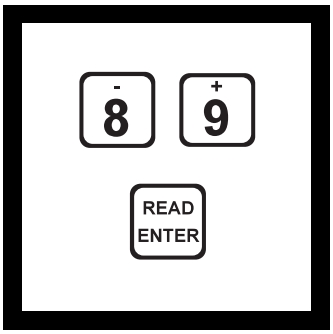
# ANALYTICAL PROCEDURES
## For DR/2000 and DR/3000 Instruments

**Method 10102**

## CHLORINE, FREE, Test 'N Tube™ (0.00-5.00 mg/L as $Cl_2$)
**DPD Method***

***Scope and Application:*** *For water, wastewater, and seawater.*




**1.** Enter the stored program for Test 'N Tube Free Chlorine ($Cl_2$).

Press: **8 9 READ/ENTER**

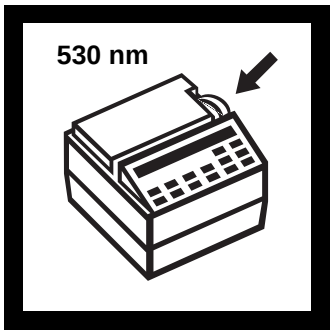
The display will show:

**Dial nm to 530**

***Note:*** *DR/2000s with software version 3.0 and greater will not display "Dial nm to" message if the wavelength is already set correctly. The display will show the message in Step 3. Proceed with Step 4.*

***Note:*** *For DR/2000s without this stored program, see Instrument Setup following these steps.*

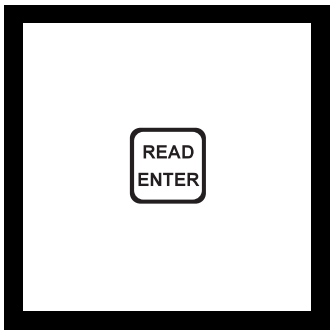
***Note:*** *For DR/3000s, make the following keystrokes:*
*Press:* **MANUAL PROGRAM**
*Press:* **2.98 CONC FACTOR**
*Press:* **ZERO**
*Press:* **2 CONC**




**2.** Rotate the wavelength dial until the display shows:

**530 nm**

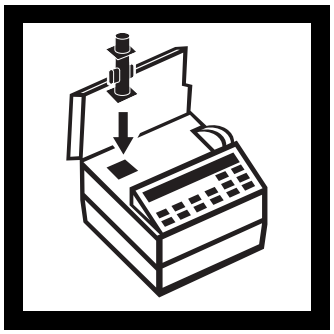
***Note:*** *For DR/3000s, set the wavelength to 530 nm and press* **CLEAR**.




**3.** Press: **READ/ENTER**

The display will show:

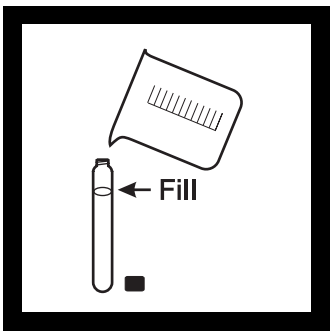
**mg/l $Cl_2$ TNT**



**4.** Place the COD Vial Adapter into the cell holder with the marker to the right.

***Note:*** *For the DR/3000, place the COD/TNT Vial Adapter into the cell holder with the groove in the adapter facing the front of the instrument.*

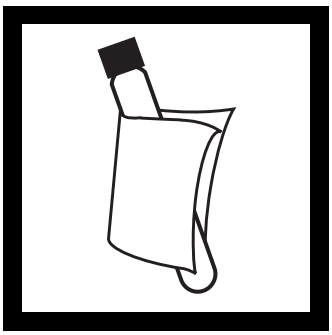
* Adapted from *Standard Methods for the Examination of Water and Wastewater.*




