



## ✓ Method 8021

DPD Method\*

### Powder Pillows or AccuVac® Ampuls

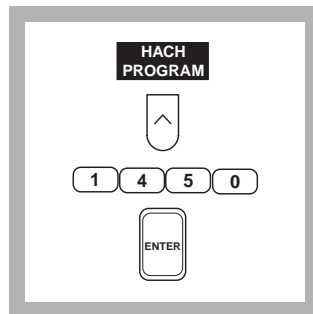
(0 to 2.00 mg/L)

**Scope and Application:** For testing free chlorine (hypochlorous acid and hypochlorite ion) in water, treated waters, estuary and seawater. USEPA accepted for reporting for drinking water analyses\*\*. The estimated detection limit for program numbers 1450 and 1460 is 0.01 mg/L Cl<sub>2</sub>.

\* Adapted from *Standard Methods for the Examination of Water and Wastewater*

\*\* Procedure is equivalent to USEPA method 330.5 and Standard Method 4500-Cl G for drinking water.

## Using Powder Pillows



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

Select the stored program number for free chlorine (Cl<sub>2</sub>) by pressing **1450** 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.

**Note:** The Flow Cell and Sipper Modules can be used with this procedure if rinsed between samples. Use a 25-mL sample and reagents with the Flow Cell Module.



**2.** The display will show: **HACH PROGRAM: 1450 Chlorine, F&T**

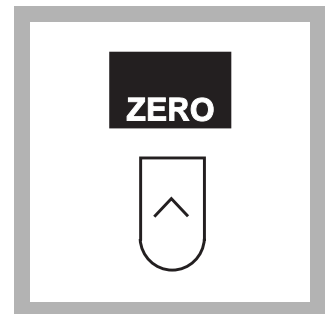
The wavelength ( $\lambda$ ), **530 nm**, is automatically selected.

**Note:** For best results, determine a reagent blank for each new lot of reagent as follows. Prepare a reagent blank by repeating Steps 3 through 7, 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 reagent.



**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 sample with extreme pH, see *Interferences* section.



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

The display will show:

**0.00 mg/L Cl<sub>2</sub>**

**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.

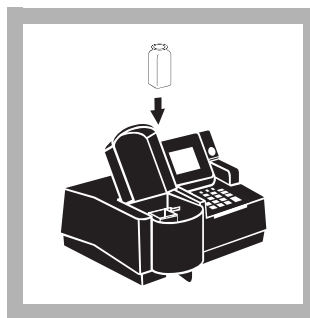


**5.** Fill another cell with 10 mL of sample.



**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. Proceed to Step 7 immediately.

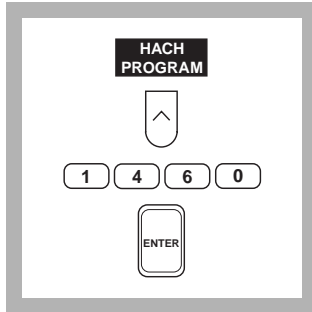
**Note:** A pink color will develop if free chlorine is present.



**7.** Place the prepared sample into the cell holder. Close the light shield. Read results in mg/L chlorine (or chosen units) within 1 minute of reagent addition.

**Note:** If the chlorine 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 may occur due to the dilution. Multiply the result by the appropriate dilution factor; See Section 1.2.6 Sample Dilution Techniques.

## Using AccuVac Ampuls



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

Select the stored program number for free chlorine ( $\text{Cl}_2$ ) by pressing **1460** 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.



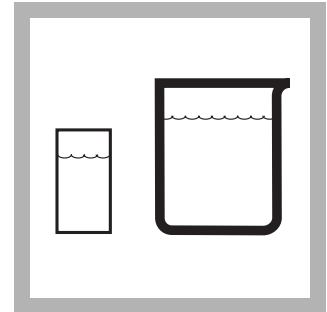
**2.** The display will show: **HACH PROGRAM:1460 Chlorine, F&T AV**

The wavelength ( $\lambda$ ), **530 nm**, is automatically selected.

