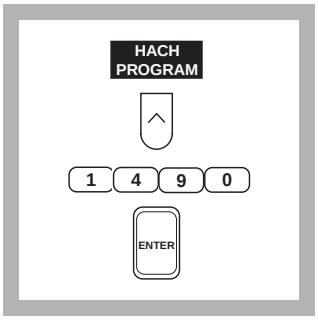
CHLORINE, Total

✔ Method 10014 **DPD Method* ****

ULR (0 to 500 µg/L as Cl_2)

Scope and Application: *For testing trace levels of chlorine and chloramines in treated domestic and industrial wastewater. USEPA accepted for reporting wastewater analyses. The estimated detection limit for program number 1490 is 3 µg/L Cl_2.*

* Adapted from *Standard Methods for the Examination of Water and Wastewater*
** U.S. Patent number 5,362,650 covers the procedure. U.S. Patent 5,549,816 covers the OriFlo filter.



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. See Sample Collection, Storage and Preservation following these steps.*

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.*

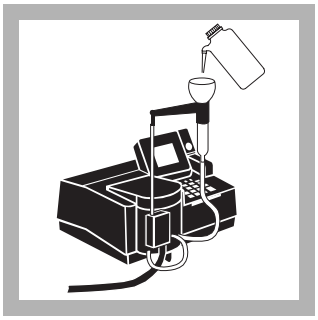
Note: *The Single Cell Module cannot be used in this procedure.*

2. The display will show:

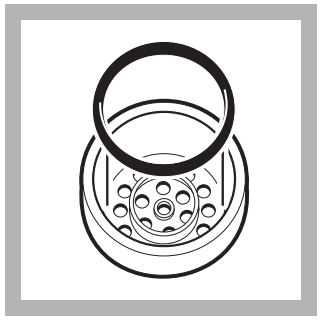
HACH PROGRAM: 1490
Chlorine, Tot. ULR

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

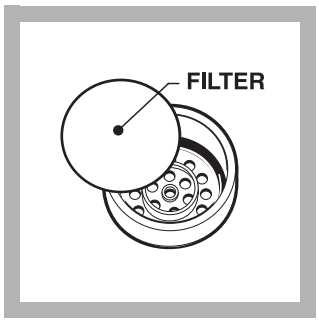
Note: *A reagent blank value for a combined lot of Indicator/Buffer reagent solutions should be determined at least once a day. Determine the reagent blank as described in* Determining the Reagent Blank Value *after this procedure.*



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

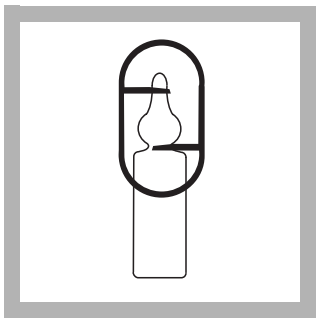


4. Unscrew the cap from the OriFlo plunger assembly. Be sure the O-ring is properly seated in the cap.

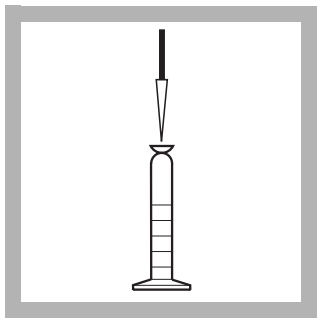


5. Install a new 3-micron filter into the cap well. Wet the filter with a few drops of deionized water. Re-assemble and hand-tighten the cap onto the plunger.

Note: *Use a new filter for each test. Using an unspecified filter may give low analysis results or inability to filter the required volume.*



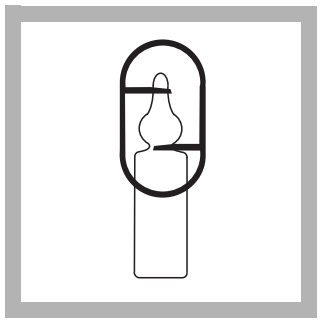
6. Break open 1 ampule of ULR Chlorine Buffer Solution.



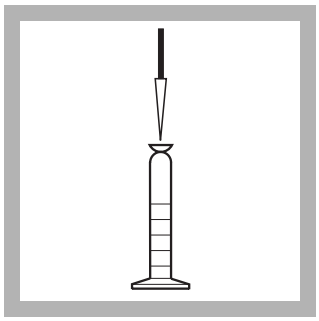
7. Using a TenSette Pipet and clean tip, transfer 1.0 mL of buffer from the ampule to a clean, treated 50-mL graduated mixing cylinder.

