



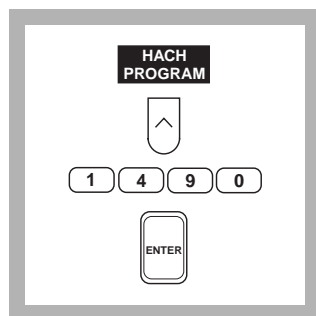
✓ Method 8370

DPD Method*

ULR (0 to 500 µg/L as Cl₂)

Scope and Application: For testing trace levels of chlorine and chloramines in clean waters relatively free of color and turbidity. USEPA accepted for reporting for drinking water analysis. The estimated detection limit for program number 1490 is 3 µg/L Cl₂.

* U.S. Patent 5,362,650



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

Select the stored program number for ultra low range (ULR) chlorine by pressing **1490** with the numeric keys.

Press: **ENTER**

Note: Samples should be analyzed immediately after collection, as chlorine is not stable in aqueous solution.

Note: See Treating Analysis Labware section for more information on cleaning labware. The Flow-Thru and Sipper Cells must be cleaned and treated for chlorine demand.

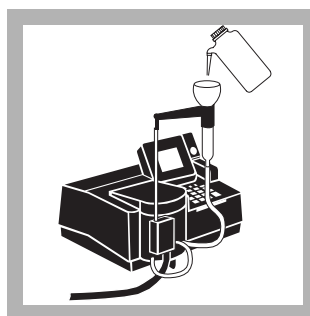
Note: The Single Cell Module cannot be used in this procedure. See the Summary of Method section.



2. The display will show: **HACH PROGRAM: 1490 Chlorine, Tot. ULR**

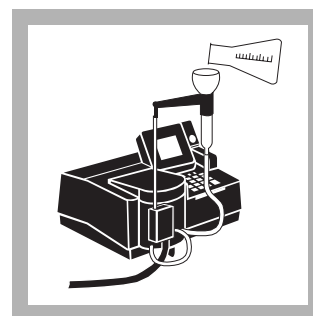
The wavelength (λ), **515 nm**, is automatically selected.

Note: A reagent blank value for a combined lot of indicator/buffer reagent solutions should be determined at least once a day. If sample color or turbidity fluctuates frequently during the day, determine a reagent blank for each sample. See Determining the Reagent Blank Value after this procedure.



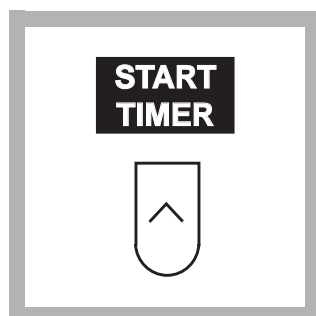
3. Install the 1-inch Flow-Thru or Sipper Cell Module in the instrument. Flush it with at least 50 mL of deionized water.

Note: See the DR/4000 Optional Modules Instrument Manual for operation of the Flow-Thru or Sipper Cell modules.



4. Pour at least 50 mL of sample into the Flow-Thru or Sipper Cell.

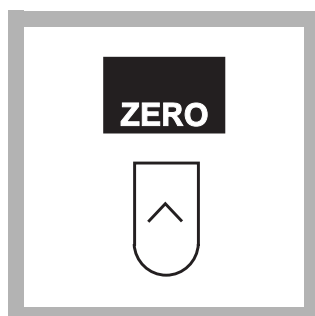
CHLORINE, Total, continued



5. After the flow stops, press the soft key under **START TIMER**.

A 3-minute reaction period will begin.

Note: Wait 3 minutes before zeroing the sample to allow any turbidity or solids in the sample to settle. This ensures a stable reading.



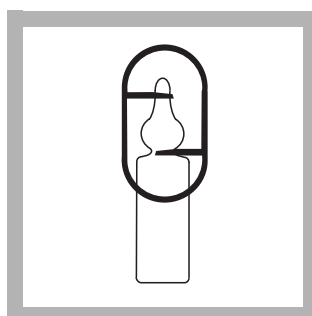
6. When the timer beeps, press the soft key under **ZERO**.

