Chlorine Dioxide

DOC316.53.01021

DPD Method[1]

Method 10126

0.04 to 5.00 mg/L ClO_2

Powder Pillows

Scope and application: For water and wastewater. USEPA accepted for reporting for drinking water analysis.[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 Standard Methods, 18 ed., 4500 ClO_2 D.

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 orientation requirements for reagent addition tests, such as powder pillow or bulk reagent tests.

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

Table 1 Instrument-specific information

Instrument	Sample cell orientation	Sample cell
DR6000 DR3800 DR2800 DR2700 DR1900	The fill line is to the right.	2495402 
DR5000 DR3900	The fill line is toward the user.	
DR900	The orientation mark is toward the user.	2401906 

Before starting

Samples must be analyzed immediately after collection and cannot be preserved for later analysis.
Install the instrument cap on the DR900 cell holder before ZERO or READ is pushed.
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.
If the chlorine dioxide concentration in the sample exceeds the upper limit of the test, the color may fade or the sample color may change to yellow. Dilute the sample with a known volume of high quality, chlorine demand-free water and repeat the test. Some loss of chlorine dioxide may occur due to the dilution. Multiply the result by the dilution factor.
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

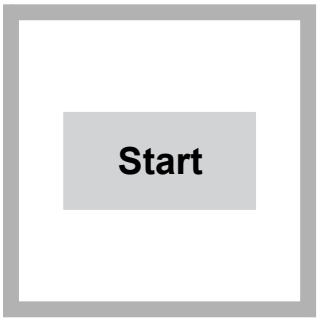
Description	Quantity
DPD Free Chlorine Powder Pillow, 10 mL	1
Glycine Reagent	4 drops
Sample cells. (For information about sample cells, adapters or light shields, refer to Instrument-specific information on page 1.)	2
Stopper for 18-mm tubes	2

Refer to Consumables and replacement items on page 5 for order information.

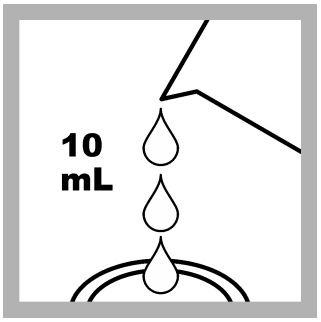
Sample collection

- Analyze the samples immediately. The samples cannot be preserved for later analysis.
- Chlorine dioxide 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 dioxide in water.
- Collect samples in clean glass bottles. Do not use plastic containers because these can have a large chlorine dioxide demand.
- Pretreat glass sample containers to remove chlorine dioxide 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.

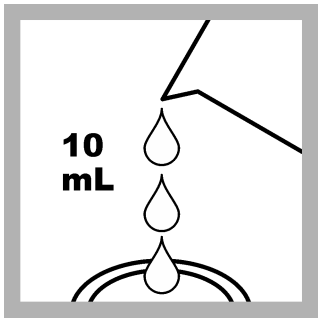
Test procedure



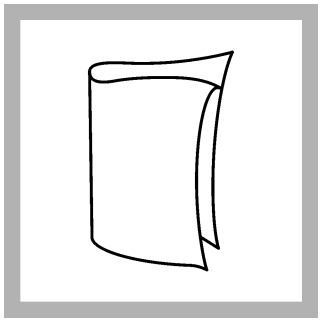
1. Start program **76 Chlor Diox DPD**. For information about sample cells, adapters or light shields, refer to Instrument-specific information on page 1.



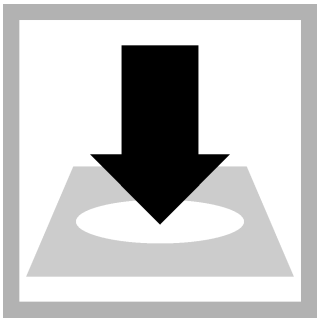
2. Prepare the blank: Fill the sample cell with 10 mL of sample.
Put the stopper in the blank.



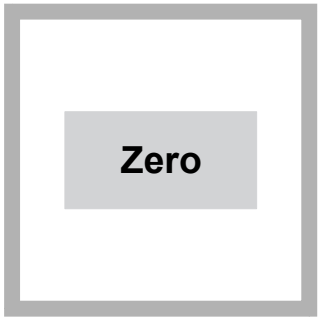
3. Prepare the sample: Fill a second sample cell with 10 mL of sample.
Put the stopper in the prepared sample.



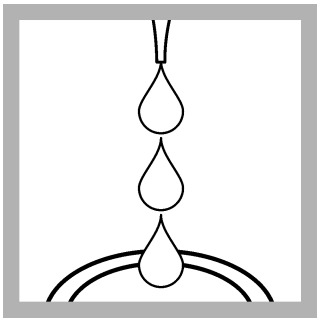
4. Clean the blank sample cell.



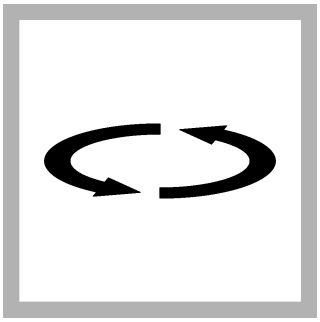
5. Insert the blank into the cell holder.



