monochloramine is present in the sample, its interference in the free chlorine test depends on the sample temperature, relative amount of monochloramine to free chlorine and the time required to do the analysis. Typical interference levels of monochloramine as mg/L Cl<sub>2</sub> in the free chlorine test are shown in [Table 2](#) (1 minute test time). Measure the monochloramine levels with method 10200 for Chloramine (Mono) and Free Ammonia.

**Table 2 Monochloramine interference at different sample temperatures**

NH <sub>2</sub> Cl (as Cl <sub>2</sub> )	5 °C (41 °F)	10 °C (50 °F)	20 °C (68 °F)	30 °C (83 °F)
1.2 mg/L	0.15	0.19	0.30	0.29
2.2 mg/L	0.35	0.38	0.55	0.61
3.2 mg/L	0.38	0.56	0.69	0.73

### 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 (or 50–75) mg/L
- Ampule breaker
- 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.
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.

## Verification of on-line analyzers

This procedure can be used to meet the requirements of USEPA Method 334.0 - Determination of Residual Chlorine in Drinking Water Using an On-line Chlorine Analyzer. The procedure and requirements for compliance with EPA Method 334.0 can be downloaded directly from <http://www.hach.com/method334>.

## 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
87	2.68 mg/L Cl <sub>2</sub>	2.63–2.73 mg/L Cl <sub>2</sub>	0.03 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, 25 mL	1	100/pkg	1407099
Sample cell, 10-mL round, 25 mm x 60 mm	1	6/pkg	2427606

### Recommended standards

Description	Unit	Item no.
Chlorine Standard Solution, 2-mL PourRite <sup>®</sup> Ampules, 25–30 mg/L	20/pkg	2630020
Ampule Breaker, 10-mL Voluette <sup>®</sup> Ampules	each	2196800
PourRite <sup>®</sup> Ampule Breaker, 2-mL	each	2484600
Chlorine Standard Solution, 2-mL PourRite <sup>®</sup> Ampules, 50–75 mg/L	20/pkg	1426820
Chlorine Standard Solution, 10-mL Voluette <sup>®</sup> Ampule, 50–75 mg/L	16/pkg	1426810

### Optional reagents and apparatus

Description	Unit	Item no.
Sodium Hydroxide Standard Solution, 1.0 N	100 mL MDB	104532
Sulfuric Acid Standard Solution, 1 N	100 mL MDB	127032
Potassium Iodide, 30-g/L	100 mL	34332
Sodium Arsenite, 5-g/L	100 mL	104732
Pipet, TenSette <sup>®</sup> , 0.1–1.0 mL	each	1970001

**Optional reagents and apparatus (continued)**

<b>Description</b>	<b>Unit</b>	<b>Item no.</b>
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
Paper, pH, 0–14 pH range	100/pkg	2601300
DPD Free Chlorine Reagent Powder Pillows, 25 mL	1000/pkg	1407028
SpecCheck™ Secondary Standard Kit, Chlorine DPD, MR	each	2980500
Water, organic-free	500 mL	2641549
Freechlor F Reagent Solution	50 mL SCDB	2964926
Monochlor F Reagent Powder Pillows	100/pkg	2802299



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