The display will show:

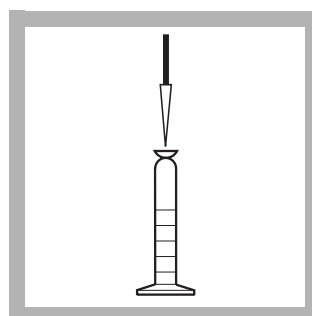
0 $\mu\text{g/L Cl}_2$

Note: If you are using a reagent blank correction, the display will show the correction.

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.



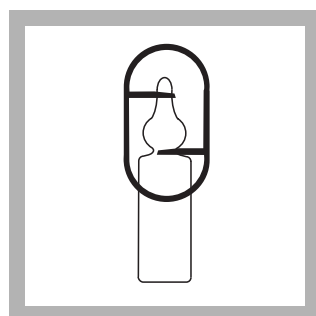
7. Break open 1 ampule of ULR Chlorine Buffer Solution.



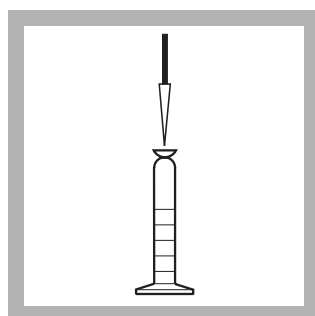
8. Using a TenSette Pipet and clean tip, transfer 1.0 mL of buffer from the ampule to a clean, treated 50-mL graduated mixing cylinder.

Note: See *Treating Analysis Labware* following these steps for cleaning glassware.

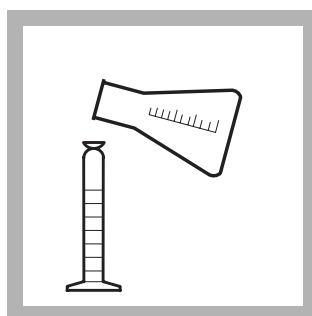
Note: The ampules contain more than 1.0 mL of solution for ease of reagent transfer. Discard any excess reagent in the ampule.



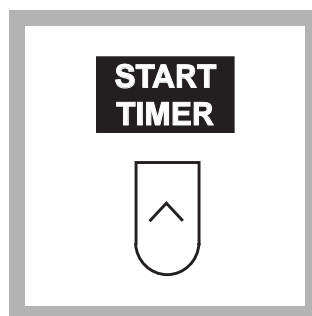
9. Break open 1 ampule of DPD Indicator Solution for Ultra Low-Range Chlorine.



10. Using a TenSette Pipet and clean tip, transfer 1.0 mL of indicator from the ampule to the graduated mixing cylinder. Swirl to mix the reagents. Proceed with Step 11 within 1 minute.

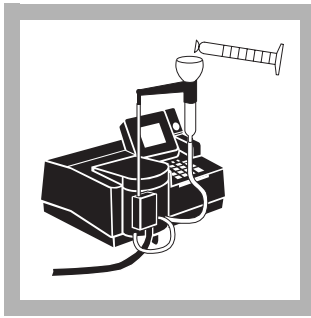


11. Avoiding extra agitation, carefully fill the cylinder to the 50-mL mark with sample. Stopper the cylinder. Gently invert it twice to mix (the prepared sample).



12. Press the soft key under **START TIMER**. A 3-minute reaction time will begin.

Note: Measure the reacted sample 3–4 minutes after mixing the sample and reagents. If less than 3 minutes elapses, reaction with chloramines may be incomplete. A reading after 4 minutes may result in higher reagent blank values.



