



Method 10069

DPD method*

UHR (0.1–10.0 mg/L as Cl₂)

Scope and Application: For testing higher levels of free chlorine (hypochlorous acid and hypochlorite ion) in drinking water, cooling water, and industrial process waters.

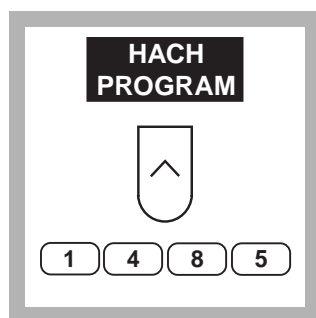
* Adapted from *Standard Methods for the Examination of Water and Wastewater*.

Tips and Techniques

- Analyze samples immediately. Do not preserve for later analysis.
- If chlorine is present, a pink color will develop after adding DPD Free Chlorine Reagent
- If the chlorine concentration is typically less than 2 mg/L, use method 8021, program number 1450.

Powder Pillow

Method 10069



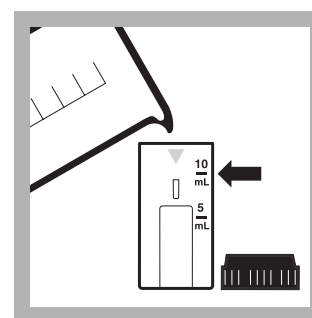
1. Press the soft key under **HACH PROGRAM**. Select the stored program number for Chlorine, HR by pressing **1485**. Use the numeric keys.



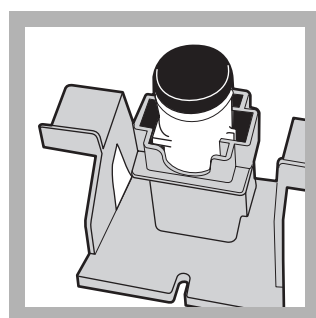
2. Press: **ENTER**. The display will show: **HACH PROGRAM 1485 Chlorine, UHR**. The wavelength (λ), **530 nm**, is automatically selected.



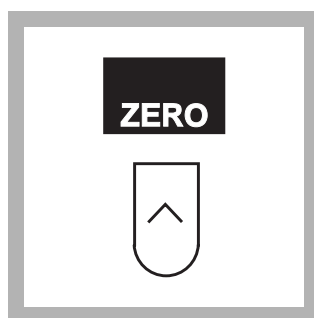
3. Insert the AccuVac[®] adapter into the sample cell module by sliding it under the thumbscrew and into the alignment grooves. Fasten with the thumbscrew.



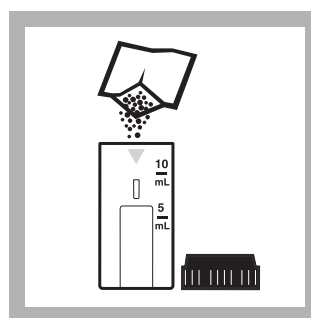
4. Fill the 10-mL/1-cm cell to the 5-mL line with sample.



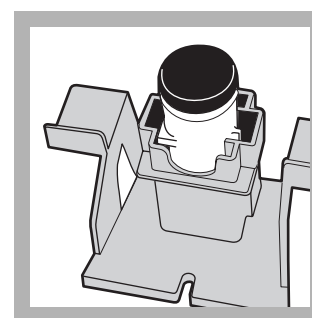
5. Place the cell into the cell holder so that the locking ridge on the cell is oriented to the left. Press the top rim of the cell on the right side to lock it in place. Close the light shield.



6. Press the soft key under **ZERO**. The display will show: **0.0 mg/L Cl₂**



7. Remove the cell from the cell holder and add the contents of one pillow of DPD Free Chlorine to the sample. Proceed immediately to step 8. Cap and shake the cell about 20 seconds to dissolve.



8. Place the cell into the cell holder so the locking ridge on the cell is oriented to the left. Press the top rim of the cell on the right side to lock it in place.



9. Close the light shield. Within 1 minute after reagent addition, read the results in mg/L chlorine (as Cl₂).

Sampling and Storage

Analyze samples for chlorine immediately after collection. free and combined chlorine are strong oxidizing agents and react 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 containers to remove chlorine demand by soaking in a dilute bleach solution (1 mL commercial bleach to 1 L 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.

Do not use the same sample cells for free and total chlorine. If trace iodide from the total chlorine reagent is carried over to the free chlorine test, monochloramine could interfere. It is best to use separate, dedicated sample cells for free and total chlorine determinations.

A common error in testing for chlorine is obtaining a representative 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 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.

