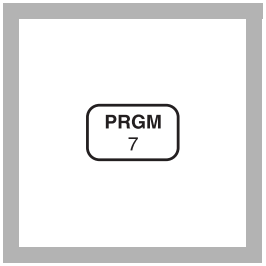
Using Powder Pillows

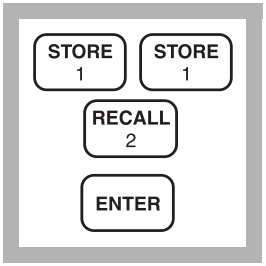


1. Enter the stored program number for chlorine dioxide (ClO_2) powder pillows.

Press: **PRGM**

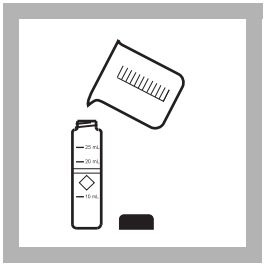
The display will show:

PRGM ?



2. Press: **112 ENTER**

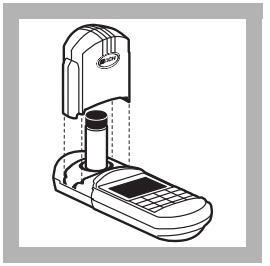
The display will show **mg/L, ClO2**, and the **ZERO** icon.



3. Fill a sample cell with 10 mL of sample (the blank).

Note: *Samples must be analyzed immediately and cannot be preserved for later analysis.*

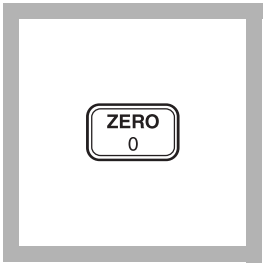
Note: *Wipe off any liquid or fingerprints before inserting the sample cell into the instrument.*



4. Place the blank into the cell holder. Tightly cover the sample cell with the instrument cap.

Note: *For best results, run a reagent blank using deionized water as the sample. Subtract the blank value from the sample reading to obtain the final result. See* Reagent Blank Correction *in Section 1 of the DR/800 Procedure Manual.*

* Procedure is equivalent to *Standard Method 4500, $Cl0_2P$*

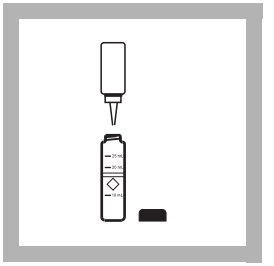


5. Press: **ZERO**

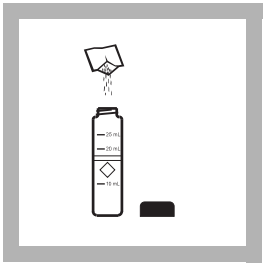
The cursor will move to the right, then the display will show:

0.00 mg/L ClO2

Note: *If Reagent Blank Correction is on, the display may flash* **"limit"***. See Section 1 of the DR/800 Procedures Manual.*



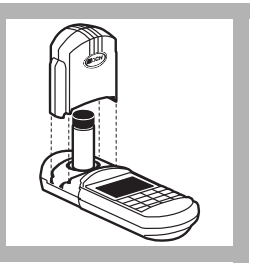
6. Add four drops of Glycine Reagent to the sample cell. Swirl to mix.



7. Add the contents of one DPD Free Chlorine Powder Pillow to the sample cell (the prepared sample). Cap the cell and swirl to mix.

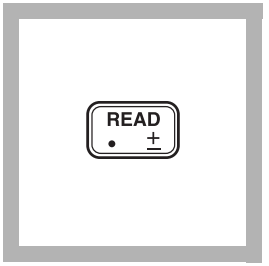
Note: *A pink color will develop if free chlorine dioxide is present.*

Note: *Perform step 9 within one minute of reagent addition.*



8. Allow 30 seconds for undissolved powder to settle. Place the prepared sample into the cell holder. Tightly cover the sample cell with the instrument cap.

Note: *Wipe off any liquid or fingerprints before inserting the sample cell into the instrument.*

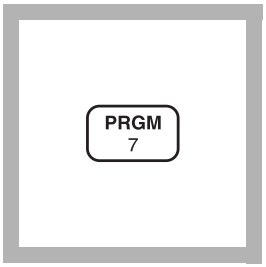


9. Press: **READ**

The cursor will move to the right, then the result in mg/L chlorine dioxide will be displayed.

Note: *If the sample temporarily turns yellow after reagent addition, or the display flashes* **"limit"***, it is due to high chlorine dioxide levels. Dilute a fresh sample with chlorine dioxide-free water and repeat the test. A slight loss of chlorine dioxide may occur during dilution. Multiply the result by the dilution factor.*

Using AccuVac® Ampuls

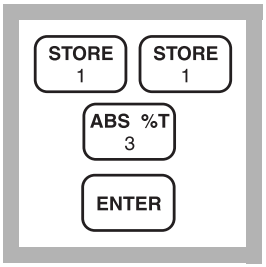


1. Enter the stored program number for chlorine dioxide (ClO_2) AccuVac Ampuls.

Press: **PRGM**

The display will show:

PRGM ?



