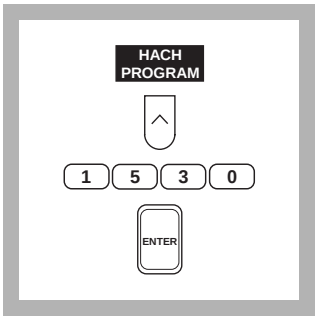
CHLORINE DIOXIDE

Method 10126 **DPD Method***

Powder Pillows and AccuVac® Ampuls **(0 to 5.00 mg/L)**

Scope and Application: *For testing chlorine dioxide in water; USEPA accepted for reporting for drinking water analyses***
The estimated detection limit for program numbers 1530 and 1535 is 0.04 mg/L ClO_2.

* Adapted from *Standard Methods for the Examination of Water and Wastewater.*
** Procedure is equivalent to Std. Methods, 18th Ed. 4500 ClO_2 D.



1. Press the soft key under ***HACH PROGRAM***.

Select the stored program number for chlorine dioxide (ClO_2) by pressing **1530** with the numeric keys.

Press: **ENTER**

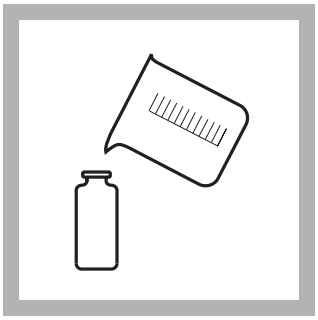
Note: *Samples must be analyzed immediately and cannot be preserved for later analysis. See Sample Collection, Storage and Preservation following these steps.*

2. The display will show:

HACH PROGRAM: 1530 ClO_2 DPD

The wavelength (λ), **530 nm**, is automatically selected.

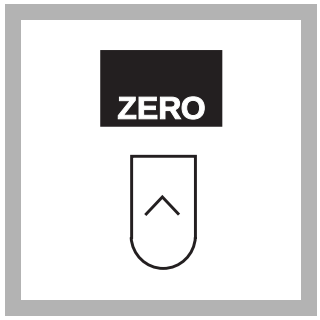
Note: *For best results, determine a reagent blank for each new lot of reagent as follows. Prepare a reagent blank by repeating steps 3–8, using deionized water as the sample. Zero the instrument on deionized water by pressing the soft key under* ***ZERO****. Insert the reagent blank and the blank value will be displayed. Correct for the reagent blank by pressing the soft keys under* ***OPTIONS, (MORE)****, and then* ***BLANK:OFF****. Enter the reagent blank value and press* **ENTER.** *Repeat for each new lot of reagents.*



3. Fill a sample cell with 10 mL of sample (the blank). Place it into the cell holder and close the light shield.

Note: *For samples with extreme pH, see Interferences.*

Note: *Wipe off any liquid or fingerprints before putting the cell in the instrument.*



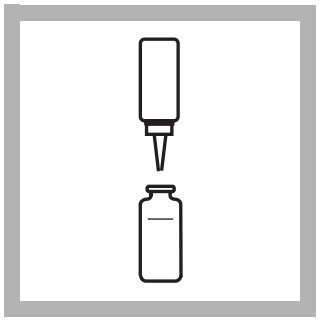
4. Press the soft key under ***ZERO***.

The display will show:

0.00 mg/L ClO_2

Note: *If you are using a reagent blank correction, the display will show the correction.*

Note: *For alternate concentration units, press the soft key under* ***OPTIONS****. Then press the soft key under* ***UNITS*** *to scroll through the available options. Press* **ENTER** *to return to the read screen.*

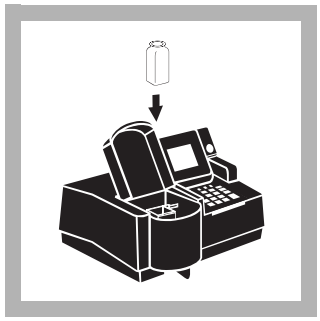


5. Add four drops of Glycine Reagent to the sample. Swirl to mix. This is the prepared sample.

6. Add the contents of one DPD Free Chlorine Powder Pillow to the sample cell (the prepared sample). Swirl the sample cell for 20 seconds to mix. Wait 30 seconds for any undissolved powder to settle. Proceed to step 7 immediately.

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

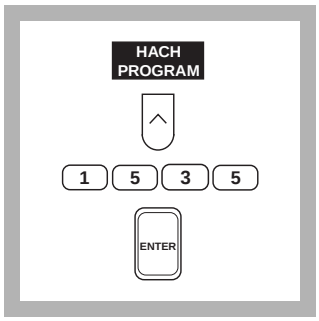
Note: *Wipe off any liquid or fingerprints before putting the cell in the instrument.*



7. Place the prepared sample into the cell holder. Close the light shield. Read results in mg/L chlorine dioxide (or chosen units) within one minute of reagent addition.