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

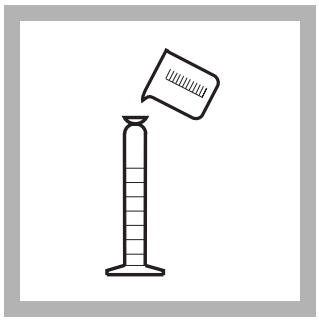
Note: *The ampules contain more than 1.0 mL of solution for ease of reagent transfer. Discard any excess reagent in the ampule.*



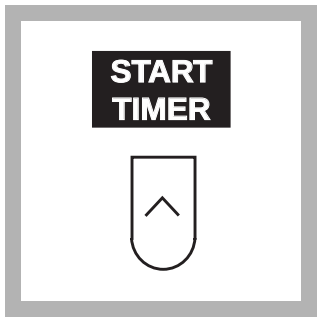
8. Break open 1 ampule of DPD Indicator Solution for Ultra Low-Range Chlorine.



9. 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 10 within 1 minute.



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

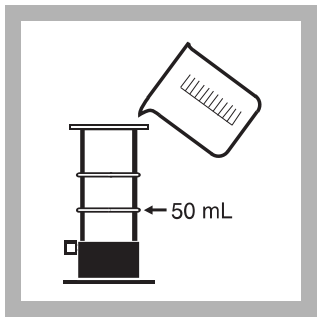


11. Press the soft key under ***START TIMER***.

A 3-minute reaction period will begin.

Note: *Measure the reacted sample 3– 6 minutes after mixing the sample and reagents. If less than 3 minutes elapses, reaction with chloramines may be incomplete. A reading after 6 minutes may result in higher reagent blank values.*

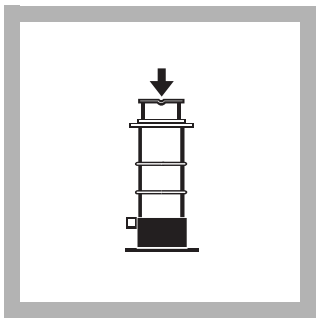
Note: *Perform Steps 12-17 during the 3-minute reaction period.*



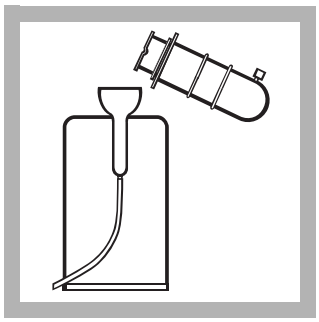
12. During the 3-minute reaction period, push the valve button on the OriFlo barrel assembly to the "closed" position. Place the barrel assembly into its stand. Pour approximately 50-mL of the original sample into the barrel.

Note: *Perform steps 11-16 within the 3-minute reaction period.*

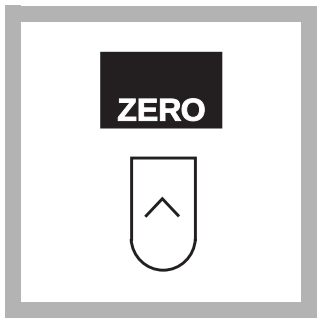
Note: *The lower ring on the barrel assembly represents about a 50-mL volume.*



13. Insert the plunger into the barrel and slowly push the plunger down with even pressure, until the plunger is fully seated.



14. Introduce the filtered sample in the beaker into the Flow-Thru or Sipper Cell.



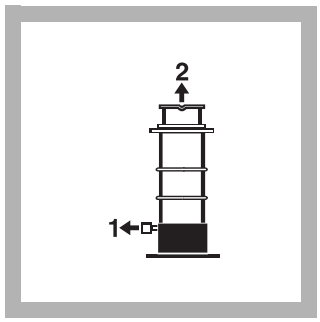
15. After the flow stops, press the soft key under ***ZERO***.

