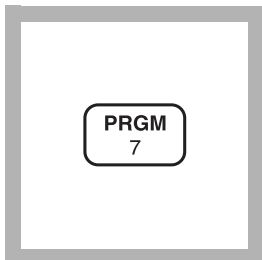


DPD Method

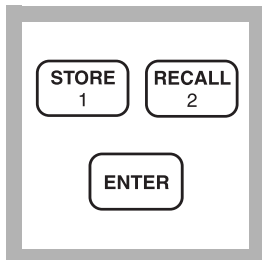
USEPA accepted for reporting drinking water analyses*
For testing higher levels of free chlorine (hypochlorous acid and hypochlorite) in drinking water, cooling water, and industrial process waters



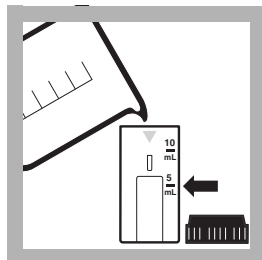
1. Enter the user program number for Chlorine, UHR.

Press: **PRGM**
 The display will show:
PRGM?

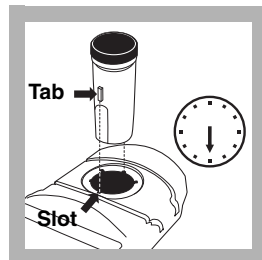
Note: If the chlorine is typically less than 2.0 mg/L, use method 8021, program number 9.



2. Press:
12 ENTER
 The display will show
mg/L Cl₂
 then: **ZERO**



3. Fill the 10-mL/1-cm cell to the 5-mL line with sample.

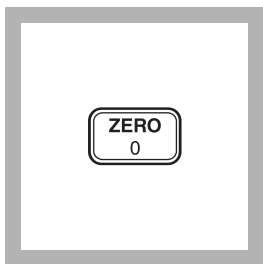


4. Place the cell into the instrument. Cover the sample cell tightly with the instrument cap.

Note: Place the cell into the cell holder as illustrated. The sample cell tab should be at the 6 o'clock position and completely seated in the cell holder slot.

* Procedure is equivalent to USEPA method 330.5 for wastewater and Standard Method 4500-C1-G for drinking water.

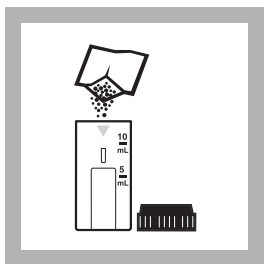
CHLORINE, FREE, Ultra-high Range, continued



5. Press: ZERO

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

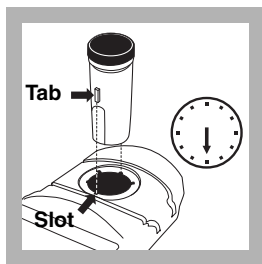
0.0 mg/L Cl₂



6. Remove the sample cell from the cell holder and add the contents of one 25-mL DPD Free Chlorine Reagent pillow to the sample. Cap and shake the sample cell about 20 seconds to dissolve.

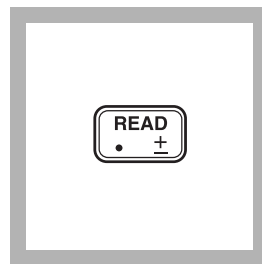
Proceed **immediately** to step 7.

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



7. Place the sample cell into the instrument. Cover the sample cell tightly with the instrument cap.

Note: Place the sample cell into the cell holder as illustrated. The sample cell tab should be at the 6-o'clock position and completely seated in the cell holder slot.



8. Within one minute after reagent addition, press: **READ**.

The cursor will move to the right. The result in mg/L chlorine (as Cl₂) will be displayed.

Note: See "Interferences" on page 120 for samples with high monochloramine concentrations.

Sampling and Storage

Analyze samples for chlorine immediately after collection. Free chlorine is a strong oxidizing agent and reacts rapidly with various compounds. Many factors such as sunlight, pH, temperature, and sample composition will influence decomposition of free chlorine in water.

