Chlorine, Total

DOC316.53.01032

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

ULR (2 to 500 µg/L as 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[2]

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

[2] U.S. Patent 5,362,650 covers the procedure. U.S. Patent 5,549,816 covers the OriFlo™ Filtration System.

Test preparation

How to use instrument-specific information

The *Instrument-specific information* table displays requirements that may vary between instruments. To use this table, select an instrument then read across to find the corresponding information required to perform this test.

Table 118 Instrument-specific information

Instrument	Pour-thru Kit	Cell orientation[1]	Adapter
DR 6000	LQV175.99.20002	Arrow faces right	—
DR 5000	LZV479	—	—
DR 3900	LQV157.99.10002	Align cell flow arrows with arrows on cell compartment	—
DR 3800, DR 2800, DR 2700	5940400	1-inch (round) path aligned with arrow on the adapter	LZV585 (B)

[1] Align for long path

Before starting the test:

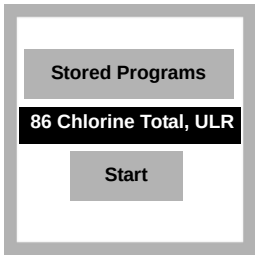
Analyze samples immediately. Samples containing chlorine cannot be preserved for later analysis.
A reagent blank value for a combined lot of indicator/buffer reagent solutions should be determined at least once a day. If sample color or turbidity fluctuates frequently during the day, determine a reagent blank for each sample. Refer to Treating Analysis Labware on page 7.
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.
Use a new filter for each test. Using an unspecified filter may give low analysis results or inability to filter the required volume.
Ampules contain more than 1.0 mL of solution for ease of transfer. Discard excess reagent in the ampule.
Refer to the instrument User Manual for Pour-Thru cell and module assembly and installation.
Protect the Pour-Thru Cell from contamination when not in use by inverting a small beaker over the top of the glass funnel.
Use forceps to handle filters.
Make sure the Pour-Thru cell is completely seated in the sample cell compartment.

Collect the following items:

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
Membrane Filters, 3-micron, 25-mm	1
OriFlo Assembly	1
Beaker, 250 mL	1
Cylinder, graduated mixing, 50-mL.	1
Pipet, TenSette®, 0.1 to 1.0 mL	1
Pipet Tips	2
Deionized water	Varies
Ampule Breaker	1
Pour-Thru Module and cell	1

See *Consumables and replacement items* for reorder information.

DPD method for Pour-Thru Cell

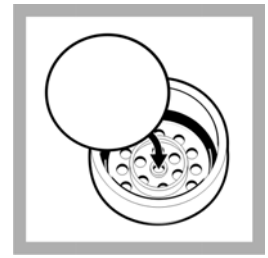


1. Select the test.

Insert an adapter if required (*Instrument-specific information*).

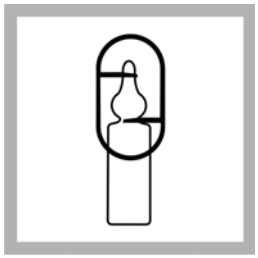
2. Flush the Pour-Thru cell with 50 mL of deionized water.

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

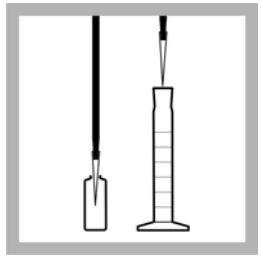


4. Install a new, 3-micron filter (white) into the cap well. Wet the filter with a few drops of deionized water. Reassemble and hand-tighten the cap onto the plunger.

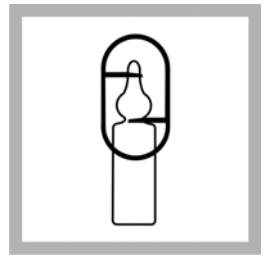
DPD method for Pour-Thru Cell (continued)



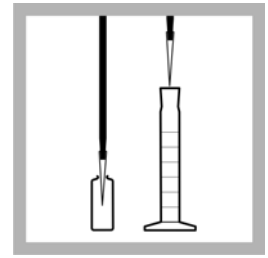
5. Open one ULR Chlorine Buffer Solution Ampule.