The display will show:

0 µg/L Cl_2

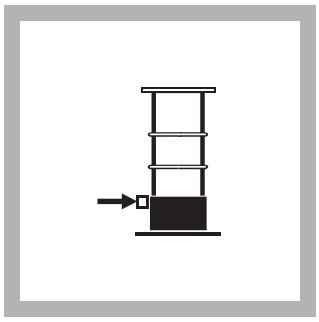
Note: *If a reagent blank value is entered, the display will show a negative number.*

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.*

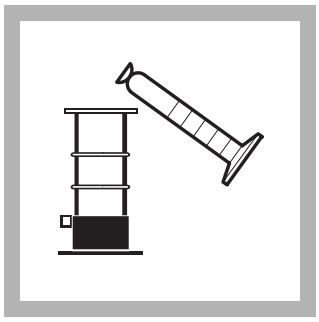


16. Pull the barrel's valve button out to the "open" position. Pull the plunger up to separate it completely from the barrel assembly. Discard the remaining unfiltered sample.

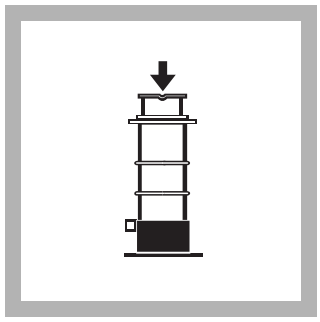
Note: *For very turbid samples, a new membrane may need to be installed. Alternatively, use a second Quick Filter unit with a new membrane filter installed.*



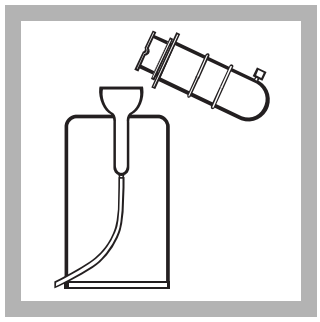
17. Push the barrel's valve button to the "closed" position. Place the barrel assembly into its stand.



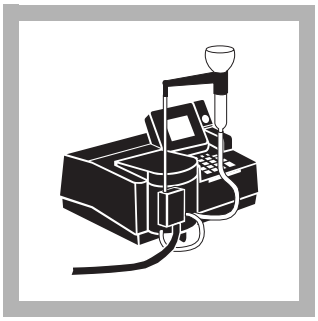
18. When the timer beeps, pour the contents of the mixing graduated cylinder into the barrel.



19. Insert the plunger into the barrel and slowly push the plunger down with even pressure, until the plunger is fully seated.

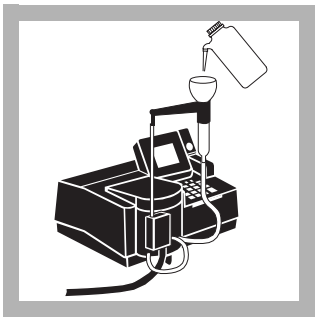


20. Introduce the filtered reacted sample from the beaker into the Flow-Thru or Sipper Cell.



21. After the flow stops and the reading stabilizes, results in µg/L (or chosen units) chlorine will be displayed.

Note: *If a dechlorinating 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.*

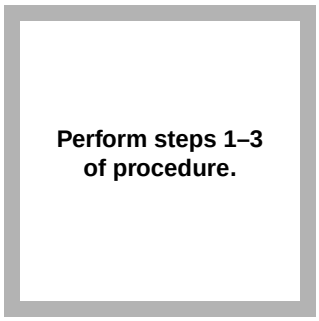


22. Flush the Flow-Thru or Sipper Cell with at least 50 mL of deionized water immediately after use.

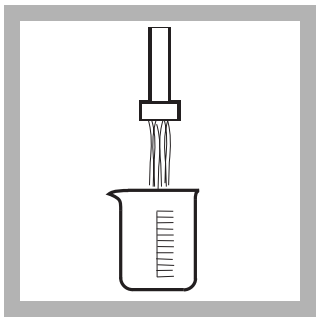
See following steps.

