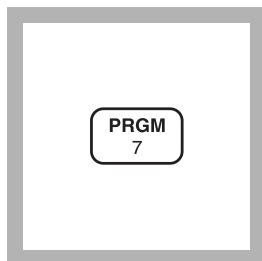


CHLORINE, FREE (0 to 2.00 mg/L)

For water, wastewater, and seawater

DPD Method (Powder Pillows or AccuVac Ampuls)

USEPA accepted for reporting wastewater and drinking water analyses*

Using Powder Pillows

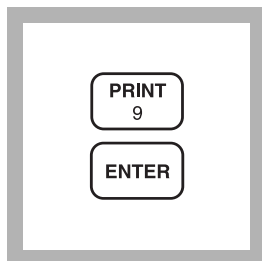
1. Enter the stored program number for free and total chlorine (Cl₂) powder pillows.

Press: **PRGM**

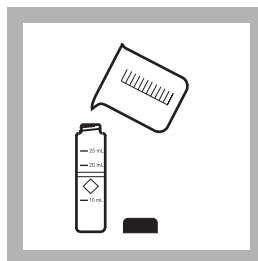
The display will show:

PRGM ?

Note: For most accurate results, perform a Reagent Blank Correction using deionized water (see Section 1).

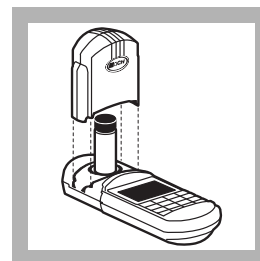


2. Press: **9 ENTER**
The display will show **mg/L, Cl₂** and the **ZERO** icon.



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

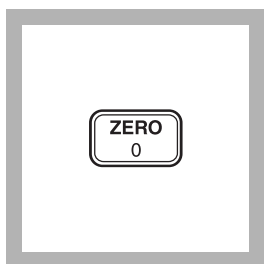
Note: Samples must be analyzed immediately and cannot be preserved for later analysis.



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

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

CHLORINE, FREE, continued



5. Press: ZERO

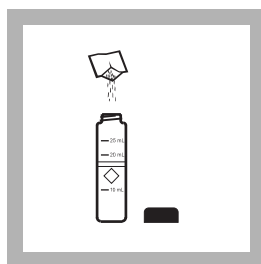
The cursor will move to the right, then the display will show:

0.00 mg/L Cl₂

Note: If Reagent Blank Correction is on, the display may flash "limit". See Section 1.

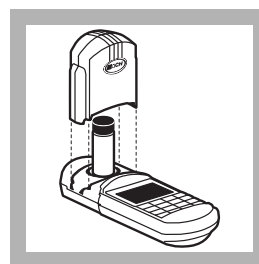


6. Fill another cell with 10 mL of sample.



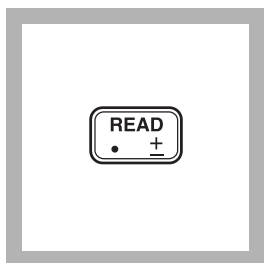
7. Add the contents of one DPD Free Chlorine Powder Pillow to the sample cell (the prepared sample). Cap the cell and swirl vigorously to dissolve the powder.

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



8. Immediately place the prepared sample into the cell holder. Tightly cover the sample cell with the instrument cap.

Note: Perform Step 9 within one minute of reagent addition.



9. Press: READ

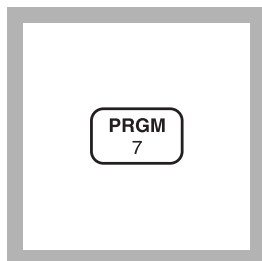
The cursor will move to the right, then the result in mg/L chlorine will be displayed.

Note: Standard Adjust may be performed using a prepared standard (see Section 1).

Note: If the sample temporarily turns yellow after reagent addition, or the display flashes "limit", it is due to high chlorine levels. Dilute a fresh sample and repeat the test. A slight loss of chlorine may occur during dilution. Multiply the result by the dilution factor; see Section 1. Or, use the High Range Free Chlorine test, program #8.

