Chlorine Dioxide

DOC316.53.01021

DPD Method[1] **Method 10126**

(0.04 to 5.00 mg/L) **Powder Pillows and AccuVac® Ampuls**

Scope and Application: For water and wastewater. USEPA accepted for reporting for drinking water analysis.[2]

[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

How to use instrument-specific information

The *Instrument-specific information* table displays requirements that may vary between instruments. To use this table, select an instrument then read across to find the corresponding information required to perform this test.

Table 1 Instrument-specific information

Instrument	Powder pillows		AccuVac Ampuls	
	Sample cell	Cell orientation	Sample cell	Adapter
DR 5000	2495402	Fill line faces user	2427606	—
DR 3900	2495402	Fill line faces user	2427606	LZV846 (A)
DR 3800, DR 2800, DR 2700	2495402	Fill line faces right	2122800	LZV584 (C)

Before starting the test:

Analyze samples immediately because chlorine dioxide is unstable and volatile. See *Sample collection, preservation and storage*.

For more accurate results, determine a reagent blank value for each new lot of reagent. Follow the procedure using deionized water instead of the sample. Subtract the reagent blank value from the final results or perform a reagent blank adjust.

After adding the DPD Free Chlorine Powder Pillow to the sample, a pink color will develop if chlorine dioxide is present.

If the chlorine dioxide concentration in the sample exceeds the upper limit of the test, the color may fade or the sample may turn yellow. Dilute the sample with high quality water that is chlorine demand-free, and repeat the test. Some loss of chlorine dioxide may occur. Multiply the result by the appropriate dilution factor.

Collect the following items:

Description	Quantity
Powder Pillow Test:	
DPD Free Chlorine powder pillow, 10-mL	1
Glycine Reagent	4 drops
Sample cells (see *Instrument-specific information*)	2
Stopper for 18 mm tube	2
AccuVac Test:	
DPD Free Chlorine Reagent AccuVac® Ampuls	1
Glycine Reagent	16 drops
Beaker, 50-mL	1
Sample Cell (see *Instrument-specific information*)	1
Stopper for 18 mm tube	1

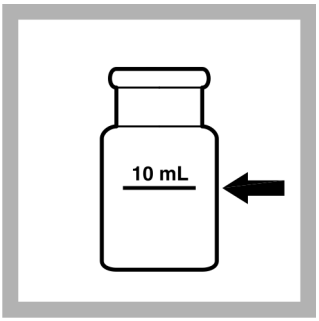
See *Consumables and replacement items* for reorder information.

DPD method, powder pillows

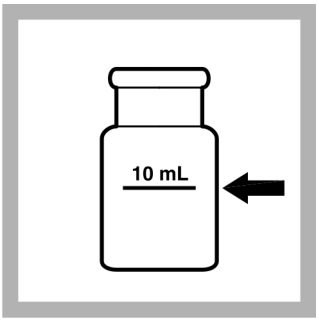
1. Select the test.

Insert an adapter if required (see *Instrument-specific information*).

Refer to the user manual for orientation.



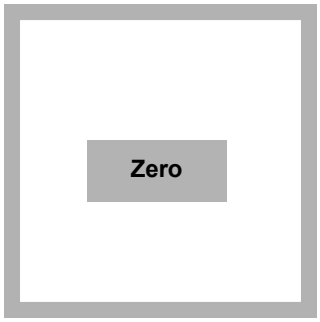
2. Blank Preparation: Fill a sample cell with 10 mL of sample. Close the sample cell.



3. Prepared Sample: Fill a second sample cell with 10 mL of sample. Close the sample cell.

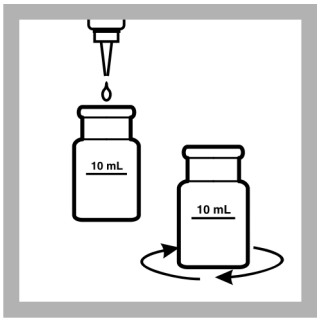
4. Wipe the blank and insert it into the cell holder.

DPD method, powder pillows (continued)

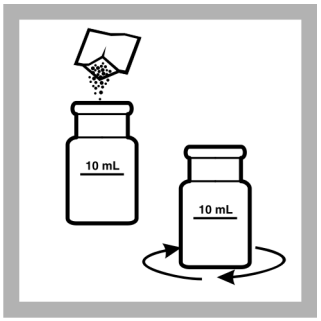


5. **ZERO** the instrument.

The display will show: 0.00 mg/L ClO_2



6. Add four drops of Glycine Reagent to the sample. Swirl to mix.



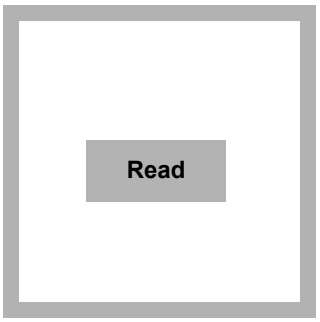
7. Add the contents of one DPD Free Chlorine Powder Pillow to the prepared sample cell.