**5.** Fill an empty Test 'N Tube vial with sample. This is the sample blank.

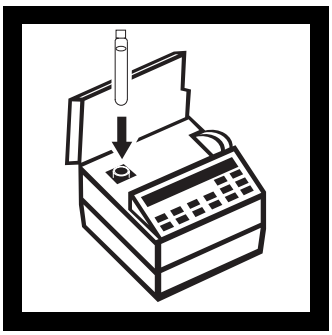
***Note:*** *Fill to the top of the Hach logo "oval" mark.*

***Note:*** *Analyze samples immediately after collection. See Sampling and Storage following these steps.*

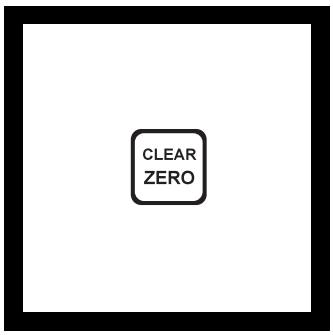


**6.** Clean the outside of the Test 'N Tube vial with a towel.

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



**7.** Place the sample blank into the vial adapter with the Hach logo facing the front of the instrument. Place the cover on the adapter.




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

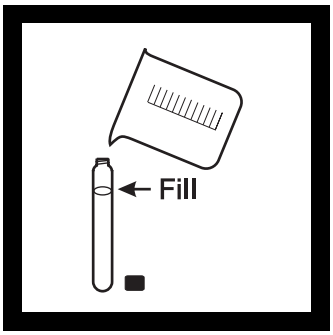
The display will show:

**WAIT**

then:

**0.00 mg/l $Cl_2$ TNT**

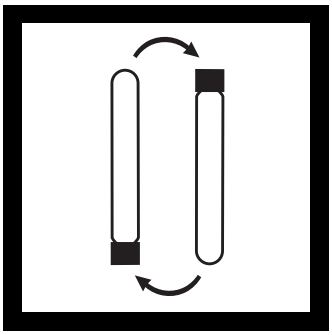
***Note:*** *For the DR/3000, press* **ZERO** *then* **CONC**.




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

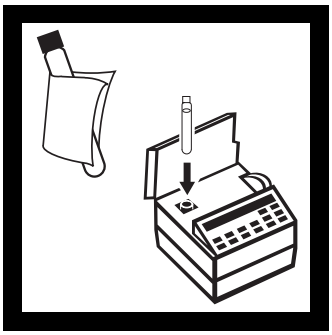
***Note:*** *Fill to the top of the Hach logo "oval" mark.*

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

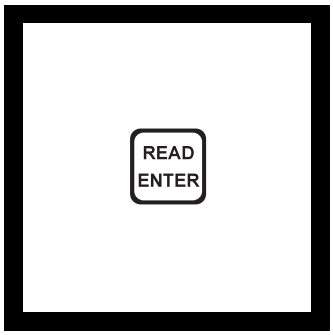


**10.** Cap and invert at least 10 times to dissolve the powder (the prepared sample).

***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.*



**11.** Within 30 seconds after mixing, wipe the vial containing the prepared sample. Place it in the adapter with the Hach logo facing the front of the instrument. Place the cover on the adapter.




**12.** Press: **READ/ENTER**

The display will show:

**WAIT**

then the results in mg/L chlorine will be displayed.

***Note:*** *In the Constant-On mode or using the DR/3000, pressing* **READ/ENTER** *is not required. When the display stabilizes, read the result.*

## INSTRUMENT SETUP

**DR/2000 with software version 3.0 and higher**

**1.** Turn the instrument on. Press **SHIFT CONFIG** to enter the configuration mode. The display will show:

**MOMENTARY or CONSTANT ON**

**2.** Press the **UP ARROW** key twice to select **HACH UPDATE**. Press **READ/ENTER**. The display will show:

**ENTER #:**

**3.** Press: 


The display will show:

**P89 ENTER nm**

***Note:*** *If you make an error, press* **SHIFT CLEAR** *and re-enter the number. When the number is correct, press* **READ/ENTER.**

**4.** Press: 


The display will show:

**P89 Decimal? 00.00**

**5.** The decimal point is correctly positioned. Press: **READ/ENTER**. The display will show:

**P89 UNITS?**

**6.** Use the arrow keys to select the appropriate unit of measure. Press the **DOWN ARROW** key twice. The display will show:

**P89 mg/l**

**7.** Press **READ/ENTER** when the correct unit of measure is displayed. This display will show:

**P89 mg/l _**

**8.** Construct the display to read the correct symbol. The symbol must be entered exactly as shown including spaces between characters:

**$Cl_2$ TNT**

To enter the display symbol, press the following number sequences. Press **ENTER** after each number sequence to place the character. Press **ENTER** again to accept the number and move to the next position.

