Chlorine Total

DOC316.53.01032

USEPA DPD Method[1] **Method 10014**

2 to 500 µg/L Cl_2 **Pour-Thru Cell and OriFlo™ Filtration**

Scope and application: For testing trace levels of chlorine and chloramines in treated domestic and industrial wastewater. USEPA accepted for reporting for wastewater analysis. This product has not been evaluated to test for chlorine and chloramines in medical applications in the United States.

[1] USEPA accepted for reporting for wastewater analysis. Adapted from *Standard Methods for the Examination of Water and Wastewater*.

Test preparation

Instrument-specific information

Table 1 shows all of the instruments that have the program for this test. The table also shows sample cell and orientation requirements.

To use the table, select an instrument, then read across to find the applicable information for this test.

Table 1 Instrument-specific information

Instrument	Sample cell orientation	Pour-Thru Kit	Adapter
DR 6000	The flow path is to the right.	LQV157.99.20002	—
DR 3800		5940400	LZV585 (B)
DR 2800		5940400	LZV585 (B)
DR 2700		5940400	LZV585 (B)
DR 1900		LZV899	—
DR 5000	The flow path is toward the user.	LZV479	—
DR 3900		LQV157.99.10002	—

Before starting

Samples must be analyzed immediately after collection and cannot be preserved for later analysis.
The reagent blank value is normally less than 5 µg/L. If the value is more than 5 µg/L, an interfering substance may be in the blanking water or the DPD Indicator may be degrading. If there is doubt about the reagents, do the reagent blank determination again with chlorine-demand-free water for the sample. Do not use blanks with a concentration that is more than 5 µg/L.
Use a new filter for each test. Use of an unspecified filter can result in low values or an inability to filter the necessary volume.
Use forceps to install or remove the filters. Do not touch the filters by hand.
Determine a reagent blank value for a combined lot of indicator/buffer reagent solutions at least once a day. If sample color or turbidity changes frequently during the day, determine a reagent blank for each sample.
Ampules contain more than 1.0 mL of solution for ease of transfer. Discard the excess reagent.
Refer to the instrument documentation for Pour-Thru cell and module assembly and installation. Make sure to install the Pour-Thru cell correctly.
To protect the Pour-Thru Cell from contamination when not in use, invert a small beaker over the top of the glass funnel.
Review the Safety Data Sheets (MSDS/SDS) for the chemicals that are used. Use the recommended personal protective equipment.
Dispose of reacted solutions according to local, state and federal regulations. Refer to the Safety Data Sheets for disposal information for unused reagents. Refer to the environmental, health and safety staff for your facility and/or local regulatory agencies for further disposal information.

Sample collection

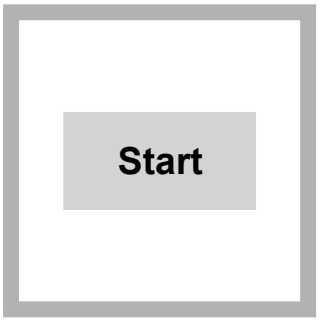
- Analyze the samples immediately. The samples cannot be preserved for later analysis.
- Chlorine is a strong oxidizing agent and is unstable in natural waters. Chlorine reacts quickly with various inorganic compounds and more slowly with organic compounds. Many factors, including reactant concentrations, sunlight, pH, temperature and salinity influence the decomposition of chlorine in water.
- Collect samples in clean glass bottles. Do not use plastic containers because these can have a large chlorine demand.
- Pretreat glass sample containers to remove chlorine demand. Soak the containers in a weak bleach solution (1 mL commercial bleach to 1 liter of deionized water) for at least 1 hour. Rinse fully with deionized or distilled water. If sample containers are rinsed fully with deionized or distilled water after use, only occasional pretreatment is necessary.
- Make sure to get a representative sample. If the sample is taken from a spigot or faucet, let the water flow for at least 5 minutes. Let the container overflow with the sample several times and then put the cap on the sample container so that there is no headspace (air) above the sample.