- Avoid plastic containers which may have a large chlorine demand.
- Pretreat glass sample containers to remove chlorine demand by soaking in a dilute bleach solution (1 mL of commercial bleach to 1 liter of deionized water) for at least one 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.
- Use separate, dedicated sample cells for free and total chlorine determinations. If trace iodide from the total chlorine reagent is carried over to the free chlorine test, monochloramine could interfere.

CHLORINE, FREE, Ultra-high Range, continued

- A common error in testing for chlorine is failure to obtain a representative sample. If sampling from a tap, let the water flow for at least five minutes to ensure a representative sample. Let the sample container overflow with sample several times. Cap the container so there is no air above the sample.
- If sampling with a sample cell, rinse the cell several times with the sample, then carefully fill to the 5-mL mark. Proceed with the chlorine test immediately.

Accuracy Check

1. Fill three mixing cylinders (Cat. No. 20886-38) with 5-mL of sample.
2. Snap the neck of a HR Chlorine Ampule Standard, 50–75 mg/L Cl₂. Using the TenSette[®] Pipet, add 0.1 mL, 0.2 mL, and 0.3 mL of standard, respectively, to each cylinder and mix thoroughly.
3. Analyze each standard addition sample as described in the procedure. Record each result.
4. Calculate the concentration of mg/L chlorine added to each sample.

$$\text{mg/L chlorine added} = \frac{\text{volume of standard added} \times \text{label value of Cl}_2\text{ standard ampule}}{\text{sample volume} + \text{volume of standard added}}$$

The spiked sample results should reflect the analyzed sample result plus the calculated mg/L Cl₂ added to each sample. If these increases do not occur, see Standard Additions in Section 1 of a DR/800 Procedure Manual for more information.

CHLORINE, FREE, Ultra-high Range, continued

Method Performance

Precision

In a single laboratory, using a chlorine standard solution of 5.05 mg/L Cl₂ and representative lots of reagent, a single operator obtained a standard deviation of ± 0.05 mg/L Cl₂.

Estimated Detection Limit

The estimated detection limit for Method 10069 is 0.1 mg/L Cl₂. For more information on the estimated detection limit, see Section 1 of the DR/800 Procedure Manual.

Interferences

Interfering Substance	Interference Levels and Treatments
Acidity	Greater than 150 mg/L CaCO ₃ . May not develop full color or color may fade instantly. <ol style="list-style-type: none">1. Neutralize to pH 6–7 with 1 N Sodium Hydroxide.2. Determine amount to be added on a separate sample aliquot, then add the same amount to the sample being tested.3. Correct for volume addition.
Alkalinity	Greater than 250 mg/L CaCO ₃ . May not develop full color or color may fade instantly. <ol style="list-style-type: none">1. Neutralize to pH 6–7 with 1 N Sulfuric Acid.2. Determine amount to be added on a separate sample aliquot, then add the same amount to the sample being tested.3. Correct for volume addition.
Bromine, Br ₂	Interferes at all levels
Chlorine Dioxide, ClO ₂	Interferes at all levels
Chloramines, organic	May interfere
Iodine, I ₂	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 2 drops Potassium Iodide (30 g/L) to a 5-mL sample.3. Mix and wait 1 minute.4. Add 2 drops of Sodium Arsenite (5 g/L) and mix.5. Analyze 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.