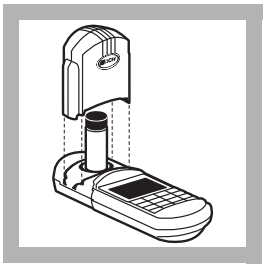
2. Press: **113 ENTER**

The display will show **mg/L, ClO2** and the **ZERO** icon.

3. Fill a sample cell with at least 10 mL of sample (the blank). Fill a 50-mL beaker with 40 mL of sample. Using the correct sample volume is important.

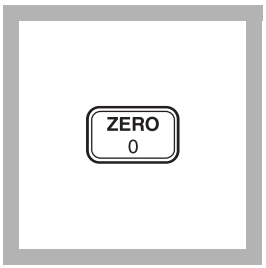
Note: *Samples must be analyzed immediately and cannot be preserved for later analysis.*

Note: *Wipe off any liquid or fingerprints before inserting the sample cell into the instrument.*



4. Place the blank into the cell holder. Tightly cover the sample cell with the instrument cap.

Note: *For best results, run a reagent blank using deionized water as the sample. Subtract the blank value from the sample reading to obtain the final result. See* Reagent Blank Correction *in Section 1 of the DR/800 Procedure Manual.*

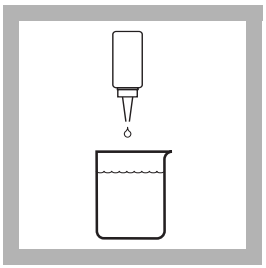


5. Press: **ZERO**

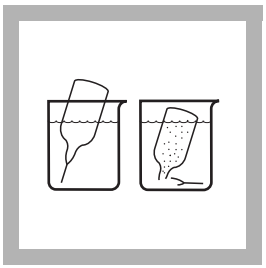
The cursor will move to the right, then the display will show:

0.00 mg/L ClO2

Note: *If Reagent Blank Correction is on, the display may flash "limit". See Section 1 of the DR/800 Procedures Manual.*



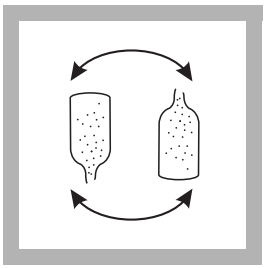
6. Add 16 drops of Glycine Reagent to the sample in the beaker. Swirl to mix.



7. Fill a DPD Free Chlorine Reagent AccuVac Ampul with sample.

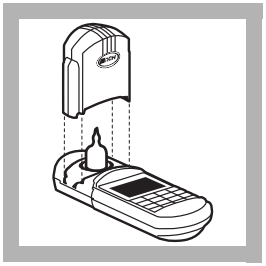
Note: *Keep the tip immersed while the ampul fills completely.*

Note: *Perform step 10 within one minute of reagent addition.*

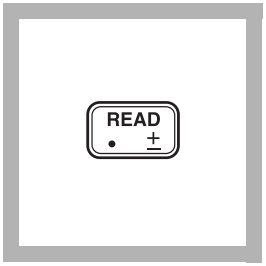


8. Quickly invert the ampul several times to mix. Wipe off any liquid or fingerprints.

Note: *A pink color will form if chlorine dioxide is present.*



9. Allow 30 seconds for undissolved powder to settle. Place the AccuVac Ampul into the cell holder. Tightly cover the ampul with the instrument cap.



10. Press: **READ**

The cursor will move to the right, then the result in mg/L chlorine dioxide will be displayed.

Note: *If the sample temporarily turns yellow after reagent addition, or the display flashes "limit", it is due to high chlorine dioxide levels. Dilute a fresh sample with chlorine dioxide-free water and repeat the test. A slight loss of chlorine dioxide may occur during dilution. Multiply the result by the dilution factor.*

Sampling and Storage

Analyze samples for chlorine dioxide **immediately** after collection. Chlorine dioxide is a strong oxidizing agent, and it is unstable in natural waters. It reacts rapidly with various inorganic compounds and slowly oxidizes organic compounds. 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 demand. **Pretreat glass** sample containers to remove any chlorine dioxide demand by soaking in a dilute bleach solution (1 mL commercial bleach to l liter of deionized water) for at least 1 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 introduced when a representative sample is not obtained. 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 container 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 analysis immediately.

Accuracy Check

Because chlorine dioxide is difficult and hazardous to produce, check the DPD and glycine reagents by using chlorine standards. Proceed as follows:

1. Prepare a 1-mg/L free chlorine standard.

Method 1

a. Obtain Free Chlorine Standards, (Cat. No. 14268-10).

b. Determine the concentration of the standard from the certificate of analysis shipped with the standard (50-75 mg/L). Calculate the volume of standard needed as follows:

mL standard needed = 100 ÷ standard concentration

c. Pipet the volume of standard needed into a 100-mL volumetric flask. Dilute to the line with chlorine demand-free deionized water. Invert to mix.