Items to collect

Description	Quantity
ULR Chlorine Buffer Solution, 1.5-mL ampules	1 mL
DPD Indicator Solution for ULR Chlorine, 1.5-mL ampules	1 mL
Blanking Reagent for ULR Chlorine	1 mL
Beaker, 250-mL	1
Mixing cylinder, graduated, 50-mL, with glass stopper	1
Pipet, TenSette®, 0.1–1.0 mL	1
Pipet Tips, for TenSette® Pipet, 0.1–1.0 mL	2
Filter, membrane, 25-mm, 3-micron	1
OriFlo™ Assembly	1
PourRite® Ampule breaker	1
Deionized water	varies
Pour-Thru Module and Cell (Refer to instrument specific information)	1
Forceps, flat square tip	1

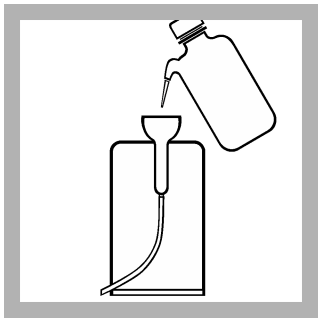
Refer to Consumables and replacement items on page 9 for order information.

Test procedure

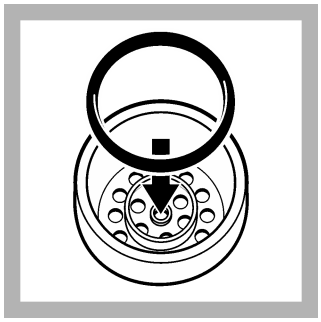


1. Start program **86 Chlorine Total, ULR**. For information about sample cells, adapters or light shields, refer to Instrument-specific information on page 1.

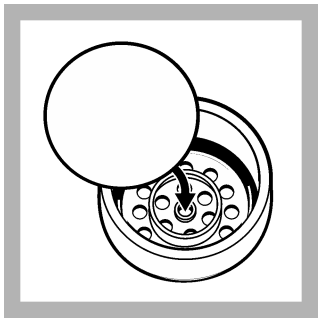
Note: *Although the program name can be different between instruments, the program number does not change.*



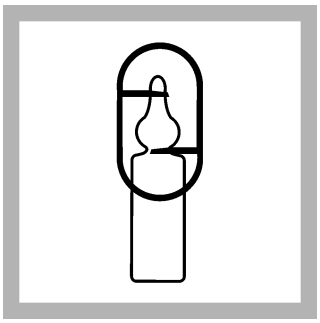
2. Flush the Pour-Thru Cell with at least 50-mL of deionized water.



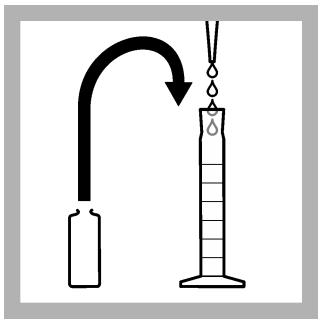
3. Remove the cap from the OriFlo plunger assembly. Make sure that the O-ring is seated correctly in the cap.



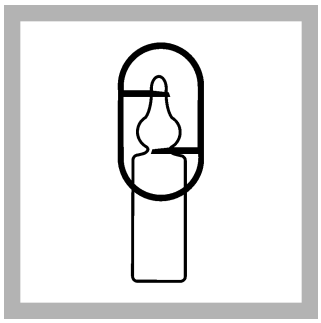
4. Install a new, 3-micron filter (white) into the cap recess. Wet the filter with drops of deionized water. Reassemble and hand-tighten the cap onto the plunger.



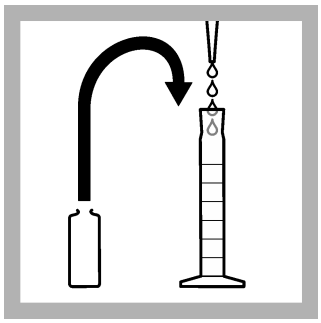
5. Open one ampule of ULR Chlorine Buffer Solution.



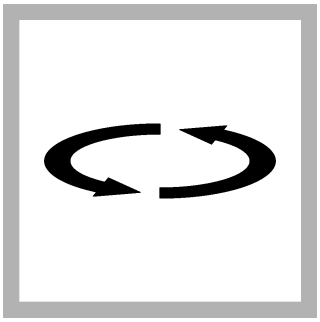
6. Use a TenSette Pipet with a clean tip to add 1 mL of buffer from the ampule to a clean and prepared 50-mL mixing cylinder.