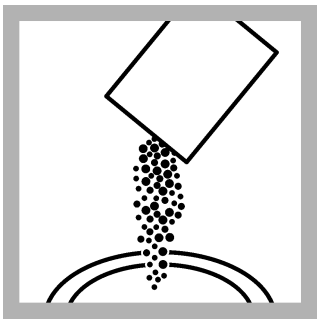
6. Push **ZERO**. The display shows 0.00 mg/L ClO_2.



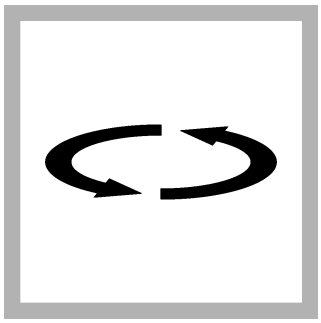
7. Add 4 drops of Glycine Reagent to the sample cell.



8. Swirl to mix.

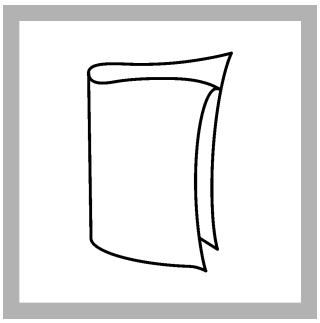


9. Add the contents of one DPD Free Chlorine Powder Pillow to the sample cell.

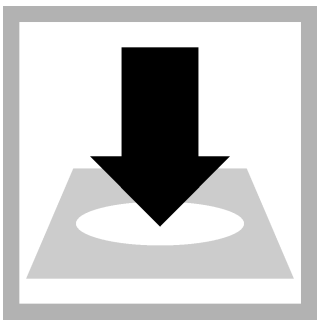


10. Swirl the sample cell for 20 seconds to mix.

11. Wait 30 seconds for any undissolved powder to settle. Undissolved powder will not affect accuracy.



12. Clean the prepared sample cell.



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

14. Push **READ**. Results show in mg/L ClO_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, Cl_2	May interfere at more than 6 mg/L Cl_2. Additional glycine may be able to remove this interference.

Interfering substance	Interference level
Inorganic chloramines	Positive interference at all levels
Chloramines, organic	May interfere in the result for total chlorine analysis
Flocculating agents	High levels of most flocculating agents are acceptable. The acceptable level is decreased when chlorine is present. Refer to the information about metals in this table. In the presence of 0.6 mg/L Cl_2, $Al(SO_4)_3$ (< 500 mg/L) and $FeCl_2$ (<200 mg/L) may be tolerated.
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: **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.
Metals	Various metals can combine with the glycine that is used to remove chlorine from the sample. Metal interference is minimal except when chlorine is present. In the presence of 0.6 mg/L Cl_2, both copper (>10 mg/L) and nickel (>50 mg/L) interfere. Other metals that combine with glycine may also interfere. It may be necessary to add more glycine to overcome this interference.
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	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.

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 solution method

The preparation of chlorine dioxide standards is difficult and hazardous. These standards are explosive and volatile! Only a trained chemist should prepare the standards with applicable safety equipment and precautions. The manufacturer does not recommend preparation of chlorine dioxide standards. If an independent standard preparation is required, refer to the instructions in *Standard Methods for the Examination of Water and Wastewater*, Part 4500-ClO_2 Chlorine Dioxide, under the headings "Stock chlorine dioxide solution" and "Standard chlorine dioxide solution". Prepare a chlorine dioxide standard.

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
76	3.00 mg/L ClO_2	2.89–3.11 mg/L ClO_2	0.04 mg/L ClO_2

Summary of method

Chlorine dioxide reacts with DPD (N, N-diethyl-p-phenylenediamine) to the extent of one-fifth of its total available chlorine content, which corresponds to the reduction of chlorine dioxide to chlorite. A pink color forms, the intensity of which is proportional to the chlorine dioxide concentration in the sample. Chlorine interference is removed with the addition of glycine, which converts free chlorine to chloroaminoacetic acid, but has no effect on chlorine dioxide at the test pH. 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.
Chlorine Dioxide DPD/Glycine Reagent Set	1	100/pkg	2770900
Includes:			
DPD Free Chlorine Reagent Powder Pillow, 10 mL	1	100/pkg	2105569
Glycine Reagent	4 drops	29 mL	2762133

Required apparatus

Description	Quantity/test	Unit	Item no.
Beaker, 50 mL	1	each	50041H
Stoppers for 18-mm tubes	2	6/pkg	173106
Sample cell, 10-mL round, 25 mm x 54 mm	1	each	2122800
Sample cell, 10-mL round, 25 mm x 60 mm	1	6/pkg	2427606
Sample cells, 10-mL square, matched pair	2	2/pkg	2495402

Recommended standards and apparatus

Description	Unit	Item no.
Chlorine Standard Solution, 10-mL Voluette® Ampule, 50–75 mg/L	16/pkg	1426810
Ampule Breaker, 10-mL Voluette® Ampules	each	2196800
Water, organic-free	500 mL	2641549

Optional reagents and apparatus

Description	Unit	Item no.
DPD Free Chlorine Reagent Powder Pillows, 10 mL	1000/pkg	2105528
DPD Free Chlorine Reagent Powder Pillows, 10 mL	300/pkg	2105503
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
Standard Methods for the Examination of Water and Wastewater (current edition)	each	2270800
Stoppers for 18-mm tube	25/pkg	173125
Sulfuric Acid Standard Solution, 1 N	100 mL MDB	127032

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