Note: *If the chlorine dioxide concentration in the sample exceeds the upper limit of the test, the color may fade or the display may show* **OVER!**. *Dilute the sample with high quality water that is chlorine demand-free, and repeat the test. Some loss of chlorine dioxide may occur due to the dilution. Multiply the result by the appropriate dilution factor.*

Using AccuVac® Ampuls



1. Press the soft key under ***HACH PROGRAM***.

Select the stored program number for chlorine dioxide (ClO_2) by pressing **1535** with the numeric keys.

Press: **ENTER**

Note: *Samples must be analyzed immediately and cannot be preserved for later analysis. See Sample Collection, Storage and Preservation following these steps.*

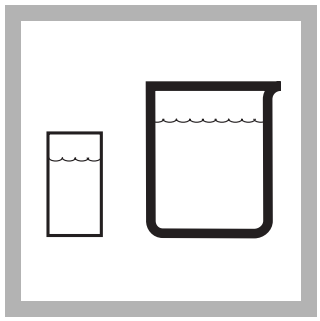
2. The display will show:

HACH PROGRAM: 1535 ClO_2 DPD, AV

The wavelength (λ), **530 nm**, is automatically selected.

Note: *For best results, determine a reagent blank. See Step 2 in the powder pillow procedure for instructions.*

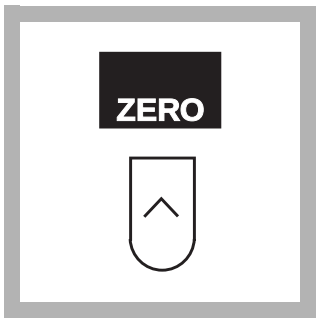
3. Insert the AccuVac Ampul Adapter into the sample cell module by sliding it under the thumb screw and into the alignment grooves. Fasten with the thumb screw.



4. Fill a zeroing vial (the blank) with at least 10 mL of sample. Fill a 50-mL beaker with 40 mL of sample.

5. Place the blank into the cell holder. Close the light shield.

Note: *Wipe off any liquid or fingerprints before putting the cell in the instrument.*



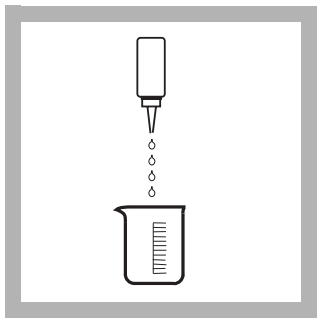
6. Press the soft key under ***ZERO***.

The display will show:

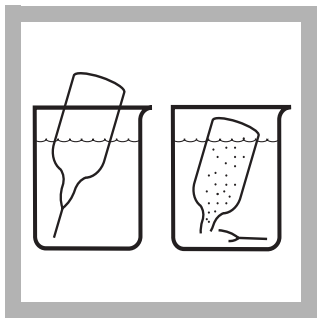
0.00 mg/L ClO_2

Note: *If you are using a reagent blank correction, the display will show the correction.*

Note: *For alternate concentration units, press the soft key under* ***OPTIONS****. Then press the soft key under* ***UNITS*** *to scroll through the available options. Press* **ENTER** *to return to the read screen.*

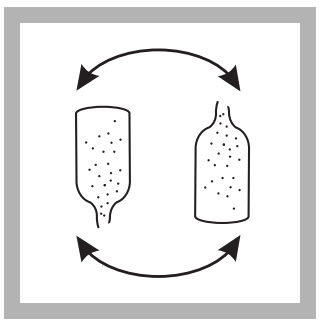


7. Add 16 drops of Glycine Reagent to the sample in the beaker. Swirl gently to mix.



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

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



9. Quickly invert the ampul several times to mix. Wait 30 seconds for any undissolved powder to settle. Wipe off any liquid or fingerprints.

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

10. Immediately (within one minute of sample addition) place the AccuVac Ampul into the cell holder. Close the light shield. Results in mg/L chlorine dioxide (or chosen units) will be displayed.

Note: *If the chlorine dioxide concentration in the sample exceeds the upper limit of the test, the color may fade or the display may show* **OVER!.** *Dilute the sample with high quality water that is chlorine demand-free, and repeat the test. Some loss of chlorine dioxide may occur due to the dilution. Multiply the result by the appropriate dilution factor.*

Interferences

A substance interferes if it changes the final reading by 0.1 mg/L 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 1.22, Correction For Volume Additions.*
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 *1.2.2 Correcting for Volume Additions*).
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 $CaCO_3$.
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 *1.3, pH Interference.*
Highly buffered samples	Adjust to pH 6-7. See Section *1.3, pH Interference.*

Sample Collection, Storage and Preservation

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 l 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 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, the carefully fill to the 10-mL mark. Perform then chlorine dioxide 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, Hach 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
Dilute 1 drop of 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* for program 1530 or *step 7* for program 1535).

