



### Method 10102

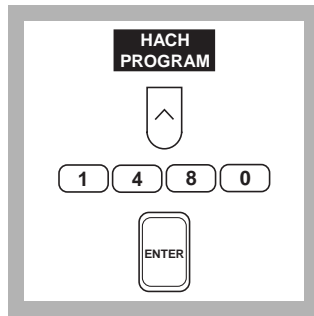
DPD Method\*

### Test 'N Tube™ Vials

(0 to 5.00 mg/L)

**Scope and Application:** For testing higher levels of free chlorine (hypochlorous acid and hypochlorite ion) in drinking water, cooling water, and industrial process waters. The estimated detection limit for program number 1480 is 0.04 mg/L Cl<sub>2</sub>.

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



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

Select the stored program number for Test 'N Tube free chlorine (Cl<sub>2</sub>) by pressing **1480** with the numeric keys.

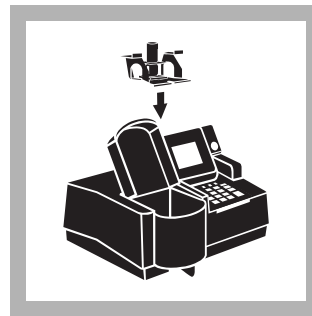
Press: **ENTER**

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

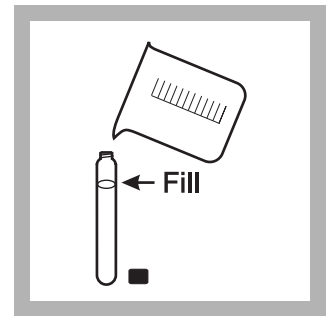


**2.** The display will show:  
**HACH PROGRAM: 1480  
Chlorine, TNT**

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

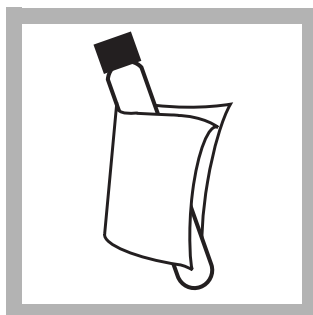


**3.** Insert the COD adapter into the sample module by sliding it under the thumbscrew and into the alignment grooves. Fasten with the thumbscrew.



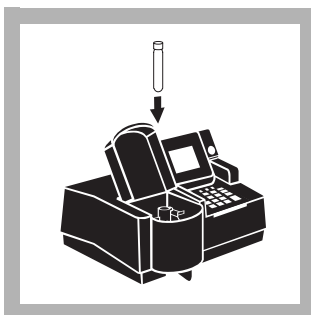
**4.** Fill an empty Test 'N Tube (TNT) vial with sample (the blank).

**Note:** Fill to the top of the label.

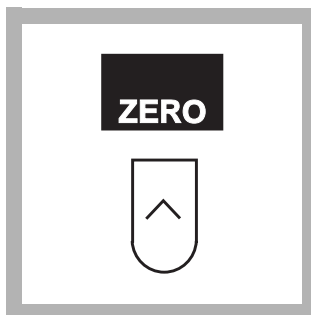


**5.** Clean the outside of the sample blank vial with a towel.

**Note:** Wiping with a damp towel followed by a dry one will remove fingerprints and other marks.



**6.** Place the blank into the adapter with the Hach logo facing the front of the instrument. Close the light shield.

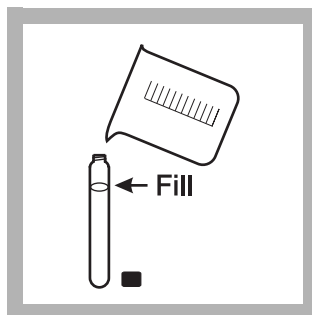


**7.** Press the soft key under **ZERO**.

The display will show:

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

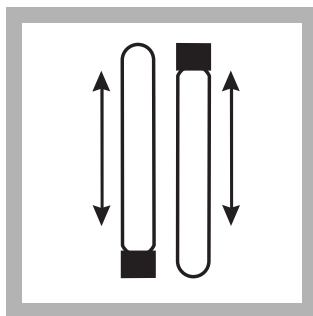
**Note:** For alternate concentration units, press the soft key under **OPTIONS**. Then press the soft key under **UNITS** to scroll through the available options. Press **ENTER** to return to the read screen.



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

**Note:** Fill to the top of the label.

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



**9.** Cap and invert at least 10 times to dissolve the powder (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.



**10.** Within 30 seconds after mixing, wipe the vial containing the prepared sample.



**11.** Place the sample in the adapter with the Hach logo facing the front of the instrument. Close the light shield.

Results in mg/L chlorine (or chosen units) will be displayed.

