



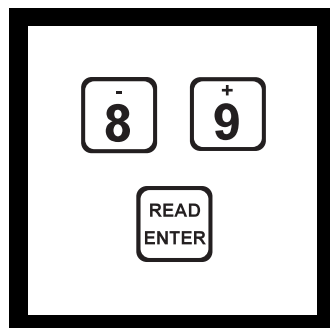
ANALYTICAL PROCEDURES

For DR/2000 and DR/3000 Instruments

Method 10101

CHLORINE, TOTAL, Test 'N Tube™ (0.00-5.00 mg/L Cl₂) **DPD Method***

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



1. Enter the stored program for Test 'N Tube Total Chlorine (Cl₂).

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 following these steps.

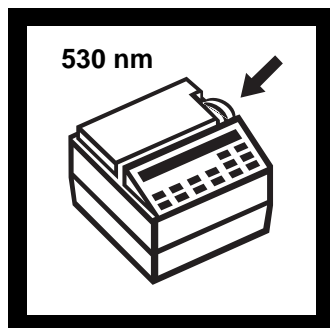
Note: For DR/3000s, make the following keystrokes:

Press: **MANUAL PROGRAM**

Press: **2.98 CONC FACTOR**

Press: **ZERO**

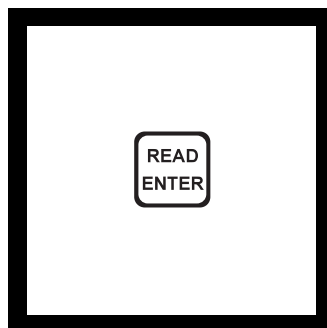
Press: **2 CONC**



2. Rotate the wavelength dial until the display shows:

530 nm

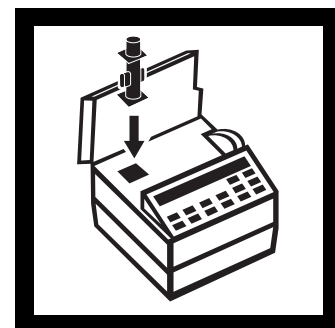
Note: For DR/3000s, set the wavelength to 530 nm and press **CLEAR**.



3. Press: **READ/ENTER**

The display will show:

mg/l Cl₂ TNT

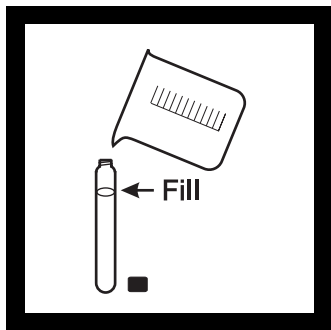


4. Place the COD/TNT Vial Adapter into the cell holder with the marker to the right.

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*.

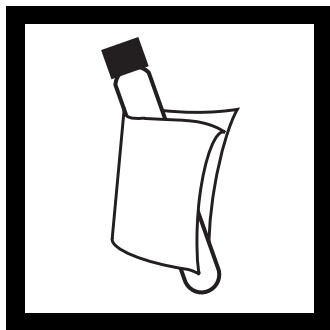
CHLORINE, TOTAL, Test 'N Tube, continued



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

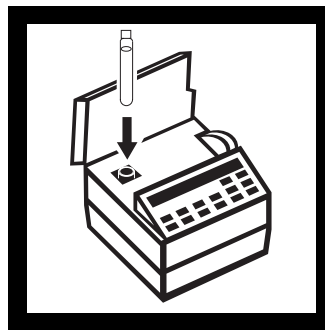
Note: Fill to the top of the Hach logo "oval" mark.

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

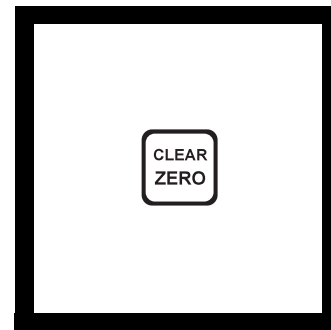


6. Wipe the outside of the Test 'N Tube vial with a towel.

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**

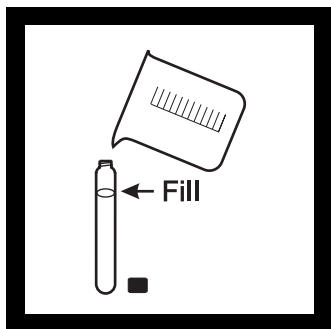
The display will show:

WAIT

then:

0.00 mg/l Cl₂ TNT

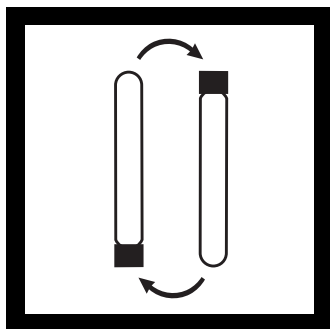
Note: For the DR/3000, press **ZERO** then **CONC**.