23. Determine a reagent blank using the procedure following these steps.

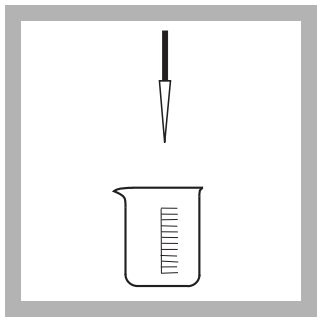
Determining the Reagent Blank Value



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

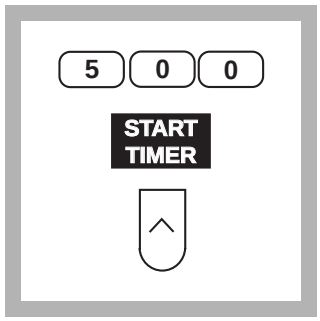


2. Collect about 100 mL deionized or tap water in a clean 250-mL beaker.



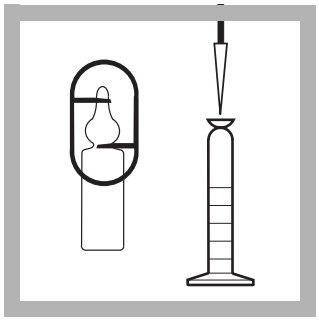
3. Using a TenSette Pipet, add 1.0 mL of Blanking Reagent to the beaker. Swirl several times to mix.

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

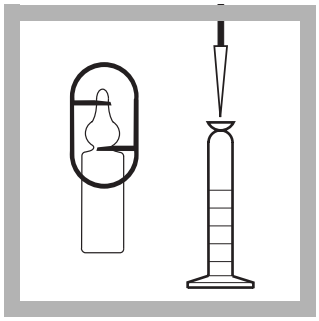


4. Press **500** followed by the soft key under ***START TIMER***.

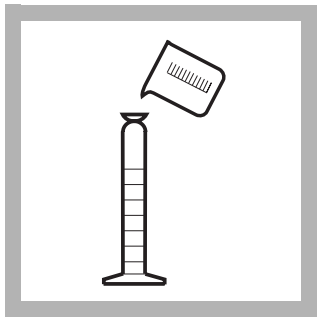
A 5-minute dechlorination period will begin.



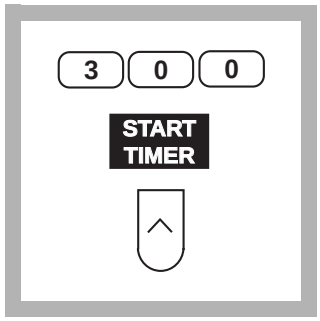
5. After the timer beeps, break open 1 ampule of ULR Chlorine Buffer Solution. Using a TenSette Pipet and clean tip, transfer 1.0 mL of buffer from the ampule to a clean 50-mL mixing graduated cylinder.



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.

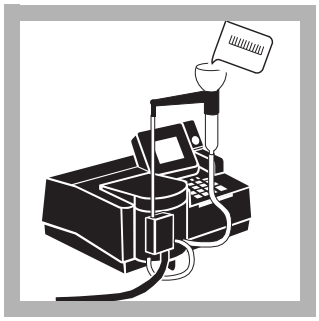


7. Fill the cylinder to the 50-mL mark with the dechlorinated water from Step 3. Cap and invert twice to mix. Save the remaining water for Step 9.

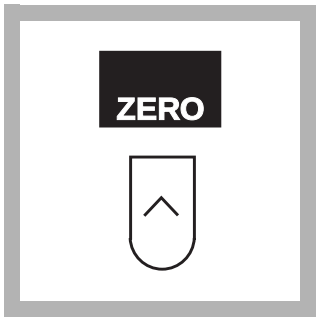


8. Press **300** followed by the soft key under ***START TIMER***.

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.

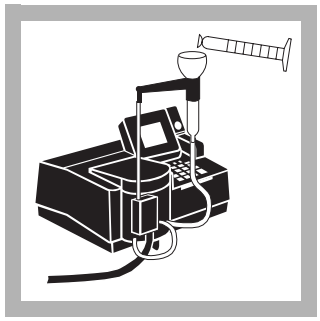


10. When the flow stops, press the soft key under ***ZERO***.

The display will show:

0 µg/L Cl_2

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

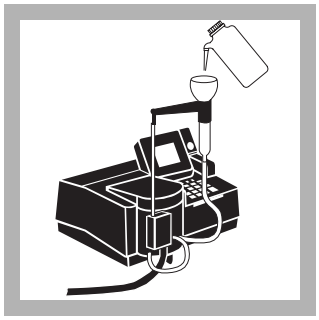


11. When the timer beeps, introduce the contents of the cylinder into the Flow-Thru Cell or Sipper Cell.

12. After the flow stops, the reagent blank value will be displayed in µg/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 for each new combined lot of reagent.*