**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 <i>Correcting for Volume Additions</i> in the <i>DR/4000 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>Correcting for Volume Additions</i> in the <i>DR/4000 Procedures Manual</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 1 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 in the sample.</li> </ol>																								
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 levels of monochloramine in the free chlorine test are listed below (as mg/L Cl<sub>2</sub>).</p> <table border="1" style="margin-left: auto; margin-right: auto;"> <thead> <tr> <th rowspan="2">NH<sub>2</sub>Cl (as Cl<sub>2</sub>)</th> <th colspan="4">Sample Temp. °C (°F)</th> </tr> <tr> <th>5 (40)</th> <th>10 (50)</th> <th>20 (68)</th> <th>30 (83)</th> </tr> </thead> <tbody> <tr> <td>1.2 mg/L</td> <td>+0.15</td> <td>+0.19</td> <td>+0.30</td> <td>+0.29</td> </tr> <tr> <td>2.5 mg/L</td> <td>0.35</td> <td>0.38</td> <td>0.55</td> <td>0.61</td> </tr> <tr> <td>3.5 mg/L</td> <td>0.38</td> <td>0.56</td> <td>0.69</td> <td>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
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Ozone, O <sub>3</sub>	Interferes at all levels																								
Peroxides	May interfere																								
Extreme sample pH	Adjust to pH 6-7. See <i>pH Interferences</i> in the <i>DR/4000 Procedures Manual</i> .																								
Highly Buffered Samples	Adjust to pH 6-7. See <i>pH Interferences</i> in the <i>DR/4000 Procedures Manual</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 containers for free and total chlorine determinations.

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 chlorine analysis immediately.

## Accuracy Check

### Standard Additions Method

- a. Leave the unspiked sample in the cell 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 HR Chlorine PourRite® Ampules. 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 HR Chlorine PourRite Ampule Standard, 50-75 mg/L Cl<sub>2</sub>.
- f. Use the TenSette® Pipet to add 0.1 mL to a 10-mL sample. Mix thoroughly.
- g. Analyze the standard addition sample as described above. Accept the standard addition readings by pressing the soft key under **READ** each time. Each addition should reflect approximately 100% recovery.
- h. See *Standard Additions* in the *DR/4000 Procedures Manual* for more information.

## Method Performance

### Precision

at mg/L Cl <sub>2</sub>	95% Confidence Limits
0.10	±0.01 mg/L
2.50	±0.01 mg/L
3.40	±0.01 mg/L

For more information on determining precision data and method detection limits, refer to *Section 1.5 of the DR/4000 Procedures Manual*.

### Estimated Detection Limit

The estimated detection limit for program 1480 is 0.04 mg/L Cl<sub>2</sub>. For more information on derivation and use of Hach's estimated detection limit, see *Section 1.5.2 of the DR/4000 Procedures Manual*. To determine a method detection limit (MDL) as defined by the 40 CFR part 136, Appendix B, see *Section 1.5.1 of the DR/4000 Procedures Manual*.

### Sensitivity

Portion of Curve	ΔAbs	ΔConcentration
0.10	0.010	0.032 mg/L
2.50	0.010	0.035 mg/L
3.40	0.010	0.036 mg/L

See *Section 1.5.3 Sensitivity Explained* in the *DR/4000 Procedures Manual* 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.

## 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 of the DR/4000 Procedures Manual*.

## 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 of the DR/4000 Procedures Manual* for further information on proper disposal of these materials.

# CHLORINE, Free, continued

## REQUIRED REAGENTS AND STANDARDS

Description	Quantity Required per test	Unit	Cat. No.
Test 'N Tube DPD Free Chlorine Reagent.....	1 vial.....	25/pkg.....	21055-45
Test 'N Tube Vials.....	1 vial.....	25/pkg.....	25831-25

## REQUIRED EQUIPMENT AND SUPPLIES

COD/TNT Vial Adapter, DR/4000 .....	1 .....	each.....	48189-00
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## OPTIONAL REAGENTS AND STANDARDS

Chlorine Standard Solution, 2-mL PourRite Ampule, 50-75mg/L .....	20/pkg.....	14268-20
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
Water, deionized .....	4 liters .....	272-56

## OPTIONAL EQUIPMENT AND SUPPLIES

Ampule Breaker Kit .....	each.....	21968-00
Beaker, 50-mL.....	each.....	500-41
pH Indicator Paper, 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
Test Tube Rack .....	each.....	18641-00

\* Contact Hach for larger sizes.



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