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



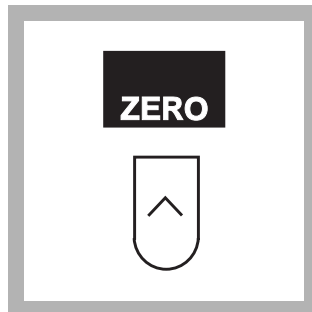
**3.** Insert the AccuVac Ampul Adapter into the sample cell module by sliding it under the thumb screw and into the alignment grooves. Fasten with the thumb screw.



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



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



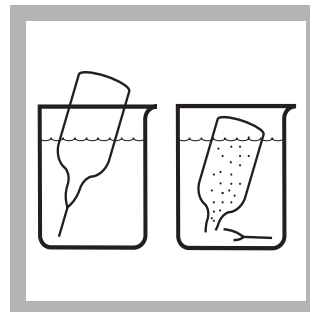
**6.** Press the soft key under **ZERO**.

The display will show:

**0.00 mg/L  $\text{Cl}_2$**

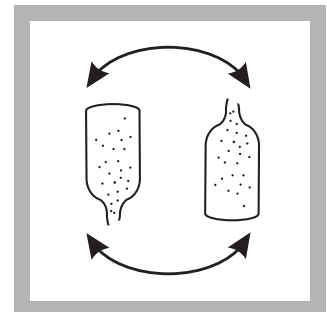
**Note:** If you are using a reagent blank correction, the display will show the correction.

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

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



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

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



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

**Note:** *If the chlorine 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 may occur due to the dilution. Multiply the result by the appropriate dilution factor; see Section 1.2.6 Sample Dilution Techniques.*

**Interferences**

Interfering Substance	Interference Levels and Treatments
Acidity	Greater than 150 mg/L CaCO <sub>3</sub> . 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 1.2.2 <i>Correcting for Volume Additions</i> ).
Alkalinity	Greater than 250 mg/L CaCO <sub>3</sub> . 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 <i>Correcting for Volume Additions</i> ).
Bromine, Br <sub>2</sub>	Interferes at all levels
Chlorine Dioxide, ClO <sub>2</sub>	Interferes at all levels
Chloramines, organic	May interfere
Hardness	No effect at less than 1,000 mg/L as CaCO <sub>3</sub>
Iodine, I <sub>2</sub>	Interferes at all levels
Manganese, Oxidized (Mn <sup>4+</sup> , Mn <sup>7+</sup> ) or Chromium, Oxidized (Cr <sup>6+</sup> )	<ol style="list-style-type: none"> <li>1. Adjust sample pH to 6–7.</li> <li>2. Add 3 drops potassium iodide (30-g/L) to a 25-mL sample.</li> <li>3. Mix and wait one minute.</li> <li>4. Add 3 drops sodium arsenite (5-g/L) and mix.</li> <li>5. Analyze 10 mL of the treated sample as described in the procedure.</li> <li>6. Subtract the result from this test from the original analysis to obtain the correct chlorine concentration.</li> </ol>
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	Interferes at all levels
Peroxides	May interfere
Extreme sample pH	Adjust to pH 6-7. See Section 1.3.1 <i>pH Interference</i> .
Highly Buffered Samples	Adjust to pH 6-7. See Section 1.3.1 <i>pH Interference</i> .

**Sample Collection, Storage and Preservation**

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

Avoid plastic containers since these may have a large chlorine demand. Pretreat glass sample containers to remove any chlorine demand by soaking in a dilute bleach solution (1 mL commercial bleach to 1 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 pre-treatment is necessary.

Do not use the same sample cells for free and total chlorine. If trace iodide from the total chlorine reagent is carried over into the free chlorine determination, monochloramine will interfere. It is best to use separate, dedicated sample cells for free and total chlorine determinations.

A common error in testing for chlorine 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 the chlorine analysis immediately.