4. For program 1530, the chlorine dioxide reading should be 2.38 times greater than the chlorine result. For program 1535, the chlorine dioxide reading should be 2.48 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* or *7*). The reading should be less than 0.10 mg/L. This verifies that the glycine is eliminating free chlorine interference.

Method Performance

Precision
Standard: 0.35 mg/L ClO_2

Program	95% Confidence Limits
1530	0.33–0.37 mg/L ClO_2
1535	0.32–0.38 mg/L ClO_2

Standard: 3.70 mg/L ClO_2

Program	95% Confidence Limits
1530	3.54–3.86 mg/L ClO_2
1535	3.59–3.81 mg/L ClO_2

For more information on determining precision data and method detection limits, refer to *Section 1.5*.

Estimated Detection Limit

Program	EDL
1530	0.04 mg/L ClO_2
1535	0.04 mg/L ClO_2

For more information on derivation and use of Hach's estimated detection limit, see Section *1.5.2*. To determine a method detection limit (MDL) as defined by the 40 CFR part 136, Appendix B, see *Section 1.5.1*.

Sensitivity
Program Number: 1530

Portion of Curve	ΔAbs	ΔConcentration
0.40	0.010	0.042 mg/L
2.50	0.010	0.045 mg/L
4.00	0.010	0.049 mg/L

Program Number: 1535

Portion of Curve	ΔAbs	ΔConcentration
0.40	0.010	0.048 mg/L
2.50	0.010	0.051 mg/L
4.00	0.010	0.054 mg/L

See Section *1.5.3, Sensitivity Explained,* for more information.

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 chloroaminoascorbic acid, but has no effect on chlorine dioxide at the test pH.

Safety

Good safety habits and laboratory techniques should be used throughout the procedure. Consult the *Material Safety Data Sheet* for information specific to the reagents used. For additional information, refer to Section *1*.

Pollution Prevention and Waste Management

Samples treated with sodium arsenite for interferences will be hazardous waste as regulated by Federal RCRA for arsenic (D004). See Section *1* for further information on proper disposal of these materials.

REQUIRED REAGENTS AND STANDARDS (Using Powder Pillows)

Chlorine Dioxide DPD/Glycine Reagent Set (100 tests) 27709-00
Includes: (1) 21055-69, (1) 27621-33

Description	Quantity Required per test	Unit	Cat. No.
DPD Free Chlorine Reagent Powder Pillows, 10 mL	1 pillow	100/pkg	21055-69
Glycine Reagent	4 drops	29 mL	27621-33

REQUIRED REAGENTS AND STANDARDS (Using AccuVac Ampuls)

Chlorine Dioxide DPD/Glycine AccuVac® Ampul Reagent Set (25 tests) 27710-00
Includes: (1) 25020-25, (1) 27621-33

DPD Free Chlorine Reagent AccuVac® Ampuls	1 ampul	25/pkg	25020-25
Glycine Reagent	16 drops	29 mL	27621-33

REQUIRED EQUIPMENT AND SUPPLIES (Using Powder Pillows)

DR/4000 1-inch Cell Adapter	1	each	48190-00
Stopper, rubber, No. 2	1	12/pkg	2118-02

REQUIRED EQUIPMENT AND SUPPLIES (Using AccuVac Ampuls)

Beaker, 50-mL	1	each	500-41
DR/4000 AccuVac Ampul Adapter	1	each	48187-00
Sample Cell, 10-mL with cap (zeroing vial)	1	each	21228-00

OPTIONAL REAGENTS AND STANDARDS

Chlorine Standard Solution, 10-mL Voluette™ Ampule, 50–75 mg/L		16/pkg	14268-10
Potassium Iodide Solution, 30-g/L	100 mL	* MDB	343-32
Sodium Arsenite Solution, 5-g/L	100 mL	* MDB	1047-32
Sodium Hydroxide Standard Solution, 1.00 N	100 mL	* MDB	1045-32
Sulfuric Acid Standard Solution, 1.000 N	100 mL	* MDB	1270-32
Water, deionized	4	liters	272-56

OPTIONAL EQUIPMENT AND SUPPLIES

AccuVac® Snapper		each	24052-00
Ampule Breaker Kit		each	21968-00
Cylinder, graduated, 25-mL, poly		each	1081-40
DR/4000 Carousel Module Kit		each	48070-02
DR/4000 Flow Cell Module Kit, 1-inch		each	48070-04
DR/4000 Flow Cell Module Kit, 1-cm		each	48070-05
DR/4000 Sipper Module Kit, 1-inch		each	48090-03
pH Meter, *sens**ion**™1*, portable		each	51700-00
Pipet, TenSette®, 0.1 to 1.0 mL		each	19700-01
Pipet Tips, for 19700-01 TenSette Pipet		50/pkg	21856-96

* Contact Hach for larger sizes.

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