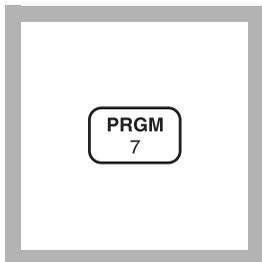


**CHLORINE, FREE (0 to 5.00 mg/L)**

For water, wastewater, and seawater

**DPD Test 'N Tube™ Method\***

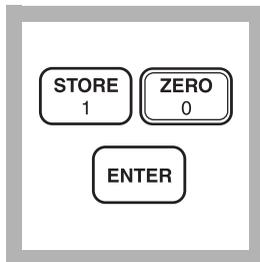
**1.** Enter the stored program number for Test 'N Tube free chlorine (Cl<sub>2</sub>).

Press: **PRGM**

The display will show:

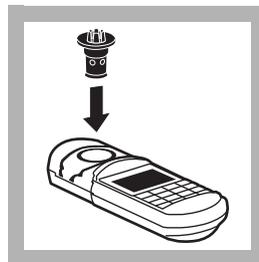
**PRGM ?**

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



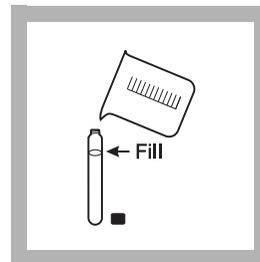
**2.** Press: **10 ENTER**

The display will show **mg/L, Cl<sub>2</sub>** and the **ZERO** icon.



**3.** Insert the COD/TNT Adapter into the cell holder by rotating the adapter until it drops into place. Then push down fully to insert it.

*Note: For increased performance, a diffuser band covers the light path holes on the adapter. Do not remove the diffuser band.*



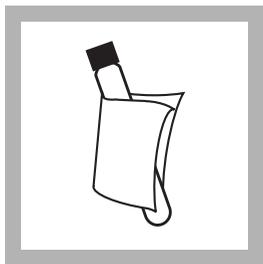
**4.** Fill an empty Test 'N Tube vial with sample (the blank).

*Note: Fill to the top of the Hach logo "oval" mark.*

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

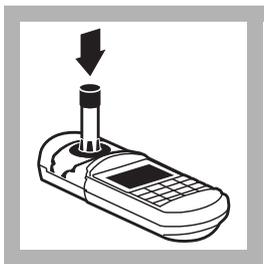
\* Adapted from *Standard Methods for the Examination of Water and Wastewater*

## CHLORINE, FREE, continued



**5.** Wipe the outside of the blank vial with a towel.

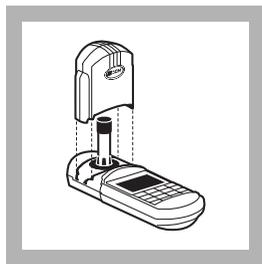
*Note: Wiping with a damp cloth followed by a dry one removes fingerprints and other marks.*



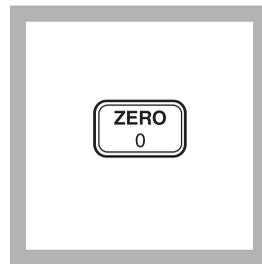
**6.** Place the blank in the adapter.

Push straight down on the top of the vial until it seats solidly into the adapter.

*Note: Do not move the vial from side to side as this can cause errors.*



**7.** Cover the vial tightly with the instrument cap.

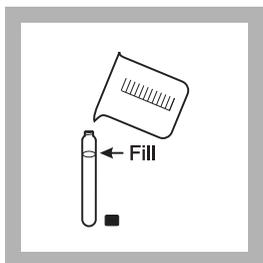


**8.** Press: **ZERO**

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

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

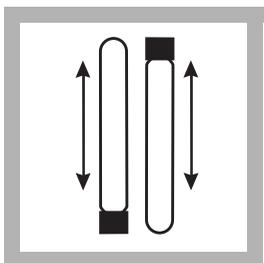
*Note: If Reagent Blank Correction is on, the display may show "limit". See Section 1.*



**9.** Remove the cap from a Free Chlorine DPD-TNT tube. Add 10 mL of sample.

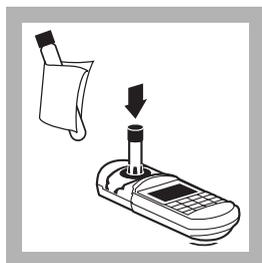
*Note: Fill to the top of the Hach logo "oval" mark.*

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



**10.** Cap and invert at least 10 times to dissolve the powder. This is the prepared sample.

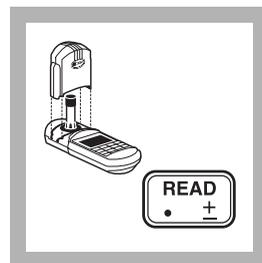
*Note: Use slow, deliberate inversion for complete recovery. Ten inversions should take at least 30 seconds. One inversion equals turning the vial upside down, then returning it to an upright position.*



**11.** Within 30 seconds after mixing, wipe the prepared sample vial with a towel, then place it in the adapter.

Push straight down on the top of the vial until it seats solidly into the adapter.

