# **Chlorine Dioxide**

#### Chlorophenol Red Method<sup>1</sup>

### 0.01 to 1.00 mg/L CIO<sub>2</sub> (LR)

Scope and application: For water and wastewater.

<sup>1</sup> Adapted from Harp, Klein and Schoonover, Jour. Amer. Water Works Assn., 73 387–388 (1981).

## ☐ 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 specific instruments.

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

Instrument	Sample cell orientation	Sample cell
DR 6000	The fill line is to the right.	2495402
DR 3800		
DR 2800		<u>10 mL</u>
DR 2700		
DR 1900		
DR 5000	The fill line is toward the user.	
DR 3900		

#### Table 1 Instrument-specific information

#### **Before starting**

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

Make sure that each portion of sample is at the same temperature for best results.

Measure the volume of Chlorine Dioxide Reagent 2 accurately. Use a volumetric pipet. Use a TenSette Pipet to dispense Chlorine Dioxide reagents 1 and 3.

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
Chlorine Dioxide Reagent Set	1
Mixing cylinder, graduated, 50-mL, with stopper	2
Pipet, volumetric, Class A, 1.00-mL	1
Pipet filler, safety bulb	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.

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### 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 dioxide 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 72 Chlor Diox CPR LR. For information about sample cells, adapters or light shields, refer to Instrumentspecific information on page 1.

**Note:** Although the program name can be different between instruments, the program number does not change.





**2.** Fill two mixing cylinders to the 50-mL mark with sample.

**3.** Use a pipet to add 1.0 mL of Chlorine Dioxide Reagent 1 to each mixing cylinder.

**4.** Put the stopper on the mixing cylinders. Invert the mixing cylinders several times to mix.



**5. Prepare the blank:** Add the contents of one Dechlorinating Reagent powder pillow to one mixing cylinder. The other mixing cylinder is the prepared sample.



**6.** Put the stopper on the mixing cylinder. Invert the mixing cylinder several times to dissolve the powder.



7. Use a volumetric pipet to accurately add 1.00 mL of Chlorine Dioxide Reagent 2 to each mixing cylinder.



8. Put the stopper on the mixing cylinders. Invert the mixing cylinders several times to mix.



**9.** Use a pipet to add 1.0 mL of Chlorine Dioxide Reagent 3 to each mixing cylinder.



**10.** Put the stopper on the mixing cylinders. Invert the mixing cylinders several times to mix.



**11.** Pour 10 mL from each mixing cylinder into two sample cells.



**12.** Clean the blank sample cell.



**13.** Insert the blank into the cell holder.



**14.** Push **ZERO**. The display shows 0.00 mg/L CIO<sub>2</sub>.



**15.** Clean the prepared sample cell.



**16.** Insert the prepared sample into the cell holder.



**17.** Push **READ**. Results show in mg/L CIO<sub>2</sub>.

#### Interferences

Interfering substance	Interference level
Highly acidic or alkaline water	2.0 mL each of Chlorine Dioxide Reagent 1 and Chlorine Dioxide Reagent 3 instead of 1.0 mL can be necessary
CIO-	More than 5.5 mg/L
CIO <sub>2</sub> -	More than 6 mg/L
CIO <sub>3</sub> -	More than 6 mg/L
CrO <sub>4</sub> <sup>2–</sup>	More than 3.6 mg/L
Fe <sup>3+</sup>	More than 5 mg/L
Hardness	More than 1000 mg/L
Ozone	More than 0.5 mg/L
Turbidity	More than 1000 NTU

## 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-CIO<sub>2</sub> Chlorine Dioxide, under the headings "Stock chlorine dioxide solution" and "Standard chlorine dioxide solution". Prepare a 0.50-mg/L 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
72	0.53 mg/L ClO <sub>2</sub>	0.50–0.55 mg/L CIO <sub>2</sub>	0.01 mg/L ClO <sub>2</sub>

#### **Summary of Method**

Chlorine dioxide (ClO<sub>2</sub>) combines with chlorophenol red at pH 5.2 to form a colorless complex. The resulting decrease in color is proportional to the chlorine dioxide concentration. The method is specific for  $ClO_2$  and is unreactive to other active chlorine or moderate oxidizing compounds. The measurement wavelength is 575 nm.

## Consumables and replacement items

#### **Required reagents**

Description	Quantity/test	Unit	ltem no.
Chlorine Dioxide Reagent Set, includes:	_	each	2242300
Chlorine Dioxide Reagent 1 (2x)	2 mL	100 mL	2070042
Chlorine Dioxide Reagent 2 (2x)	2 mL	100 mL	2070142
Chlorine Dioxide Reagent 3 (2x)	2 mL	100 mL	2070242
Dechlorinating Reagent Powder Pillows	1	100/pkg	1436369

#### **Required apparatus**

Description	Quantity/test	Unit	ltem no.
Mixing cylinder, graduated, 50-mL, with glass stopper	1	each	189641
Pipet, volumetric, Class A, 1.00-mL	1	each	1451535
Pipet filler, safety bulb	1	each	1465100

#### Optional reagents and apparatus

Description	Unit	ltem no.
Pipet, TenSette <sup>®</sup> , 0.1–1.0 mL	each	1970001
Pipet tips for TenSette <sup>®</sup> Pipet, 0.1–1.0 mL	50/pkg	2185696
Standard Methods Book, most current edition	each	2270800



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