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

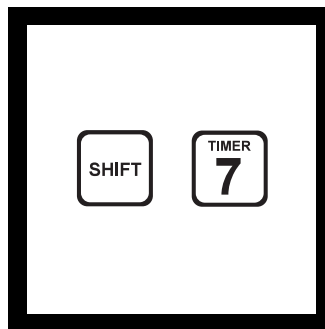
Note: Fill to the top of the Hach logo "oval" mark.

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



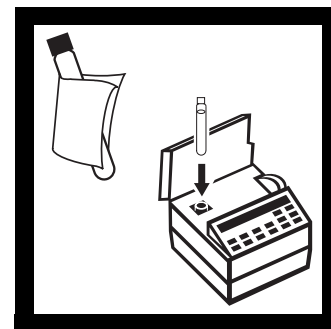
10. Cap and invert at least 10 times to dissolve the powder (the prepared sample).

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.

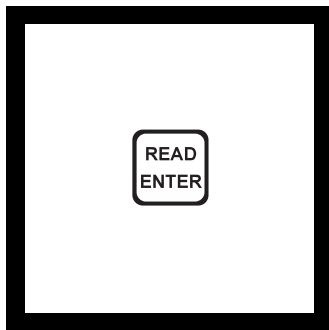


11. Press: **SHIFT TIMER**

A three-minute reaction period will begin.



12. When the timer beeps, 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.



13. 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

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

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

CHLORINE, TOTAL, Test 'N Tube, continued

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:

Cl₂ 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:

- Select letters and numbers by scrolling to the correct character with the up and down arrow keys. Press **ENTER** to accept each character.
 - To make a letter upper case, press the **SHIFT** key.
 - Make the number 2 a subscript by pressing **SHIFT** until the symbol is correct.
 - The space is the character displayed after one press of the **DOWN ARROW**.
 - Make sure to enter the display line exactly as shown, including all spaces. Do not enter trailing spaces.
 - 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?**

CHLORINE, TOTAL, Test 'N Tube, continued

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

CHLORINE, TOTAL, Test 'N Tube, continued

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 Cl₂ 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 and combined chlorine are strong oxidizing agents and are unstable in natural waters. They react rapidly with various inorganic compounds and more slowly oxidize 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.

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. Cap the 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:
$$\text{mg/L chlorine added} = \frac{0.1 (\text{vol. standard added}) \times \text{Certificate value (mg/L Cl}_2\text{)}}{10.1 (\text{sample} + \text{standard volume})}$$
- e) The spiked sample result (step c) should reflect the analyzed sample result + the calculated mg/L Cl₂ 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.

CHLORINE, TOTAL, Test 'N Tube, continued

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 10101 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 <i>Correcting for Volume Additions</i> in Section 1 of the <i>DR/2000 Procedures Manual</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>Correcting for Volume Additions</i> in Section 1 of the <i>DR/2000 Procedures Manual</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.
Ozone	Interferes at all levels
Peroxides	May interfere
Extreme sample pH and highly buffered samples	Adjust to pH 6-7. See <i>Interferences</i> in Section 1 of the <i>DR/2000 Procedures Manual</i> .

SUMMARY OF METHOD

Chlorine can be present in water as free available chlorine and as combined available chlorine. Both forms can exist in the same water and be determined together as the total available chlorine. Free chlorine is present as hypochlorous acid and/or hypochlorite ion. Combined chlorine exists as monochloramine, dichloramine, nitrogen trichloride and other chloro derivatives.

CHLORINE, TOTAL, Test 'N Tube, continued

The combined chlorine oxidizes iodide in the reagent to iodine. The iodine reacts with DPD (N, N-diethyl-p-phenylenediamine) along with free chlorine present in the sample to form a red color which is proportional to the total chlorine concentration. To determine the concentration of combined chlorine, run free chlorine and total chlorine tests. Subtract the results of the free chlorine test from the results of the total chlorine test to obtain combined chlorine.

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 Total Chlorine Reagent	1 vial.....	50/pkg	21056-45

REQUIRED APPARATUS

COD/TNT Vial Adapter.....	1	each	44799-00
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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, pH 1 to 11	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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