To enter "C" press **67 ENTER ENTER**

To enter "l" press **108 ENTER ENTER**

To enter "2" press **18 ENTER ENTER**

To enter " " press **32 ENTER ENTER**

To enter "T" press **84 ENTER ENTER**

To enter "N" press **78 ENTER ENTER**

To enter "T" press **84 ENTER ENTER**

Press **ENTER** again to conclude the symbol entry.

Alternately, you can scroll to each of the characters with the arrow keys and use the following procedure:

**a)** Select letters and numbers by scrolling to the correct character with the up and down arrow keys. Press **ENTER** to accept each character.

**b)** To make a letter upper case, press the **SHIFT** key.

**c)** Make the number 2 a subscript by pressing **SHIFT** until the symbol is correct.

**d)** The space is the character displayed after one press of the **DOWN ARROW**.

**e)** Make sure to enter the display line exactly as shown, including all spaces. Do not enter trailing spaces.

**f)** Accept the last character of the symbol by pressing **READ/ENTER**. Press **READ/ENTER** again to end display entry mode.

**9.** When the instrument is out of symbol entry mode, the display will read:

**P89 TIMER**

**10.** This method has one timed step, so press **SHIFT TIMER**. The display will show:

**MM:SS TIME 1?**

**11.** Enter a timer value of 3 minutes.

Press: 


**12.** Press **READ/ENTER** to accept the timer value. The display will show:

**MM:SS TIME 2?**

**13.** Press **READ/ENTER** to complete the timer entry. The display will show:

**#0 STANDARD**

**14.** Press **READ/ENTER** to display the zero data pair. The display will show:

**0.000 Abs 00.00 mg/l**

**15.** Press **READ/ENTER**. The display will show:

**#1 STANDARD**

**16.** Press **READ/ENTER**. The display will prompt for entry of the first concentration point:

**#1 00.00. mg/l**

**17.** Enter concentration point #1 by pressing **0 0 3 0** so that the display shows:

**# 1 00.30 mg/l**

**18.** Press **READ/ENTER**. The display will prompt for entry of the first absorbance point:

**# 1 0.000 Abs**

**19.** Enter the absorbance point #1 by pressing **0 1 0 0**. The display will show:

**# 1 0.100 Abs**

**20.** Press **READ/ENTER**. The display will show the first data pair:

**0.100 Abs 00.30 mg/l**

**21.** Press **READ/ENTER** to accept the first data pair. The display will show:

**#2 STANDARD**

**22.** Following Steps 16-21 above, enter the remaining data pair values from the table below, beginning with Standard #2.

| Standard | Concentration (mg/L) | Absorbance |
|---|---|---|
| # 0 | 0.00 | 0.000 |
| # 1 | 0.30 | 0.100 |
| # 2 | 0.61 | 0.200 |
| # 3 | 0.92 | 0.300 |
| # 4 | 1.23 | 0.400 |
| # 5 | 1.55 | 0.500 |
| # 6 | 1.88 | 0.600 |
| # 7 | 2.21 | 0.700 |
| # 8 | 2.54 | 0.800 |
| # 9 | 2.88 | 0.900 |
| # 10 | 3.23 | 1.000 |
| # 11 | 3.58 | 1.100 |
| # 12 | 3.93 | 1.200 |
| # 13 | 4.29 | 1.300 |
| # 14 | 4.65 | 1.400 |
| # 15 | 5.02 | 1.500 |