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

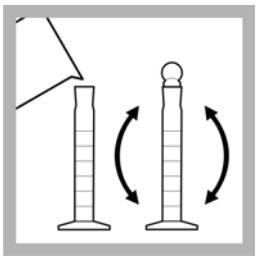


7. Open one ampule of DPD Indicator Solution for Ultra Low Range Chlorine.



8. Use a TenSette Pipet and a clean tip to transfer 1.0 mL of indicator from the ampule to the graduated mixing cylinder. Swirl to mix.

Proceed to step 9 within one minute.

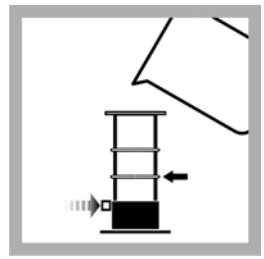


9. Prepared Sample: Avoiding extra agitation, carefully fill the cylinder to the 50-mL mark with sample. Stopper the cylinder. Gently invert it twice to mix.

10. Press **TIMER>OK**.

A three-minute reaction time will begin. Perform steps 11–16 during this period.

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

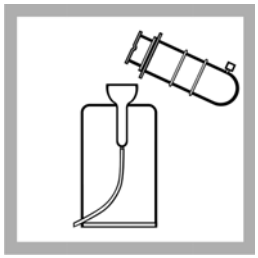


11. Push the valve button on the OriFlo™ barrel assembly in ("closed" position). Place the barrel assembly into its stand. Pour approximately 50 mL of the original sample into the barrel.

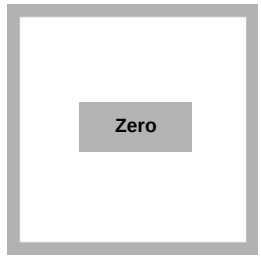
The lower ring on the barrel assembly represents about a 50-mL volume.

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

DPD method for Pour-Thru Cell (continued)



13. Pour the filtered sample from the plunger reservoir into the Pour-Thru Cell.

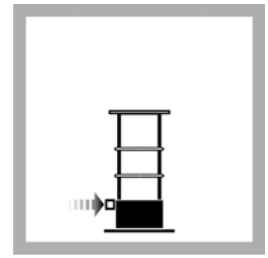


14. When the flow stops, **ZERO** the instrument.

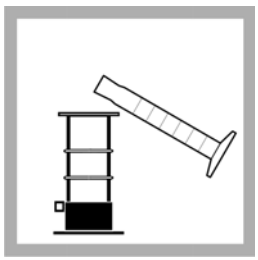
The display will show: 0 µg/L Cl_2.

15. 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 required for very turbid samples. Alternatively, use a second Quick Filter unit with a new membrane filter installed.

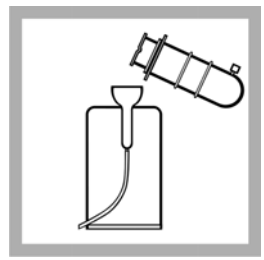


16. Push the barrel valve button to the “closed” position. Place the barrel assembly into its stand.



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

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



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

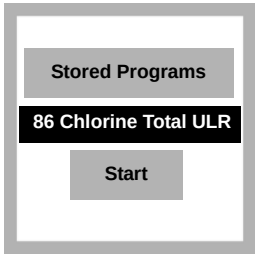
READ the results in µg/L chlorine.

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.

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

Subtract the reagent blank value (See *Determining the reagent blank value*) from the sample value obtained in step 19.

Determining the reagent blank value



1. Select the test.

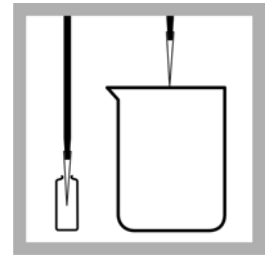
Make sure that the reagent blank setting is off.

See the user manual for information.

2. Install the Pour-Thru module.

Flush the Pour-Thru cell with 50 mL of deionized water.