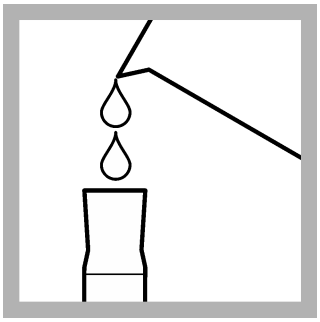
7. Open one ampule of DPD Indicator Solution for Ultra Low Range Chlorine.



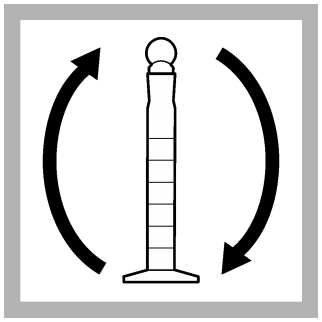
8. Use a TenSette Pipet with a clean tip to add 1 mL of indicator from the ampule to the same mixing cylinder.



9. Swirl to mix.
Continue to the next step within 1 minute

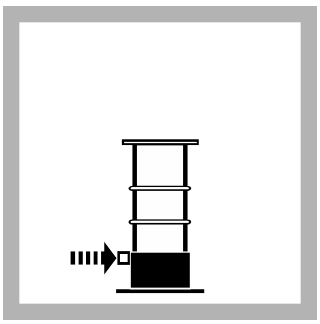


10. Prepared Sample: Prevent extra agitation while carefully filling the cylinder to the 50-mL mark with sample.

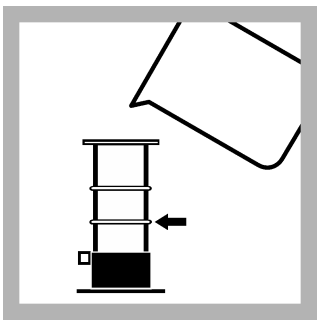


11. Put the stopper on the mixing cylinder. Carefully invert the mixing cylinder twice to mix.

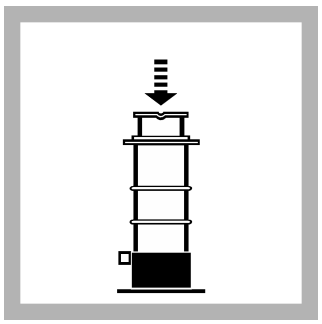
12. Start the instrument timer. A 3-minute reaction time starts.
Complete steps 13–18 during this period. Measure the reacted sample 3–6 minutes after mixing the sample and reagents.



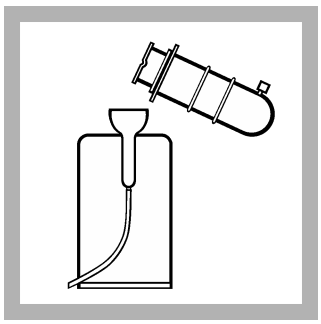
13. Push the valve button on the OriFlo barrel assembly in ("closed" position). Put the barrel assembly into its stand.



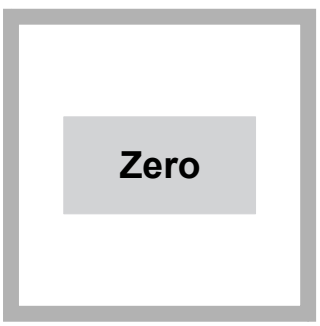
14. Pour approximately 50 mL of the original sample into the barrel. The lower ring on the barrel assembly shows about a 50-mL volume.



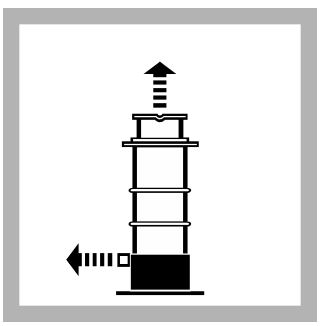
15. Insert the plunger into the barrel and slowly push the plunger down with even pressure until the plunger is fully seated.



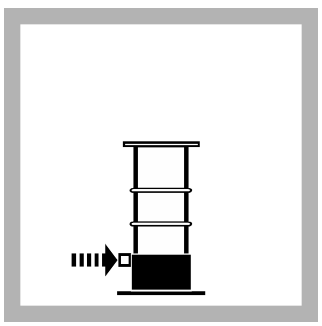
16. Pour the filtered, unreacted sample from the plunger reservoir into the Pour-Thru Cell.