**23.** When the last data pair is entered, the display will show:

**#:**

**24.** Enter the validation number **1 7 1 5 5**. The display will show:

**#: 17155**

**25.** Press **READ/ENTER**. The display will show:

**COMPLETED**

then: **P89 mg/l $Cl_2$ TNT**

***Note:*** *If the display shows* **INCORRECT #**, *then prompts for the validation number, a mistake may have been made during data entry. Make sure the validation number is correct. If so, the error occurred during some other portion of the method entry. Press* **METH** *and respond to the* **ABORT?** *message by pressing* **READ/ENTER**, *then re-enter the method.*

The instrument is now ready for use with program number 89.

## 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 l 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. Use separate, dedicated sample containers for free and total chlorine testing.

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)** 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 10-mL sample in a beaker (this is the spiked sample). Swirl to mix.

**c)** Analyze the spiked sample according to the procedure.

**d)** Calculate the concentration of mg/L chlorine added to the sample:

$$\text{mg/L chlorine added} = \frac{0.1\ (\text{vol. standard added}) \times \text{Certificate value (mg/L } Cl_2)}{10.1(\text{sample + standard volume})}$$

**e)** The spiked sample result (step c) should reflect the analyzed sample result + the calculated mg/L $Cl_2$ added (step d).

**f)** If these increases do not occur, see *Standard Additions* in *Section 1* of the *DR/2000 Procedures Manual* for more information.

## METHOD PERFORMANCE

### Precision

In a single laboratory, using a standard solution of 2.80 mg/L chlorine and two representative lots of reagents with the DR/2000, a single operator obtained a standard deviation of ±0.02 mg/L chlorine.

In a single laboratory, using a standard solution of 2.66 mg/L chlorine and two representative lots of reagents with the DR/3000, a single operator obtained a standard deviation of ±0.03 mg/L chlorine.

### Estimated Detection Limit

The estimated detection limit for method 10102 is 0.07 mg/L for the DR/2000 Spectrophotometer and 0.09 mg/L for the DR/3000 Spectrophotometer.

## 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 *Correcting for Volume Additions* in *Section 1* of the *DR/2000 Procedures Manual*). |
| 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 *Correcting for Volume Additions* in *Section 1* of the *DR/2000 Procedures Manual*). |
| 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 ($Cr^{6+}$) | **1.** Adjust sample pH to 6-7.<br>**2.** Add 3 drops potassium iodide (30 g/L) to a 25-mL sample.<br>**3.** Mix and wait one minute.<br>**4.** Add 3 drops sodium arsenite (5 g/L) and mix.<br>**5.** Analyze 10 mL of the treated sample as described in the procedure.<br>**6.** Subtract the result from this test from the original analysis to obtain the correct chlorine concentration. |
| Monochloramine | 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.<br>Typical interference levels of monochloramine in the free chlorine test are listed below (as mg/L $Cl_2$). |
| Ozone | Interferes at all levels |
| Peroxides | May interfere |
| Extreme sample pH and highly buffered samples | Adjust to pH 6-7. See *Interferences in Section 1* of the *DR/2000 Procedures Manual*. |

| $NH_2Cl$ (as $Cl_2$) | 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 |

## 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.

## 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* of the *DR/2000 Procedures Manual* for more information on proper disposal of these materials.

## REQUIRED REAGENTS

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

## REQUIRED APPARATUS

| | | | |
|---|---|---|---|
| COD/TNT Vial Adapter | 1 | each | 44799-00 |

## OPTIONAL REAGENTS

| | | | |
|---|---|---|---|
| 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 APPARATUS

| | | | |
|---|---|---|---|
| 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

**HACH** COMPANY
WORLD HEADQUARTERS
P.O. Box 389
Loveland, Colorado 80539-0389
Telephone: (970) 669-3050
FAX: (970) 669-2932

**HACH** EUROPE
Chaussée de Namur, 1
B-5150 Floriffoux (Namur), Belgium
Telephone: (32)(81) 44.71.71
FAX: (32)(81) 44.13.00

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