## Accuracy Check

### Standard Additions Method (using powder pillows)

- a. Leave the unspiked sample in the sample compartment. Verify that the units displayed are in mg/L. Select standard additions mode by pressing the soft keys under **OPTIONS, (MORE)** and then **STD ADD**.
- b. Press **ENTER** to accept the default sample volume (mL), 10.
- c. Locate the average chlorine concentration shown on the certificate enclosed with the LR Voluettes. When prompted for the standard concentration, use the numeric keys to enter the certificate value. Press **ENTER**.
- d. Press the soft key under **ENTRY DONE**.
- e. Snap the neck off a LR Chlorine Voluette Ampule Standard, 20-30 mg/L Cl<sub>2</sub>.
- f. Use the TenSette Pipet to add 0.1 mL, 0.2 mL and 0.3 mL of standard, respectively to three 10-mL samples and mix each thoroughly.
- g. Analyze each standard addition sample as described above. Accept the standard additions readings by pressing the soft key under **READ** each time. Each addition should reflect approximately 100% recovery.
- h. After completing the sequence, the display will show the extrapolated concentration value and the “best-fit” line through the standard additions data points, accounting for matrix interferences.
- i. See Section 1.4.1 *Standard Additions* for more information.

### Standard Additions Method (using AccuVac Ampuls)

- a. Leave the unspiked sample in the sample compartment. Verify that the units displayed are in mg/L. Select standard additions mode by pressing the soft keys under **OPTIONS, (MORE)** and then **STD ADD**.
- b. Press **ENTER** to accept the default sample volume (mL), 25.
- c. Locate the average chlorine concentration shown on the certificate enclosed with the LR Voluettes. When prompted for the standard concentration, use the numeric keys to enter the certificate value. Press **ENTER**.
- d. Press the soft key under **ENTRY DONE**.
- e. Snap the neck off a LR Chlorine Voluette Ampule Standard, 20-30 mg/L Cl<sub>2</sub>.
- f. Use graduated cylinder to measure 25 mL of sample into each of three 50-mL beakers. Use a TenSette Pipet to add 0.2, 0.4 and 0.6 mL of standard, respectively, to each of the 25-mL samples. Swirl gently to mix.
- g. Fill a DPD Free Chlorine AccuVac completely from each beaker and analyze each standard addition sample as described above. Accept the

standard additions readings by pressing the soft key under **READ** each time. Each addition should reflect approximately 100% recovery.

- h.** After completing the sequence, the display will show the extrapolated concentration value and the “best-fit” line through the standard additions data points, accounting for matrix interferences.
- i.** See Section 1.4.1 *Standard Additions* for more information.

## Method Performance

### Precision

Standard: 1.00 mg/L Cl<sub>2</sub>

Program	95% Confidence Limits
1450	0.99–1.01 mg/L Cl <sub>2</sub>
1460	0.99–1.01 mg/L Cl <sub>2</sub>

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

### Estimated Detection Limit

Program	EDL
1450	0.01 mg/L Cl <sub>2</sub>
1460	0.01 mg/L Cl <sub>2</sub>

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: 1450

Portion of Curve	ΔAbs	ΔConcentration
Entire Range	0.010	0.019 mg/L

Program Number: 1460

Portion of Curve	ΔAbs	ΔConcentration
Entire Range	0.010	0.020 mg/L

See Section 1.5.3 *Sensitivity Explained* for more information.

## Summary of Method

Chlorine in the sample as hypochlorous acid or hypochlorite ion (free chlorine or free available chlorine) immediately reacts with DPD (N,N-diethyl-p-phenylenediamine) indicator to form a pink color which is proportional to the chlorine concentration.

# CHLORINE, Free, continued

## 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)

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

### REQUIRED REAGENTS AND STANDARDS (Using AccuVac Ampuls)

DPD Free Chlorine Reagent AccuVac Ampuls.....	1 ampul	.....	25/pkg	.....25020-25
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### 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, 2-mL Voluette Ampule, 20–30 mg/L .....	20/pkg	.....	26300-20
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
SwifTest DPD Free Chlorine Reagent, with dispenser .....	250 tests	.....	28023-00
SwifTest Replacement Vial .....	250 tests	.....	21055-60
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
Graph Paper, linear, 10 x 10.....	100/pkg	.....	22313-00
pH Meter, <i>sensio</i> <sup>TM</sup> 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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