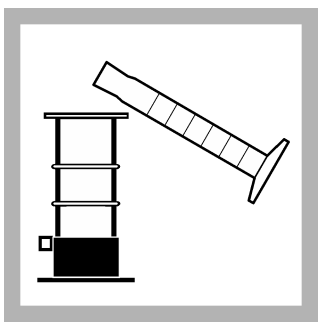
17. When the flow stops, push **ZERO**. The display shows 0 µg/L Cl_2.



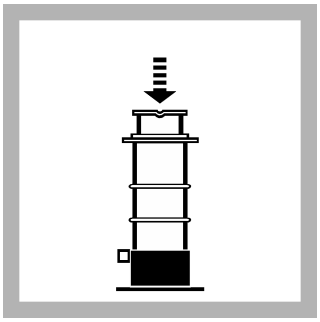
18. Pull the barrel valve button out to the “open” position. Pull the plunger up to separate it from the barrel assembly. Discard the remaining unfiltered sample. A new membrane may be necessary for very turbid samples. Alternatively, use a second Quick Filter unit with a new membrane filter installed.



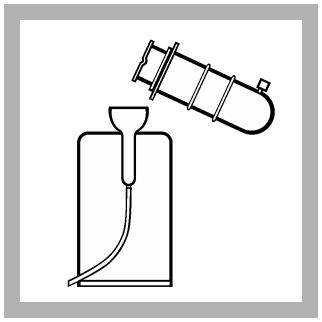
19. Push the barrel valve button to the “closed” position. Put the barrel assembly into its stand.



20. When the timer expires, pour the contents of the mixing cylinder into the barrel.

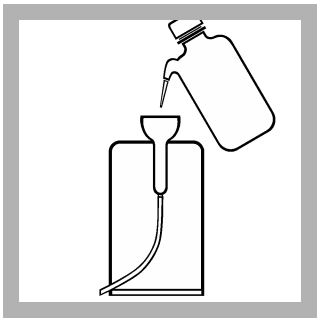


21. Insert the plunger into the barrel and slowly push the plunger down with even pressure, until the plunger is fully seated.



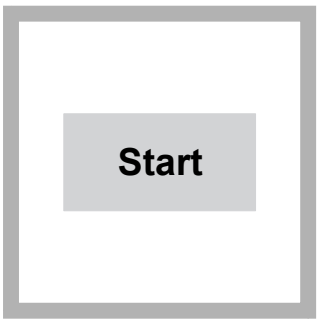
22. Pour the filtered, reacted sample from the plunger reservoir into the Pour-Thru Cell.

23. When the flow stops, push **READ**. Results show in µg/L Cl_2.
If the sample contains a dechlorinating agent (e.g. sulfite or sulfur dioxide), the sample result (corrected for the reagent blank) will read "0" or a slightly negative value.



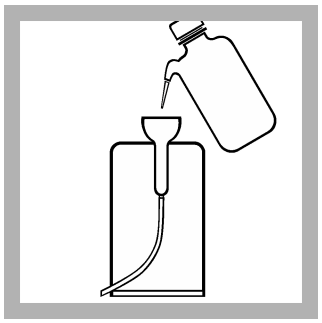
24. Flush the Pour-Thru Cell with at least 50-mL of deionized water immediately after use.

Determine the blank value

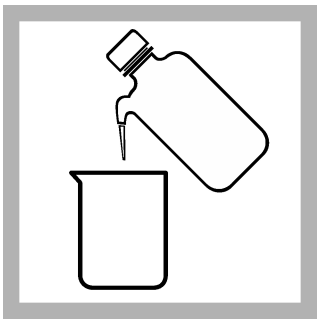


1. Start program **86 Chlorine Total, ULR**. For information about sample cells, adapters or light shields, refer to Instrument-specific information on page 1.

