

USEPA¹ DPD Method²

0.05 to 4.00 mg/L Cl₂ (MR)

Method 10250

Powder Pillows

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

¹ Procedure is equivalent to USEPA and Standard Method 4500-Cl G for drinking water and wastewater analyses.

² Adapted from Standard Methods for the Examination of Water and Wastewater.



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)	
DR900	—	2401906

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.

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.

A powder pillow for 25-mL samples is intentionally added to 10 mL of sample in this test to get the correct working range.

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.

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

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

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.

Items to collect

Description	Quantity
DPD Total Chlorine Reagent powder pillow, 25-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 5 for order information.

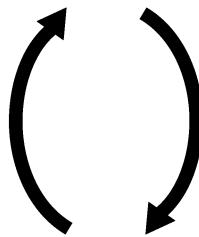
Sample collection

- 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

Start

10 mL



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.

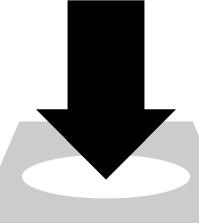
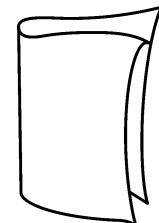
2. Prepare the sample: Fill a sample cell with 10 mL of sample.

3. Add the contents of one DPD Total Chlorine Reagent Powder Pillow (for 25-mL samples).

4. Put the stopper on the sample cell. Invert the sample cell for 20 seconds. It is not necessary for all of the reagent to dissolve.

03:00

10 mL



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

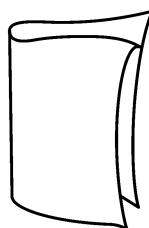
Do the next four steps during the timer period.

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.

Zero



Read

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.

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
Chloramines, organic	May interfere
Hardness	No effect at less than 1000 mg/L as CaCO ₃
Iodine, I ₂	Interferes 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 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 or 50–75 mg/L (use mg/L on label)
 - 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	2.10 mg/L Cl ₂	2.07–2.13 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 get an approximate combined chlorine concentration, compare the results of the free chlorine test and the total chlorine test on the same sample. For more accuracy, use different methods to determine total chlorine, monochloramine and free chlorine. Different methods are more accurate because of the pH-dependent equilibrium between the chlorine species and possible interferences in the DPD free chlorine test. 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, 25 mL	1	100/pkg	1406499

Recommended standards and apparatus

Description	Unit	Item no.
Chlorine Standard Solution, 2-mL PourRite® Ampules, 25–30 mg/L	20/pkg	2630020
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
Ampule Breaker, 10-mL Voluette® Ampules	each	2196800
PourRite® Ampule Breaker, 2 mL	each	2484600

Optional reagents and apparatus

Description	Unit	Item no.
Beaker, 50 mL	each	50041H
Mixing cylinder, graduated, 25 mL	each	2088640
Water, deionized	4 L	27256
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
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
Paper, pH, 0–14 pH range	100/pkg	2601300
DPD Total Chlorine Reagent Powder Pillows, 25 mL	1000/pkg	1406428
SpecCheck™ Secondary Standard Kit, Chlorine DPD, MR	each	2980500
Water, organic-free	500 mL	2641549



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