CHLORINE, FREE, Ultra-high Range, continued

Interfering Substance	Interference Levels and Treatments																									
Monochloramine	<p>For conventional free chlorine disinfection (beyond the breakpoint), monochloramine concentrations are very low. If monochloramine is present in the sample, its interference in the free chlorine test varies with the sample temperature, the relative amount of monochloramine to free chlorine, and the time required to do the analysis. Approximate interference levels of monochloramine in the free chlorine test are listed below (as mg/L Cl₂).</p> <table border="1" data-bbox="508 357 1184 562"> <thead> <tr> <th data-bbox="508 357 642 407">NH₂Cl (as Cl₂)</th> <th colspan="4" data-bbox="642 357 1184 407">Sample Temperature °C (°F)</th> </tr> <tr> <th data-bbox="508 407 642 458"></th> <th data-bbox="642 407 776 458">5 (40)</th> <th data-bbox="776 407 911 458">10 (50)</th> <th data-bbox="911 407 1045 458">20 (68)</th> <th data-bbox="1045 407 1184 458">30(83)</th> </tr> </thead> <tbody> <tr> <td data-bbox="508 458 642 491">1.2</td> <td data-bbox="642 458 776 491">0.2</td> <td data-bbox="776 458 911 491">0.2</td> <td data-bbox="911 458 1045 491">0.3</td> <td data-bbox="1045 458 1184 491">0.3</td> </tr> <tr> <td data-bbox="508 491 642 524">2.5</td> <td data-bbox="642 491 776 524">0.4</td> <td data-bbox="776 491 911 524">0.5</td> <td data-bbox="911 491 1045 524">0.6</td> <td data-bbox="1045 491 1184 524">0.6</td> </tr> <tr> <td data-bbox="508 524 642 562">3.5</td> <td data-bbox="642 524 776 562">0.5</td> <td data-bbox="776 524 911 562">0.6</td> <td data-bbox="911 524 1045 562">0.7</td> <td data-bbox="1045 524 1184 562">0.8</td> </tr> </tbody> </table>	NH ₂ Cl (as Cl ₂)	Sample Temperature °C (°F)					5 (40)	10 (50)	20 (68)	30(83)	1.2	0.2	0.2	0.3	0.3	2.5	0.4	0.5	0.6	0.6	3.5	0.5	0.6	0.7	0.8
NH ₂ Cl (as Cl ₂)	Sample Temperature °C (°F)																									
	5 (40)	10 (50)	20 (68)	30(83)																						
1.2	0.2	0.2	0.3	0.3																						
2.5	0.4	0.5	0.6	0.6																						
3.5	0.5	0.6	0.7	0.8																						
Ozone	Interferes at all levels																									
Peroxides	May interfere																									
Extreme sample pH or highly buffered samples	Adjust the sample pH to 6–7 with Sulfuric Acid or Sodium Hydroxide																									

Summary of Method

The range of analysis using the DPD method for free chlorine can be extended by adding more indicator in proportion to sample volume. Thus, a larger fill powder pillow of DPD Free Chlorine Reagent is added to a 5-mL sample portion.

Chlorine in the sample as hypochlorous acid or hypochlorite ion (free chlorine or free available chlorine) reacts immediately with DPD (N,N-diethyl-p-phenylenediamine) indicator to form a pink color which is proportional in intensity to the chlorine concentration.

Instrument Setup

The following procedure will add this method as a new Hach program to a DR/800 instrument.

1. Turn on the instrument by pressing the **ON** key.
2. Press the **SETUP** key.
3. Press the **DOWN** arrow key until the prompt line shows **USER**.
4. Press the **ENTER** key.
5. Enter “8138”, followed by **ENTER**.

CHLORINE, FREE, Ultra-high Range, continued

6. Key the number in the “Enter” column corresponding to line number 1 on the display. Press **ENTER**. Repeat for lines 2–56 on the display.

Line Number	Enter	Line Number	Enter
1	12	29	0
2	24	30	0
3	73	31	0
4	0	32	0
5	0	33	0
6	0	34	0
7	0	35	0
8	62	36	0
9	55	37	0
10	23	38	0
11	88	39	0
12	64	40	0
13	113	41	0
14	242	42	0
15	18	43	0
16	0	44	110
17	0	45	0
18	0	46	0
19	0	47	10
20	67	48	0
21	108	49	180
22	50	50	0
23	0	51	0
24	0	52	0
25	0	53	0
26	0	54	236
27	0	55	0
28	0	56	255

CHLORINE, FREE, Ultra-high Range, continued

REQUIRED REAGENTS

Description	Quantity Required		Unit	Cat. No.
	Per Test			
DPD Free Chlorine Reagent Powder Pillows, 25-mL.....	1.....	100/pkg.....		14070-99

REQUIRED APPARATUS

Sample Cell, 10-mL/1-cm.....	1.....	2/pkg.....		48643-02
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OPTIONAL REAGENTS

Chlorine Standard Solution, 2-mL Voluette® Ampule, 50–75 mg/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 L.....		272-56

OPTIONAL APPARATUS

Ampule Breaker Kit		each.....		24846-00
Cylinder, graduated, 10-mL, mixing		each.....		20886-38
pH Meter, sens <i>ion</i> ™1, portable, with electrode		each.....		51700-10
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