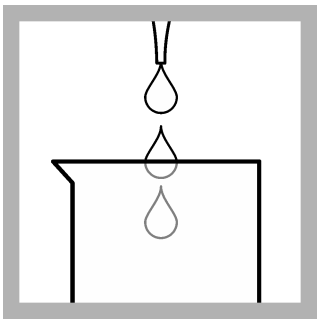
Note: *Although the program name can be different between instruments, the program number does not change.*



2. Flush the Pour-Thru Cell with at least 50-mL of deionized water.

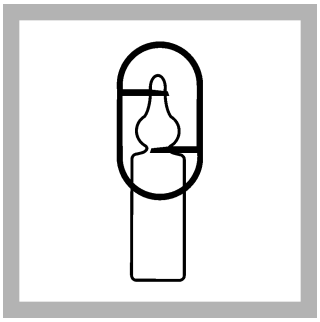


3. Collect approximately 100 mL of deionized or tap water in a clean, 250-mL beaker.

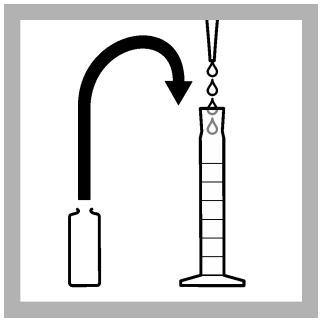


4. Use a TenSette Pipet to add 1.0 mL of Blanking Reagent to the beaker. Swirl to mix.
The Blanking Reagent removes chlorine and chloramines from the water.
Note: *Use this solution in step 11.*

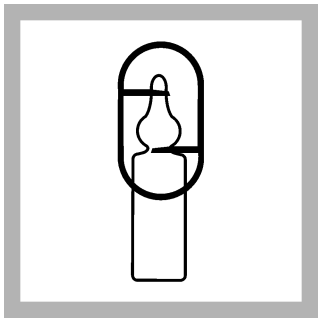
5. Start a timer for 5 minutes.



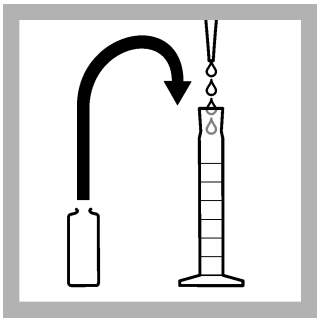
6. Open one ampule of ULR Chlorine Buffer Solution.



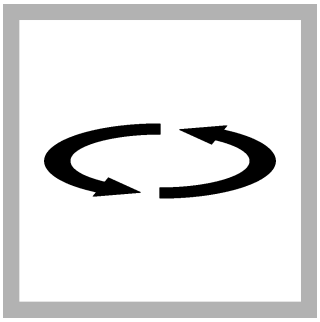
7. Use a TenSette Pipet with a clean tip to add 1 mL of buffer from the ampule to a clean and prepared 50-mL mixing cylinder.



8. Open one ampule of DPD Indicator Solution for Ultra Low Range Chlorine.

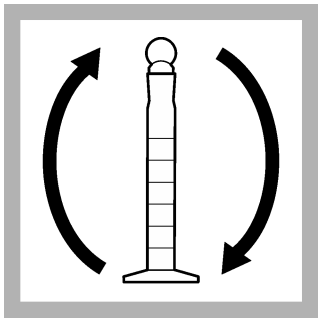


9. Use a TenSette Pipet with a clean tip to add 1 mL of indicator from the ampule to the same mixing cylinder.



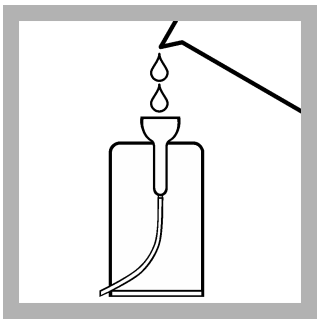
10. Swirl to mix. Continue to the next step within 1 minute

11. Fill the cylinder to the 50-mL mark with dechlorinated water from step 4. Keep the remaining dechlorinated water for step 14.

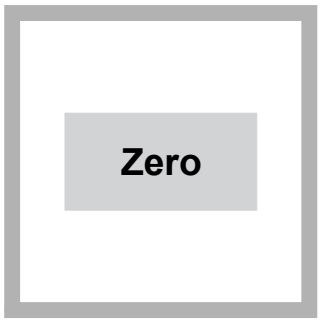


12. Put the stopper on the mixing cylinder. Invert the mixing cylinder two times to mix.

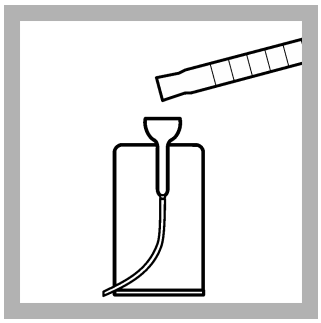
13. Start the instrument timer. A 3-minute reaction time starts.