Method Performance

Precision

Standard: 5.6 mg/L Cl₂

Program	95% Confidence Limits of Distribution
1485	5.5–5.7 mg/L Cl ₂

Sensitivity

Portion of Curve	Δ Abs	Δ Concentration
Entire range	0.010	0.1 mg/L Cl ₂

Accuracy Check**Standard Additions Method (Sample Spike)**

1. Leave the unspiked sample in the sample 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**.
2. Press **ENTER** to accept the default sample volume (mL), 10.
3. Locate the average chlorine concentration shown on the certificate enclosed with the LR Voluette® Ampules. When prompted for the standard concentration, use the numeric keys to enter the certificate value. Press **ENTER**.
4. Press the soft key under **ENTRY DONE**.
5. Snap the neck off of a Chlorine Voluette® Ampule Standard, 50–75 mg/L Cl₂.
6. Use the Tensette® Pipet to add 0.1 mL, 0.2 mL, and 0.3 mL of standard, respectively, to three 10-mL samples. Mix each thoroughly.
7. Analyze each standard addition sample as described above. Accept the standard additions readings by pressing the soft key under **READ** each time. Each additions should reflect approximately 100% recovery.
8. After completing the sequence, the display will show the extrapolated concentration value and the “best-fit” line through the standard additions data points, accounting for matrix interferences.
9. See Section 1.4.1 *Standard Additions* for more information.

Interferences

The following have been tested for interference and found to interfere at the indicated levels:

Table 1 Interfering Substances

Substance	Level	Correction
Acidity	Greater than 150 mg/L CaCO ₃ May not develop full color or color may fade instantly.	1 Neutralize to pH 6–7 with 1 N Sodium Hydroxide. 2 Determine the amount to be added on separate sample aliquot, then add the same amount to the sample being tested. 3 Correct for volume additions.
Alkalinity	Greater than 250 mg/L CaCO ₃ May not develop full color or color may fade instantly.	1 Neutralize to pH 6–7 with 1 N Sulfuric Acid. 2 Determine the amount to be added on separate sample aliquot, then add the same amount to the sample being tested. 3 Correct for volume additions.

Table 1 Interfering Substances (Continued)

Substance	Level	Correction
Bromine, Br ₂	Interferes at all levels	
Chlorine dioxide, ClO ₂	Interferes at all levels	
Chloramines, organic	May interfere	
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 Sodium Arsenite* (5 g/L) and mix. 5 Analyze the treated sample as described in the procedure. Subtract the result from this test from the original analysis to obtain the correct chlorine concentration.
Iodine, I ₂	Interferes at all levels	
Manganese, oxidized (Mn ⁴⁺ , Mn ⁷⁺)		<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 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.
Ozone	Interferes at all levels	
Peroxides	May interfere	
pH (extreme sample pH or highly buffered samples)		Adjust to pH 6–7 using acid (1.000 N Sulfuric Acid) or base (1.00 N Sodium Hydroxide).

* Samples treated with sodium arsenite for manganese or chromium interference will be hazardous wastes as regulated by the Federal RCRA for arsenic (D004).

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) immediately reacts with DPD (N, N-diethyl-p-phenylenediamine) indicator to form a magenta 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 (MSDS) for information specific to the reagent used.

REQUIRED REAGENTS

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

REQUIRED APPARATUS

Sample Cell, 10-mL/1-cm, with cap	1	2/pkg	48643-02
---	---	-------	----------

OPTIONAL REAGENTS

Sodium Hydroxide, 1 N	100 mL	MDB	1045-32
Sulfuric Acid, 1 N	100 mL	MDB	1270-32
Potassium Iodide, 30 g/L.....	100 mL	MDB	343-32
Sodium Arsenite, 5 g/L	100 mL		1047-32

OPTIONAL APPARATUS

Cylinder, graduated mixing		each	1896-40
TenSette Pipet, 0.1–1.0 mL		each	19700-01
Replacement Tips for 19700-01		50/pkg	21856-96

REQUIRED STANDARDS

Chlorine Standard Solution, PourRite™ Ampules, 50–75 mg/L.....		20/pkg	14268-20
--	--	--------	----------



FOR TECHNICAL ASSISTANCE, PRICE INFORMATION AND ORDERING:

In the U.S.A. – Call toll-free 800-227-4224

Outside the U.S.A. – Contact the HACH office or distributor serving you.

On the Worldwide Web – www.hach.com; E-mail – techhelp@hach.com

HACH COMPANY
WORLD HEADQUARTERS
Telephone: (970) 669-3050
FAX: (970) 669-2932