CHLORINE, FREE continued

Using AccuVac Ampuls



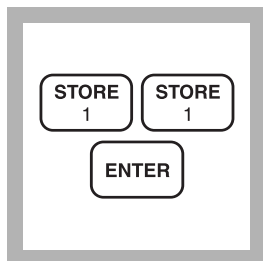
1. Enter the stored program number for free and total chlorine (Cl₂)-AccuVac Ampuls.

Press: **PRGM**

The display will show:

PRGM ?

Note: For most accurate results, perform a Reagent Blank Correction using deionized water (see Section 1).

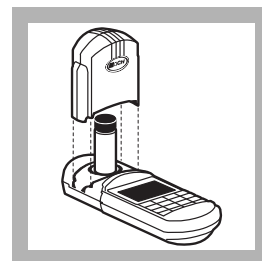


2. Press: **11 ENTER**
The display will show **mg/L, Cl₂** and the **ZERO** icon.

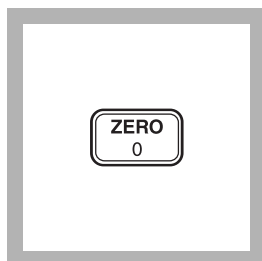


3. Fill a sample cell with at least 10 mL of sample (the blank). Collect at least 40 mL of sample in a 50-mL beaker.

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



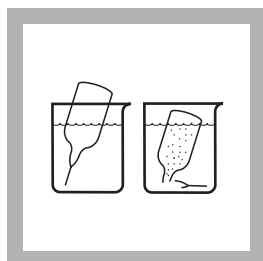
4. Place the blank into the cell holder. Tightly cover the sample cell with the instrument cap.



5. Press: **ZERO**
The cursor will move to the right, then the display will show:

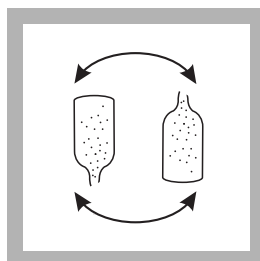
0.00 mg/L Cl₂

Note: If Reagent Blank Correction is on, the display may flash "limit". See Section 1.



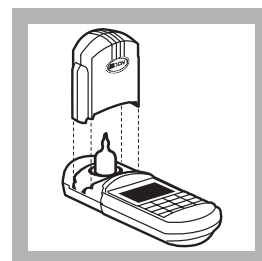
6. Fill a DPD Free Chlorine Reagent AccuVac Ampul with sample.

Note: Keep the tip immersed while the ampule fills completely.



7. Quickly invert the ampule several times to mix. Wipe off any liquid or fingerprints.

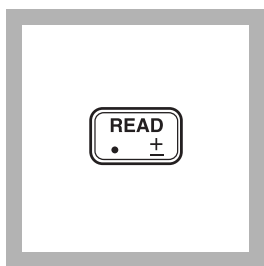
Note: A pink color will form if chlorine is present.



8. Immediately place the AccuVac Ampul into the cell holder. Tightly cover the ampule with the instrument cap.

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

CHLORINE, FREE continued



9. Press: **READ**

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

Note: Standard Adjust may be performed using a prepared standard (see Section 1).

Note: If the sample temporarily turns yellow after reagent addition, or the display flashes "limit", it is due to high chlorine levels. Dilute a fresh sample and repeat the test. A slight loss of chlorine may occur during dilution. Multiply the result by the dilution factor; see Section 1.

Sampling and Storage

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 pretreatment 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 introduced when a representative sample is not obtained. If sampling from a tap, let

CHLORINE, FREE continued

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

Standard Additions Method (using powder pillows)

- a) Snap the top off a LR Chlorine PourRite Ampule Standard Solution.
- b) Use a TenSette Pipet to add 0.1 mL of the standard to the reacted sample (this is the spiked sample). Swirl to mix.
- c) Re-zero the instrument using the original sample (the blank).
- d) Place the spiked sample in the cell holder and press **READ**. Record the results.
- e) Calculate the concentration of mg/L chlorine added to the sample:

$$\text{mg/L Chlorine added} = \frac{0.1 (\text{vol. standard added}) \times \text{Label value (mg/L Cl}_2\text{)}}{10.1 (\text{sample} + \text{standard volume})}$$

- f) The spiked sample result (step d) should reflect the analyzed sample result + the calculated mg/L Cl₂ added (step e).
- g) If this increase does not occur, see *Standard Additions* in *Section 1* for more information.