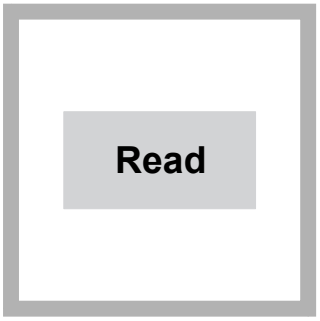
14. During the reaction period, flush the Pour-Thru Cell with the remaining dechlorinated water from step 4.



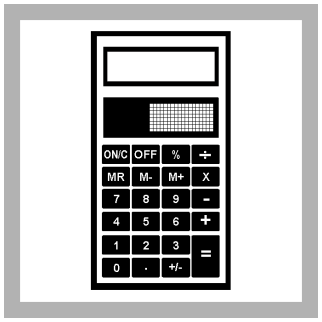
15. When the flow stops, push **ZERO**. The display shows 0 µg/L Cl_2.



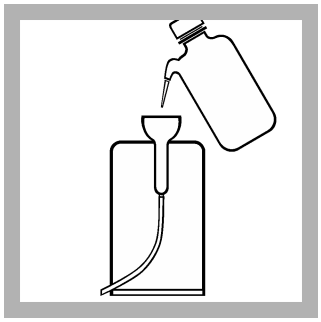
16. When the timer expires, pour the contents of the cylinder into the Pour-Thru Cell.



17. Push **READ**. Results show in µg/L Cl_2.



18. Subtract this value from the sample results received in this procedure. Refer to the instrument documentation for more information on blank adjustment.



19. Flush the Pour-Thru Cell with at least 50-mL of deionized water immediately after use.

Interferences

Interfering substance	Interference level	
Bromine, Br_2	Interferes at all levels.	
Chlorine Dioxide, ClO_2	Interferes at all levels.	
Chloramines, organic	Can interfere.	
Copper, Cu^{2+}	More than 1000 µg/L.	
Iodine, I_2	Interferes at all levels.	
Iron (Fe^{3+})	More than 1000 µg/L.	
Manganese, oxidized (Mn^{4+}, Mn^{7+}) or Chromium, oxidized (Cr^{6+})	**1.** Adjust sample pH to 6-7 with 1.000 N Sulfuric Acid. **2.** Add 9 drops Potassium Iodide (30 g/L) to an 80-mL sample. **3.** Mix and wait 1 minute. **4.** Add 9 drops of Sodium Arsenite[1] (5 g/L) and mix. **5.** Analyze the treated sample as described in the procedure above. **6.** Subtract the result of this test from the original analysis to obtain the correct concentration.	
Nitrite, NO_2^- (uncommon in clean waters)	**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	Interferes at all levels.	
Peroxides	Can interfere.	
Extreme sample pH or highly buffered samples	Adjust to pH 6–7.	

[1] Samples that are treated with sodium arsenite will contain arsenic and may require special disposal consideration. Refer to the current MSDS/SDS for safe handling and disposal instructions.

Prepare analysis labware

Pretreat the labware to remove any chlorine demand. Do not use the same mixing cylinder for a Free Chlorine analysis and Total Chlorine analysis.

1. Add 1 mL of commercial bleach to 1 liter of water.
2. Fill the mixing cylinder, the sample container and the Pour-Thru Cell with the diluted chlorine bleach solution.
3. Soak the labware in this solution for a minimum of 1 hour.
4. Rinse fully with deionized water. Let the mixing cylinder and sample container dry. If the mixing cylinder is fully rinsed with deionized water and dried after each use, only occasional pretreatment is necessary.

Clean the Pour-Thru Cell

The Pour-Thru Cell can collect a buildup of products with color, especially if the reacted solutions stay in the cell for long periods of time after measurement.

1. Rinse the Pour-Thru Cell with 5.25 N Sulfuric Acid to remove the color.
2. Fully rinse with deionized water.
3. Put a cover on the Pour-Thru Cell funnel when it is not in use.