Method 2

a. Dilute 1 drop of commercial 5% chlorine bleach in 1 liter of chlorine demand-free deionized water. Use this as the standard.

2. Verify the standard's concentration using the Hach Free Chlorine Method, #8021.

3. Perform the chlorine dioxide test on the standard without adding glycine (*step 6*).

4. The chlorine dioxide reading should be about 2.45 times greater than the chlorine result. If so, this verifies the DPD and the instrument are functioning properly.

5. Repeat the chlorine dioxide test on the chlorine standard, including the glycine addition (*step 6*). The reading should be less than 0.10 mg/L. This verifies that the glycine is eliminating free chlorine interference.

Method Performance

Precision

Program	Standard	95% Confidence Limits
112	0.24 mg/L	0.22–0.26 mg/L ClO_2
112	4.79 mg/L	4.67–4.91 mg/L ClO_2
113	0.26 mg/L	0.21–0.27 mg/L ClO_2
113	4.83 mg/L	4.71–4.97 mg/L ClO_2

For more information on determining precision data and method detection limits, see *Section 1* of the *DR/800 Procedures Manual*.

Estimated Detection Limit (EDL)

Program	EDL
112	0.04 mg/L ClO_2
113	0.04 mg/L ClO_2

For more information on derivation and use of Hach's estimated detection limit, see *Section 1* of the *DR/800 Procedures Manual*.

Interferences

A substance interferes if it changes the final reading by 0.1 mg/L ClO_2 or more.

Interfering Substance	Interference Levels and Treatments
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. Determine amount to be added on separate sample aliquot, then add the same amount to the sample being tested. Correct for volume addition (see *Section 1, Correction For Volume Additions, in the DR/800 Procedures Manual).*
Alkalinity	Greater than 250 mg/L $CaCO_3$. May not develop full color or color may fade instantly. Neutralize to pH 6–7 with 1 N sulfuric acid. Determine amount to be added on separate sample aliquot, then add the same amount to the sample being tested. Correct for volume addition (see *Section 1*, *Correction For Volume Additions, in the DR/800 Procedures Manual).*
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 1,000 mg/L as $CaCO_3$.

Interfering Substance	Interference Levels and Treatments
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 (30 g/L) to a 25-mL sample. **3.** Mix and wait one minute. **4.** Add 3 drops sodium arsenite (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.
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. See *Section 1, pH Interferences, in the DR/800 Procedures Manual.*
Highly buffered samples	Adjust to pH 6–7. *See Section 1, pH Interferences, in the DR/800 Procedures Manual.*

Pollution Prevention and Waste Management

Samples treated with sodium arsenite for manganese or chromium interferences will be hazardous wastes as regulated by Federal RCRA for arsenic (D004).

Summary of Method

Chlorine dioxide reacts with DPD (N,N-diethyl-p-phenylenediamine) Indicator Reagent (to the extent of one-fifth of its total available chlorine content corresponding to reduction of chlorine dioxide to chlorite) to form a pink color. The 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.

REQUIRED REAGENTS (Using Powder Pillows)

Description	Quantity Required per test	Unit	Cat. No.
Chlorine Dioxide DPD/Glycine Reagent Set (100 tests)			27709-00
Includes one of each:			
DPD Free Chlorine Reagent Powder Pillows, 10 mL	1 pillow	100/pkg	21055-69
Glycine Reagent	4 drops	29 mL	27621-33

REQUIRED REAGENTS (Using AccuVac® Ampuls)

Chlorine Dioxide DPD/Glycine AccuVac® Ampul Reagent Set (25 tests)			27710-00
Includes one of each:			
DPD Free Chlorine Reagent AccuVac® Ampuls	1	25/pkg	25020-25
Glycine Reagent	16 drops	29 mL	27621-33

OPTIONAL REAGENTS

Chlorine Standard Solution, Voluette™ ampule, 50-75 mg/L, 10 mL		16/pkg	14268-10
DPD Free Chlorine Reagent, SwifTest™		250 tests	28023-00
Potassium Iodide Solution, 30 g/L		100 mL* MDB	343-32
Sodium Arsenite, 5 g/L		100 mL* MDB	1047-32
Sodium Hydroxide Standard Solution, 1.000 N		100 mL* MDB	1045-32
Sulfuric Acid Standard Solution, 1.000 N		100 mL* MDB	1270-32
Water, deionized		4 L	272-56
Water, sterile, chlorine dioxide-free		500 mL	26415-49

OPTIONAL APPARATUS

AccuVac® Snapper Kit		each	24052-00
Cylinder, graduated, 25 mL		each	508-40
pH Meter, *sens**ion***™*1*, portable, with electrode		each	51700-10
pH Paper, 1 to 11 pH units		5 rolls/pkg	391-33
Pipet, TenSette®, 0.1 to 1.0 mL		each	19700-01
Pipet Tips, for 19700-01 TenSette® Pipet		50/pkg	21856-96
Pipet Tips, for 19700-01 TenSette® Pipet		1000/pkg	21856-28
PourRite™ Ampule Breaker		each	24846-00

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* Marked Dropper Bottle - contact Hach for larger sizes.