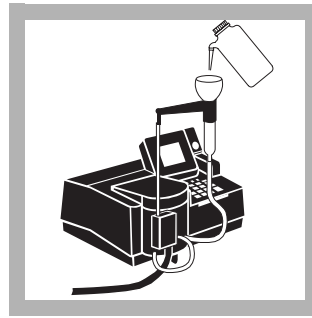
13. Introduce the contents of the graduated mixing cylinder into the Flow-Thru or Sipper Cell.



14. When the timer beeps, the result in $\mu\text{g/L}$ (or chosen units) chlorine will be displayed.

Note: If a de-chlorinating agent (e.g. sulfite or sulfur dioxide) is present, the sample result, corrected for the reagent blank, will read "0" or a slightly negative value.

Note: If a reagent blank value is entered, a correction is not necessary. If not, correct the result for the blank value (see Determining the Reagent Blank Value following these steps).

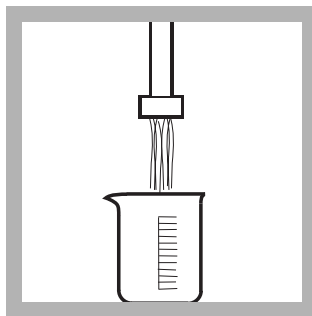


15. Flush the Flow-Thru or Sipper Cell with at least 50 mL of deionized water immediately after use.

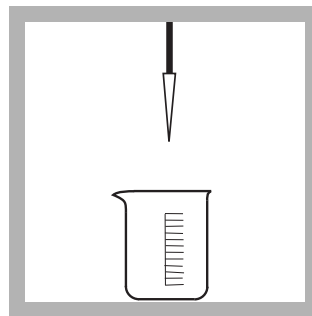
Determining the Reagent Blank Value



1. Set up the DR/4000 Spectrophotometer as described in steps 1–3 of the procedure.

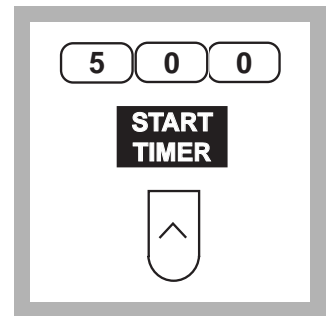


2. Collect about 100 mL of deionized or tap water in a clean 250-mL beaker.



3. Using a TenSette Pipet, add 1.0 mL of Blanking Reagent to the beaker. Swirl several times to mix.

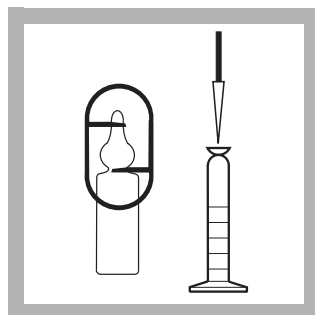
Note: The Blanking Reagent removes chlorine and chloramines from the water.



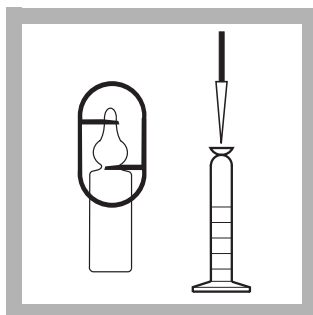
4. Press **500** followed by **START TIMER**.

A 5-minute dechlorination period will begin.

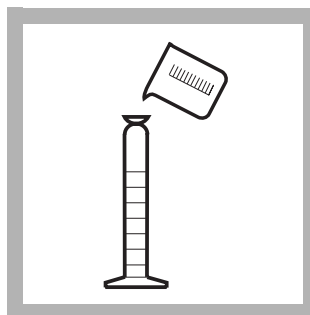
CHLORINE, Total, continued



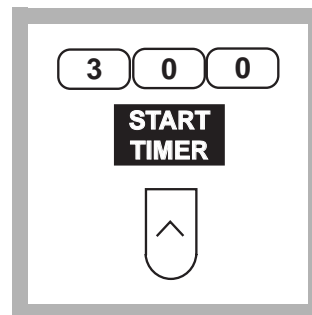
5. After the timer beeps, break open 1 ampule of ULR Chlorine Buffer Solution. Using a TenSette Pipet and clean tip, transfer 1.0 mL of buffer from the ampule to a clean 50-mL mixing graduated cylinder.