Standard Additions Method (using AccuVac Ampuls)

- a) Snap the top off a LR Chlorine PourRite Ampule Standard Solution.
- b) Use a graduated cylinder to measure 25 mL of sample into each of two beakers.
- c) Use a TenSette Pipet to add 0.2 mL of the standard to one of the beakers (this is the spiked sample). Swirl to mix.
- d) Fill a DPD Free Chlorine AccuVac completely from each beaker.

CHLORINE, FREE continued

- e) Analyze the spiked and unspiked sample as described in the procedure.
- f) Calculate the concentration of mg/L chlorine added to the sample:

$$\text{mg/L Chlorine added} = \frac{0.2(\text{vol. standard added}) \times \text{Label value (mg/L Cl}_2\text{)}}{25.2(\text{sample} + \text{standard volume})}$$

- g) The spiked sample result should reflect the analyzed sample result + the calculated mg/L Cl₂ added (step f).
- h) If this increase does not occur, see *Standard Additions* in *Section 1* for more information.

Method Performance

Precision

In a single laboratory using a standard solution of 1.00 mg/L chlorine and two representative lots of reagents with the instrument, a single operator obtained a standard deviation of ±0.01 mg/L chlorine.

In a single laboratory using a standard solution of 1.00 mg/L chlorine and two representative lots of AccuVac Ampuls with the instrument, a single operator obtained a standard deviation of ±0.01 mg/L chlorine.

Estimated Detection Limit (EDL)

The estimated detection limit for programs 9 and 11 is 0.02 mg/L Cl₂. For more information on derivation and use of Hach's estimated detection limit, see *Section 1*.

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). See *Section 3* for more information on proper disposal of these materials.

CHLORINE, FREE continued

Interferences

Interfering Substance	Interference Level and Treatment
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 <i>Section 1, Correcting for Volume Additions</i>).
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 <i>Section 1, Correcting for Volume Additions</i>).
Bromine	Interferes at all levels
Chlorine Dioxide	Interferes at all levels
Chloramines, organic	May interfere
Hardness	No effect at less than 1,000 mg/L as CaCO ₃
Iodine	Interferes at all levels
Manganese, Oxidized (Mn ⁴⁺ , Mn ⁷⁺) or Chromium, Oxidized (Cr ⁶⁺)	<ol style="list-style-type: none"> 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 from this test from the original analysis to obtain the correct chlorine concentration.
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 and highly buffered samples	Adjust to pH 6-7. See <i>Interferences, Section 1</i> .

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 magenta color which is proportional to the chlorine concentration.

CHLORINE, FREE continued

REQUIRED REAGENTS & APPARATUS (Using Powder Pillows)

Description	Quantity Required		Unit	Cat. No.
	Per Test			
DPD Free Chlorine Powder Pillows, 10 mL.....	1 pillow		100/pkg.....	21055-69
Sample Cell, 10, 20, 25 mL, w/ cap.....	2.....		6/pkg.....	24019-06

REQUIRED REAGENTS & APPARATUS (Using AccuVac Ampuls)

DPD Free Chlorine Reagent AccuVac Ampuls	1 ampul		25/pkg.....	25020-25
Beaker, 50 mL	1		each.....	500-41

OPTIONAL REAGENTS

Description		Unit	Cat. No.
Chlorine Standard Solution, PourRite ampule, 25-30 mg/L, 2 mL		20/pkg.....	26300-20
DPD Free Chlorine Reagent w/dispensing cap.....		250 tests.....	21055-29
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.....		4L	272-56

OPTIONAL APPARATUS

AccuVac Snapper Kit.....		each.....	24052-00
Cylinder, graduated, 25 mL		each.....	508-40
pH Meter, <i>sensio</i> TM 1, portable		each.....	51700-00
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
PourRite Ampule Breaker.....		each.....	24846-00

For Technical Assistance, Price and Ordering

In the U.S.A.—Call 800-227-4224

Outside the U.S.A.—Contact the Hach office or distributor serving you.

* Marked Dropper Bottle - contact Hach for larger sizes.