Swirl the sample for 20 seconds to mix.

8. Wait 30 seconds for any undissolved powder to settle.

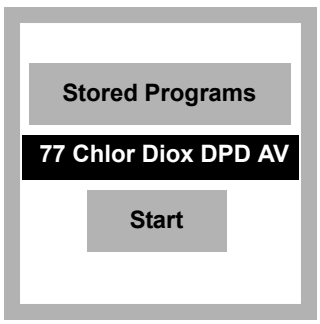
Immediately proceed to step 9.

9. Within one minute of adding the DPD reagent, wipe the sample cell and insert it into the cell holder.



10. **READ** the results in mg/L ClO_2.

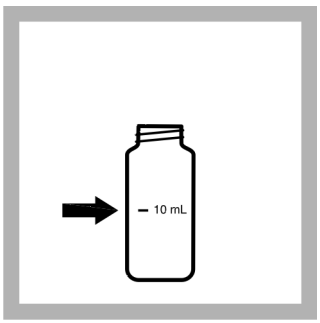
DPD method, AccuVac® Ampuls



1. Select the test.

Insert an adapter if required (see *Instrument-specific information*).

Refer to the user manual for orientation.

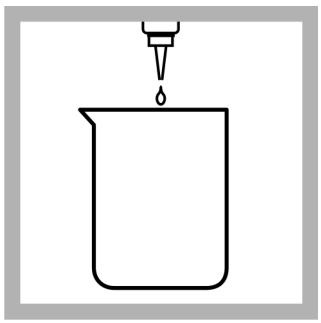


2. **Blank Preparation:** Fill a round sample cell with 10-mL of sample.

3. Wipe the blank and insert it into the cell holder.

ZERO the instrument.

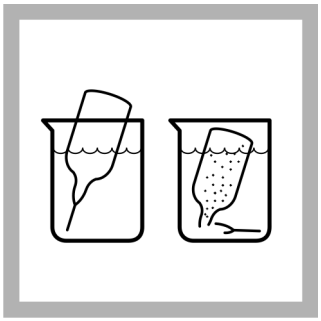
The display will show: 0.00 mg/L ClO_2



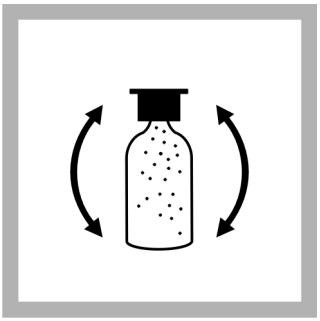
4. **Prepared Sample:** Fill a 50-mL beaker with 40 mL of sample.

Add 16 drops of Glycine Reagent to the sample in the beaker. Swirl gently to mix.

DPD method, AccuVac® Ampuls (continued)

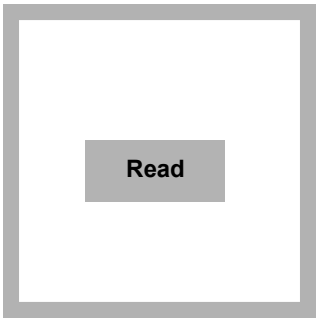


5. Fill a DPD Free Chlorine Reagent AccuVac Ampul with sample. Keep the tip immersed while the Ampul fills completely.



6. Quickly invert the Ampul several times to mix. Wait 30 seconds for any undissolved powder to settle.

7. Within one minute of adding the sample, wipe the Ampul and insert it into the cell holder.



8. **READ** the results in mg/L ClO_2.

Interferences

Table 2 Interfering substances

Interfering substance	Interference level
Acidity	Greater than 150 mg/L $CaCO_3$. May not develop full color or color may fade instantly. Neutralize to pH 6–7 with 1 N Sodium Hydroxide[1]. Determine amount to be added on a separate sample aliquot, then add the same amount to the sample being tested. Correct for volume addition.
Alkalinity	Greater than 250 mg/L $CaCO_3$. Color may not develop fully or may fade instantly. Neutralize to pH 6–7 with 1 N Sulfuric Acid[1]. Determine amount to be added on a separate sample aliquot, then add the same amount to the sample being tested. Correct for the volume addition.
Bromine, Br_2	Interferes at all levels.
Chlorine, Cl_2	May interfere at levels greater than 6 mg/L. Additional glycine may be able to compensate for this interference.
Chloramines, organic	May interfere.
Flocculating agents	High levels of most flocculating agents can be tolerated. This tolerance is decreased if chlorine is present. See 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 $CaCO_3$.
Iodine, I_2	Interferes at all levels.
Manganese, oxidized (Mn^{4+}, Mn^{7+}) or Chromium, oxidized (Cr^{6+})	Oxidized manganese interferes at all levels. Oxidized chromium interferes at levels greater than 2 mg/L. To remove the interferences: **1.** Adjust sample pH to 6–7. **2.** Add 3 drops Potassium Iodide[1] (30 g/L) to a 25-mL sample. **3.** Mix and wait one minute. **4.** Add 3 drops Sodium Arsenite[1, 2] (5 g/L) and mix. **5.** Analyze 10 mL of the treated sample as described in the procedure. **6.** Subtract the result of this test from the original analysis to obtain the correct chlorine dioxide concentration.