6. Break open 1 ampule of DPD Indicator Solution for Ultra Low-Range Chlorine. Using a TenSette Pipet and clean tip, transfer 1.0 mL of indicator from the ampule to the cylinder. Swirl to mix the reagents. Proceed with Step 7 within 1 minute.

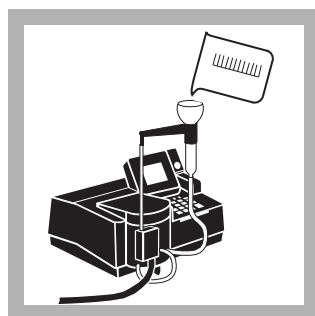


7. Fill the cylinder to the 50-mL mark with the dechlorinated water from Step 3. Cap and invert twice to mix. Save the remaining water for Step 9.

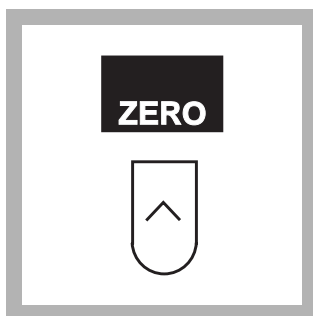


8. Press **300** followed by the soft key under **START TIMER**.

A 3-minute reaction period will begin.



9. During the reaction period flush the Flow-Thru or Sipper Cell with the remainder of the original dechlorinated water from Step 7.

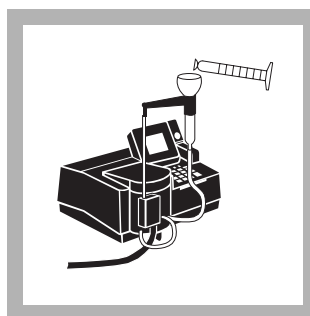


10. When the flow stops, press the soft key under **ZERO**.

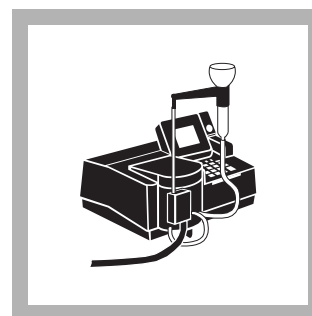
The display will show:

0 $\mu\text{g/L Cl}_2$

Note: Make sure the Blank is set to OFF under **OPTIONS, (MORE)**.



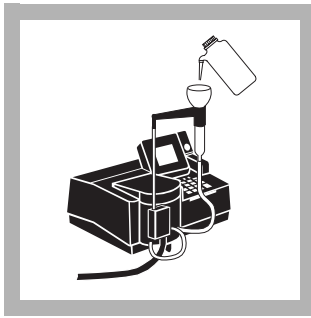
11. When the timer beeps, introduce the contents of the cylinder into the Flow-Thru Cell or Sipper Cell.



12. After the flow stops, the reagent blank value will be displayed in $\mu\text{g/L}$ (or chosen units) chlorine.

Note: Store the reagent blank value by pressing the soft keys under **OPTIONS, (MORE)**, and then **BLANK: (OFF)**. Enter the reagent blank value and press **ENTER**. Repeat daily or for each new combined lot of reagent.

Note: The reagent blank value is normally less than $5 \mu\text{g/L}$. If the value is greater than $5 \mu\text{g/L}$, an interfering substance may be present in the blanking water or the DPD Indicator may be degrading. If there is doubt about the reagents, repeat the reagent blank determination using chlorine demand-free water for the sample. Blanks up to $10 \mu\text{g/L}$ may be entered.