Note: *The reagent blank value is normally less than 5 µg/L. If the value is greater than 5 µg/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 5 µg/L may be used.*



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

Interferences

Table 1 Interfering Substances and Suggested Treatments

<table>
<tr><th>Interfering Substance</th><th>Interference Levels and Treatments</th></tr>
<tr><td>Bromine, Br_2</td><td>Interferes at all levels</td></tr>
<tr><td>Chlorine Dioxide</td><td>Interferes at all levels</td></tr>
<tr><td>Chloramines, organic</td><td>May interfere</td></tr>
<tr><td>Hardness</td><td>No effect at less than 1,000 mg/L as $CaCO_3$</td></tr>
<tr><td>Iodine, I_2</td><td>Interferes at all levels</td></tr>
<tr><td>Manganese, Oxidized (Mn^{4+}, Mn^{7+}) or Chromium, Oxidized (Cr^{6+})</td><td>1. Adjust sample pH to 6–7
2. Add 6 drops potassium iodide (30-g/L) to a 50-mL sample.
3. Mix and wait one minute.
4. Add 6 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.</td></tr>
<tr><td>Nitrite, NO_2^-</td><td>Causes a positive interference which varies with the nitrite concentration:
<table>
<tr><th>mg/L nitrite</th><th>Apparent µg/L chlorine</th></tr>
<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>
</table></td></tr>
<tr><td>Ozone, O_3</td><td>Interferes at all levels</td></tr>
<tr><td>Peroxides</td><td>May interfere</td></tr>
<tr><td>Extreme sample pH</td><td>Adjust to pH 6–7. See Section 1.3.1 pH Interference.</td></tr>
<tr><td>Highly Buffered Samples</td><td>Adjust to pH 6–7. See Section 1.3.1 pH Interference.</td></tr>
</table>

Sample Collection, Storage and Preservation

Analyze samples for chlorine immediately after collection. Free chlorine is a strong oxidizing agent and it 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. 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 and Sipper Cells

The Flow-Thru or Sipper Cell may accumulate a buildup of colored reaction products, especially of 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

Note: *The Standard Additions technique is not applicable for samples that contain excess reducing agents such as sulfur dioxide, sulfites or bisulfites.*

a. Leave the unspiked sample in the sample cell compartment. Verify that the units displayed are in µg/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 µg/L Cl_2. When prompted for the standard concentration, use the numeric keys to enter the µg/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.

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 in 150-mL beakers. Swirl gently to mix.

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 Cl_2

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

It is essential that interfering sample turbidity is removed using a 3-micron membrane filter. To avoid chlorine loss, the filtration is done after reacting the DPD with the chlorine in the sample. The filter used has been specifically selected to avoid retention of the colored reaction product. Sample color is compensated by zeroing the spectrophotometer on a filtered sample.

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 and Sipper Cell gives more stable readings than is possible with movable sample cells, resulting in more stable measurements.

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 may give a positive chlorine reading in the blank), determine a reagent blank at least once a day for each lot of reagent used. Subtract this reagent blank value from the sample result to obtain 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 *3*.

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 *3* for more information on proper disposal of these materials.

REQUIRED REAGENTS AND STANDARDS

Description	Cat. No.
ULR Chlorine Reagent Set (about 20 tests)	25630-00
Includes: (1) 24930-23, (1) 24931-20, (1) 24932-20	
ULR Chlorine Quick Filter Apparatus Set	25956-00
Includes: (1) 25940-25, (1) 49660-00	

Description	Quantity Required per test	Unit	Cat. No.
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, graduated mixing, 50-mL	1	each	1896-41
DR/4000 Flow Cell Module Kit, 1-inch	1	each	48070-04
or			
DR/4000 Sipper Module Kit, 1-inch	1	each	48090-03
Membrane Filters, 3 micron, 25-mm	1	25/pkg	25940-25
Oriflo Assembly	1	each	49660-00
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

LR Chlorine Standard Solution, 2-mL Voluette Ampules, 20–30 mg/L	20/pkg	26300-20
Sulfuric Acid Solution, 5.25 N	1 liter	2449-53
Water, deionized	4 liter	272-56

OPTIONAL EQUIPMENT AND SUPPLIES

Ampule Breaker, PourRite	each	24846-00
Bottle, wash, 250-mL	each	620-31
Membrane Filters, 3-micron, 25-mm	100/pkg	25940-00

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