Table 2 Interfering substances (continued)

Interfering substance	Interference level
Metals	Various metals may interfere by combining with the glycine needed to remove the chlorine interference. Metal interference is limited 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 may also interfere, depending on their ability to prevent glycine from reacting with any Cl_2 in the sample. 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 ClO_2 increase in the reading.
Ozone	Interferes at levels greater than 1.5 mg/L.
Peroxides	May interfere.
Extreme sample pH	Adjust to pH 6–7.
Highly buffered samples	Adjust to pH 6–7.

[1] See *Optional reagents and apparatus*.

[2] Samples treated with sodium arsenite for interferences will be hazardous waste as regulated by Federal RCRA for arsenic (D004). Refer to a current MSDS for proper disposal instructions.

Sample collection, preservation and storage

Analyze samples for chlorine dioxide immediately after collection. Chlorine dioxide is a strong oxidizing agent and is unstable in natural waters. It reacts rapidly with various inorganic compounds, but oxidizes organic compounds more slowly. Many factors, including reactant concentrations, sunlight, pH, temperature, and salinity influence decomposition of chlorine dioxide in water.

Avoid plastic containers since these may have a large chlorine dioxide demand. Pretreat glass sample containers to remove any chlorine or chlorine dioxide demand by soaking in a dilute bleach solution (1 mL commercial bleach to 1 liter of deionized water) for at least one hour. Rinse thoroughly with deionized or distilled water. If sample containers are rinsed thoroughly with deionized or distilled water after use, only occasional pretreatment is necessary.

A common error in testing for chlorine dioxide is not obtaining a representative sample. If sampling from a tap, let the water flow for at least 5 minutes to ensure a representative sample. Let the container overflow with the sample several times, then cap the sample containers so there is no headspace (air) above the sample. If sampling with a sample cell, rinse the cell several times with the sample, then carefully fill to the 10-mL mark. Perform the chlorine dioxide analysis immediately.

Accuracy check

Standard Solution Method

Preparing chlorine dioxide standards is difficult and dangerous. In addition, these standards are both explosive and volatile! Only a trained chemist should prepare the standards using appropriate safety equipment and precautions. The manufacturer does not recommend preparation of chlorine dioxide standards. If independent standard preparation is required, please see 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

Program	Instrument	Standard	Precision 95% Confidence Limits of Distribution	Sensitivity Concentration change per 0.010 Abs change
76	DR 5000	3.00 mg/L ClO_2	2.89–3.11 mg/L ClO_2	0.04 mg/L ClO_2
77	DR 5000	3.00 mg/L ClO_2	2.91–3.09 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, corresponding to reduction of chlorine dioxide to chlorite. The resulting pink color intensity is proportional to the ClO_2 in the sample. Chlorine interference is eliminated by adding glycine, which converts free chlorine to chloroaminoacetic acid, but has no effect on chlorine dioxide at the test pH. Test results are measured at 530 nm.

Consumables and replacement items

Required reagents

Description	Quantity/Test	Unit	Catalog number
Chlorine Dioxide DPD/Glycine Reagent Set (100 tests), includes:			2770900
(1) DPD Free Chlorine Reagent Powder Pillows, 10-mL	1	100/pkg	2105569
(1) Glycine Reagent	4 drops	29 mL	2762133
OR			
Chlorine Dioxide DPD/Glycine AccuVac® Ampul Reagent Set (25 tests), includes:			2771000
(1) DPD Free Chlorine Reagent AccuVac® Ampuls	1	25/pkg	2502025
(1) Glycine Reagent	16 drops	29 mL	2762133

Required apparatus

Description	Quantity	Unit	Catalog number
AccuVac Snapper	1	each	2405200
Beaker, 50-mL	1	each	50041H
Stopper for 18 mm tube	1	6/pkg	173106
Sample cell, 10 mL round, 25 x 54 mm	1	each	2122800
Sample cell, 10 mL round, 25 x 60 mm	1	6/pkg	2427606
Sample cell, 10 mL square, matched pair	2	2/pkg	2495402

Recommended standards

Description	Unit	Catalog number
Chlorine Standard Solution, 10-mL Voluette® Ampule, 50–75 mg/L	16/pkg	1426810
Voluette Ampule Breaker, for 10-mL ampules	each	2196800
Water, organic-free	500 mL	2641549

Optional reagents and apparatus

Description	Unit	Catalog number
AccuVac Vials, for sample blanks	25/pkg	2677925
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, 1 N	100 mL	104532
Standard Methods Book, most current edition	each	2270800
Stopper for 18 mm tube	25/pkg	173125
Sulfuric Acid, 1 N, 100 mL	each	127032

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