13. Flush the Flow-Thru or Sipper Cell with at least 50 mL of deionized water immediately after use.

Interferences

Table 1 Interfering Substances and Suggested Treatments

Interfering Substance	Interference Levels and Treatments												
Bromine, Br ₂	Interferes at all levels												
Chlorine Dioxide, ClO ₂	Interferes at all levels												
Chloramines, organic	May interfere												
Copper, Cu ²⁺	Greater than 1000 µg/L												
Iodine, I ₂	Interferes at all levels												
Iron (Fe ³⁺)	Greater than 1000 µg/L												
Manganese, Oxidized (Mn ⁴⁺ , Mn ⁷⁺) or Chromium, Oxidized (Cr ⁶⁺)	<ol style="list-style-type: none"> Adjust sample pH to 6–7. Add 6 drops potassium iodide (30-g/L) to a 50-mL sample. Mix and wait 3 minutes. Add 6 drops sodium arsenite (5-g/L) and mix. 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. 												
Nitrite, NO ₂ ⁻ (uncommon in clean waters)	<table border="1"> <thead> <tr> <th>mg/L nitrite</th> <th>Apparent µg/L chlorine</th> </tr> </thead> <tbody> <tr> <td>2.0 mg/L</td> <td>3 µg/L</td> </tr> <tr> <td>5.0 mg/L</td> <td>5 µg/L</td> </tr> <tr> <td>10.0 mg/L</td> <td>7 µg/L</td> </tr> <tr> <td>15.0 mg/L</td> <td>16 µg/L</td> </tr> <tr> <td>20.0 mg/L</td> <td>18 µg/L</td> </tr> </tbody> </table>	mg/L nitrite	Apparent µg/L chlorine	2.0 mg/L	3 µg/L	5.0 mg/L	5 µg/L	10.0 mg/L	7 µg/L	15.0 mg/L	16 µg/L	20.0 mg/L	18 µg/L
mg/L nitrite	Apparent µg/L chlorine												
2.0 mg/L	3 µg/L												
5.0 mg/L	5 µg/L												
10.0 mg/L	7 µg/L												
15.0 mg/L	16 µg/L												
20.0 mg/L	18 µg/L												
Ozone, O ₃	Interferes at all levels												
Peroxides	May interfere												
Extreme sample pH	Adjust to pH 6–7. See Section 1.3.1 <i>pH Interference</i> .												
Highly Buffered Samples	Adjust to pH 6–7. See Section 1.3.1 <i>pH Interference</i> .												

CHLORINE, Total, continued

Sample Collection, Storage and Preservation

Analyze samples for chlorine immediately after collection. Many factors, including reactant concentrations, sunlight, pH, temperature and salinity influence decomposition of 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 (0.5 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 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 containers so there is no headspace (air) above the sample. Perform the chlorine analysis immediately.

Treating Analysis Labware

Glassware used in this test must be chlorine demand-free. Treat all glassware with a dilute solution of chlorine bleach prepared by adding 0.5 mL of commercial bleach to 1 liter of water. Soak glassware in this solution at least one hour. After soaking, rinse the glassware with copious amounts of deionized water and allow to dry before use.

Treat the Flow-Thru or Sipper Cell similarly with dilute bleach and let stand for several minutes and then rinse several times with deionized water.

Cleaning the Flow-Thru Cell

The Flow-Thru or Sipper Cell may accumulate a buildup of colored reaction products, especially if the reacted solutions are allowed to remain in the cell for long periods after measurement. Remove the buildup by rinsing the cell with 5.25 N sulfuric acid followed by several rinsings with deionized water.

Accuracy Check

Standard Additions Method

- a. Leave the unspiked sample in the sample compartment. Verify that the units displayed are in $\mu\text{g/L}$. 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), 50.
- c. Locate the average chlorine concentration shown on the certificate enclosed with the LR Voluettes. Multiply the mg/L Voluette concentration by 1000 to convert to $\mu\text{g/L}$. When prompted for the standard concentration, use the numeric keys to enter the $\mu\text{g/L}$ value. Press **ENTER**.