Accuracy check

Standard additions method (sample spike)

Use the standard additions method (for applicable instruments) to validate the test procedure, reagents and instrument and to find if there is an interference in the sample.

Items to collect:

- Low Range Chlorine PourRite® Ampule Standard Solution, 25 to 30-mg/L (25,000 to 30,000 µg/L Cl_2). Use concentration on label.
- TenSette® Pipet and Pipet Tips
- Ampule Breaker

1. Use the test procedure to measure the concentration of the sample, then keep the (unspiked) sample in the instrument.
2. Go to the Standard Additions option in the instrument menu.
3. Select the values for standard concentration, sample volume and spike volumes.
4. Open the standard solution.
5. Prepare three spiked samples: use the TenSette pipet to add 0.1, 0.2, and 0.3 mL of the standard solution, respectively, to three 50-mL portions of fresh sample. Mix well.
6. Use the test procedure to measure the concentration of each of the spiked samples. Start with the smallest sample spike. Measure each of the spiked samples in the instrument.
7. Select **Graph** to compare the expected results to the actual results.

   Note: *If the actual results are significantly different from the expected results, make sure that the sample volumes and sample spikes are measured accurately. The sample volumes and sample spikes that are used should agree with the selections in the standard additions menu. If the results are not within acceptable limits, the sample may contain an interference.*

Method performance

The method performance data that follows was derived from laboratory tests that were measured on a spectrophotometer during ideal test conditions. Users can get different results under different test conditions.

Program	Standard	Precision (95% confidence interval)	Sensitivity Concentration change per 0.010 Abs change
86	295 µg/L Cl_2	290–300 µg/L Cl_2	17 µg/L Cl_2

Summary of Method

Some modifications to the normal DPD chlorine method are necessary to measure trace levels of chlorine. The Pour-Thru Cell must be used in the spectrophotometer. Liquid reagents are also necessary. The reproducible optics of the Pour-Thru Cell give more stable readings than are possible with movable sample cells, resulting in more stable measurements. It is essential that interfering sample turbidity is removed with a 3-micron membrane filter. To prevent chlorine loss, the filtration is done after reacting the DPD with the chlorine in the sample. The filter used is specifically selected to prevent retention of the reaction products with color. Sample color is compensated by zeroing the spectrophotometer on a filtered sample. The reagents are packaged in ampules and sealed under argon gas for stability. Use of liquid reagents eliminates any slight turbidity that might be caused by 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. The measurement wavelength is 515 nm.

Consumables and replacement items

Required reagents

Description	Quantity/test	Unit	Item no.
ULR Chlorine Reagent Set (approximately 20 tests), includes:			2563000
ULR Chlorine Buffer Solution, 1.5-mL ampules	1 mL	20/pkg	2493120
DPD Indicator Solution for ULR Chlorine, 1.5-mL ampules	1 mL	20/pkg	2493220
Blanking Reagent for ULR Chlorine	1 mL	29 mL	2493023

Required apparatus

Description	Quantity/test	Unit	Item no.
ULR Chlorine Apparatus Set, includes:			2595600
Filter, membrane, 25-mm, 3-micron	1	25/pkg	2594025
OriFlo™ Assembly	1	each	4966000
PourRite® Ampule breaker	1	each	2484600
Beaker, 250-mL	1	each	50046H
Mixing cylinder, graduated, 50-mL, with glass stopper	1	each	189641
Pipet, TenSette®, 0.1–1.0 mL	1	each	1970001
Pipet Tips, for TenSette® Pipet, 0.1–1.0 mL	2	50/pkg	2185696

Recommended standards

Description	Unit	Item no.
Chlorine Standard Solution, 2-mL PourRite® Ampules, 25–30 mg/L	20/pkg	2630020

Optional reagents and apparatus

Description	Unit	Item no.
Water, deionized	4 L	27256
Potassium Iodide, 30-g/L	100 mL	34332
Sodium Arsenite, 5-g/L	100 mL	104732
Sulfuric Acid Standard Solution, 1 N	100 mL MDB	127032

Optional reagents and apparatus (continued)

Description	Unit	Item no.
Sulfuric Acid, 5.25 N	1000 mL	244953
Forceps, flat square tip	1	1453700
pH Paper	5/pkg	39133

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

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