*Note: Do not move the vial from side to side as this can cause errors.*



**12.** Cover the vial tightly with the instrument cap.

Press: **READ**

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

## Sampling and Storage

Analyze samples for chlorine **immediately** after collection. Free chlorine is a strong oxidizing agent and 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.

A common error in testing for chlorine is obtaining an unrepresentative 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. Perform the analysis immediately.

## Accuracy Check

### Standard Additions Method

- a) Snap the top off a HR 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) Analyze the spiked sample, beginning at Step 8 of the procedure.
- d) Calculate the concentration of mg/L chlorine added to the sample:

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

- e) The spiked sample result (step c) should reflect the analyzed sample result + the calculated mg/L Cl<sub>2</sub> added (step d).
- f) If this increase does not occur, see *Standard Additions, Section 1* for more information.

# CHLORINE, FREE continued

## Method Performance

### Precision

In a single laboratory using a standard solution of 2.53 mg/L chlorine and two representative lots of reagents with the instrument, a single operator obtained a standard deviation of  $\pm 0.14$  mg/L chlorine.

### Estimated Detection Limit (EDL)

The estimated detection limit for program 10 is 0.03 mg/L Cl<sub>2</sub>. For more information on derivation and use of Hach's estimated detection limit, see *Section 1*.

## Interferences

Interfering Substance	Interference Level and Treatment
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 <i>Section 1, Correcting for Volume Additions</i> in the <i>DR/800 Series Procedures Manual</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 <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 <sub>3</sub>
Iodine	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>

## CHLORINE, FREE continued

Interfering Substance	Interference Level and Treatment																									
Monochloramine	<p>For conventional free chlorine disinfection (beyond the breakpoint), typical monochloramine concentrations are very low. If monochloramine is present in the sample, its interference in the free chlorine test depends on the sample temperature, relative amount of monochloramine to free chlorine, and the time required to do the analysis. Typical interference level of monochloramine in the free chlorine test are listed below (as mg/L Cl<sub>2</sub>).</p> <table border="1" data-bbox="548 401 1091 552"> <thead> <tr> <th data-bbox="553 401 673 461">NH<sub>2</sub>Cl as Cl<sub>2</sub></th> <th colspan="4" data-bbox="763 401 1009 430">Sample Temp. °C (°F)</th> </tr> <tr> <th data-bbox="682 430 673 461"></th> <th data-bbox="682 430 767 461">5 (40)</th> <th data-bbox="767 430 852 461">10 (50)</th> <th data-bbox="852 430 936 461">20 (68)</th> <th data-bbox="936 430 1021 461">30 (83)</th> </tr> </thead> <tbody> <tr> <td data-bbox="553 461 673 491">1.2 mg/L</td> <td data-bbox="682 461 767 491">+0.15</td> <td data-bbox="767 461 852 491">+0.19</td> <td data-bbox="852 461 936 491">+0.30</td> <td data-bbox="936 461 1021 491">+0.29</td> </tr> <tr> <td data-bbox="553 491 673 520">2.5 mg/L</td> <td data-bbox="682 491 767 520">0.35</td> <td data-bbox="767 491 852 520">0.38</td> <td data-bbox="852 491 936 520">0.55</td> <td data-bbox="936 491 1021 520">0.61</td> </tr> <tr> <td data-bbox="553 520 673 550">3.5 mg/L</td> <td data-bbox="682 520 767 550">0.38</td> <td data-bbox="767 520 852 550">0.56</td> <td data-bbox="852 520 936 550">0.69</td> <td data-bbox="936 520 1021 550">0.73</td> </tr> </tbody> </table>	NH <sub>2</sub> Cl as Cl <sub>2</sub>	Sample Temp. °C (°F)					5 (40)	10 (50)	20 (68)	30 (83)	1.2 mg/L	+0.15	+0.19	+0.30	+0.29	2.5 mg/L	0.35	0.38	0.55	0.61	3.5 mg/L	0.38	0.56	0.69	0.73
NH <sub>2</sub> Cl as Cl <sub>2</sub>	Sample Temp. °C (°F)																									
	5 (40)	10 (50)	20 (68)	30 (83)																						
1.2 mg/L	+0.15	+0.19	+0.30	+0.29																						
2.5 mg/L	0.35	0.38	0.55	0.61																						
3.5 mg/L	0.38	0.56	0.69	0.73																						
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> .																									

### 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.

### 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

Description	Quantity Required		Unit	Cat. No.
	Per Test			
Test 'N Tube DPD Free Chlorine Reagent .....	1 vial .....	50/pkg.....	21055-45	
Test 'N Tube Vials .....	1 vial .....	6/pkg.....	22758-06	

## REQUIRED APPARATUS

Caps, white.....	1 cap.....	6/pkg.....	22411-06
COD/TNT Adapter .....	1 .....	each.....	48464-00

## OPTIONAL REAGENTS

Chlorine Standard Solution, PourRite ampule, 50-75 mg/L, 2 mL .....	20/pkg.....	14268-20
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

## OPTIONAL APPARATUS

Beaker, 50 mL.....	each.....	500-41H
pH Meter, <i>sensio</i> <sup>TM</sup> 1, portable, with electrode .....	each.....	51700-10
pH Paper, pH 1 to 11 pH.....	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
Test Tube Rack .....	each.....	18641-00

---

\* Marked Dropper Bottle - contact Hach for larger sizes.