- d. Press the soft key under **ENTRY DONE**.
- e. Snap the neck off a LR Chlorine Voluette Ampule Standard, 20–30 mg/L Cl₂.
- f. Use the TenSette Pipet to add 0.1 mL, 0.2 mL and 0.3 mL of standard, respectively to three 50-mL samples and mix each thoroughly.
- g. Analyze each standard addition sample as described above. Accept the standard additions readings by pressing the soft key under **READ** each time. Each addition should reflect approximately 100% recovery.
- h. 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.
- i. See Section 1.4.1 *Standard Additions* for more information.

Method Performance

Precision

Standard: 250 µg/L Cl₂

Program	95% Confidence Limits
1490	248–252 µg/L Cl ₂

For more information on determining precision data and method detection limits, refer to Section 1.5.

Estimated Detection Limit

Program	EDL
1490	3 µg/L Cl ₂

For more information on derivation and use of Hach’s estimated detection limit, see Section 1.5.2. To determine a method detection limit (MDL) as defined by the 40 CFR part 136, Appendix B, see Section 1.5.1.

Sensitivity

Program Number: 1490

Portion of Curve	ΔAbs	ΔConcentration
Entire Range	0.010	15.8 µg/L

See Section 1.5.3 *Sensitivity Explained* for more information.

Summary of Method

This method is designed for clean water, low in color and turbidity. The main applications include monitoring for trace chlorine break-through of activated carbon beds and feedwater to reverse osmosis membranes or ion-exchange resins.

Several modifications to the normal DPD chlorine method are necessary to measure trace levels of chlorine. The 1-inch Flow-Thru or Sipper Cell must be used in the spectrophotometer. Liquid reagents are also required. The reproducible optics of the Flow-Thru or Sipper Cell gives more stable readings than is possible with movable sample cells, resulting in more stable measurements.

CHLORINE, Total, continued

The reagents are packaged in ampules and sealed under argon gas to ensure stability. Use of liquid reagents eliminates any slight turbidity that might be caused by using powdered reagents. Due to the possible oxidation of the reagents (which could give a positive chlorine reading in the blank), a reagent blank must be determined at least once a day for each lot of reagent used. This reagent blank value is subtracted from the sample result and the corrected value is the actual 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.

Pollution Prevention and Waste Management

Samples treated with sodium arsenite for manganese or chromium interferences will be hazardous wastes as regulated by the Federal RCRA for arsenic (D004). See Section 1 for more information on proper disposal of these materials.

REQUIRED REAGENTS AND STANDARDS

Description	Quantity Required Per Test	Unit	Cat. No.
ULR Chlorine Reagent Set (about 20 tests)..... Includes: (1) 24930-23, (1) 24931-20, (1) 24932-20			25630-00
ULR Chlorine Buffer Solution, 1.5 mL ampules	1 mL	20/pkg	24931-20
DPD Indicator Solution for ULR Chlorine, 1.5 mL ampules	1 mL	20/pkg	24932-20
Blanking Reagent for ULR Chlorine	1 mL	29 mL	24930-23

REQUIRED EQUIPMENT AND SUPPLIES

Beaker, 250-mL	1	each	500-46
Cylinder, mixing, graduated, 50-mL	1	each	1896-41
DR/4000 Flow Cell Module Kit, 1-inch	1	each	48070-04
DR/4000 Sipper Module Kit, 1-inch	1	each	48090-03
Pipet, TenSette, 0.1 to 1.0 mL	1	each	19700-01
Pipet Tips, for 19700-01 TenSette Pipet	2	50/pkg	21856-96

OPTIONAL REAGENTS AND STANDARDS

Chlorine Standard Solution, 2-mL Voluette Ampules, 20–30 mg/L	20/pkg	26300-20
Sodium Hydroxide Solution, 50%	500 mL	2180-49
Sulfuric Acid Standard Solution, 5.25 N	1 liter	2449-53

OPTIONAL EQUIPMENT AND SUPPLIES

Beaker, 150-mL	each	500-44
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