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

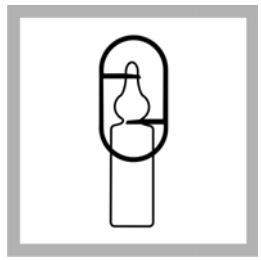


4. Use a TenSette® Pipet to add 1.0 mL of Blanking Reagent to the beaker. Swirl several times to mix.

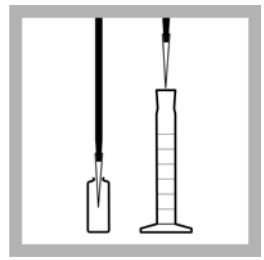
The Blanking Reagent removes chlorine and chloramines from the water.

Note: *The solution from step 4 will be used in Step 10.*

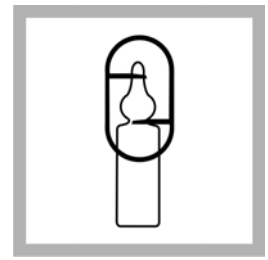
5. Access the general timer and set it for five minutes. Start the timer.



6. After the timer expires, open one ampule of ULR Chlorine Buffer Solution.

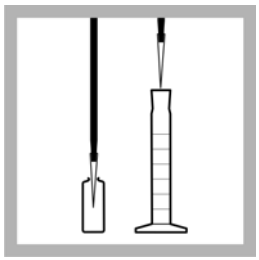


7. Use a TenSette Pipet and a clean tip to transfer 1.0 mL of buffer from the ampule a clean 50 mL mixing graduated cylinder.

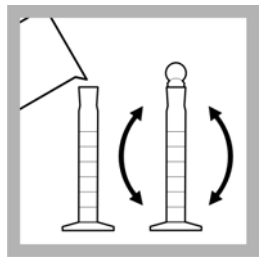


8. Open one ampule of DPD Indicator Solution for Ultra Low Range Chlorine.

Determining the reagent blank value (continued)



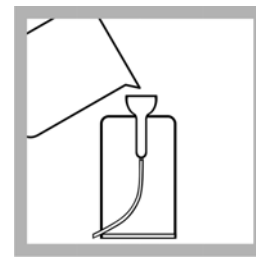
9. Use a TenSette Pipet and a clean tip to transfer 1.0 mL of indicator from the ampule to the cylinder. Swirl to mix the reagents. Proceed to step 10 within one minute.



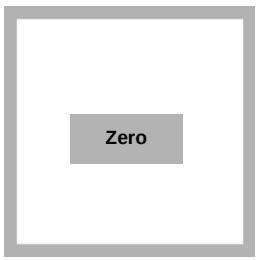
10. Fill the cylinder to the 50-mL mark with dechlorinated water from step 4. Cap and invert twice to mix. Save the remaining water for step 12.

11. Start the instrument timer.

A three-minute reaction time will begin.



12. During the reaction period, flush the Pour-Thru Cell with the remainder of original dechlorinated water from step 10.



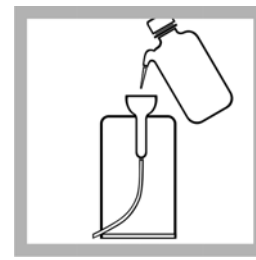
13. When the flow stops, **ZERO** the instrument.

The display will show: 0 µg/L Cl_2.

14. When the timer expires, pour the contents of the cylinder into the Pour-Thru Cell. **READ** the results in µg/L chlorine.

15. Use this value to correct the sample result obtained in this procedure.

See the user manual for details on saving the reagent blank value.



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

Interferences

Table 119 Interfering substances and levels

<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, ClO_2</td><td>Interferes at all levels</td></tr>
<tr><td>Chloramines, organic</td><td>May interfere</td></tr>
<tr><td>Copper, Cu^{2+}</td><td>Greater than 1000 µg/L</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 with 1.0 N Sulfuric Acid[1].
2. Add 9 drops Potassium Iodide (30 g/L)[1] to an 80-mL sample.
3. Mix and wait 1 minute.
4. Add 9 drops Sodium Arsenite[1, 2] (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.</td></tr>
<tr><td>Nitrite, NO_2^- (uncommon in clean waters)</td><td><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</td><td>Interferes at all levels.</td></tr>
<tr><td>Peroxides</td><td>May interfere</td></tr>
<tr><td>Extreme sample pH or highly buffered samples</td><td>Adjust to pH 6–7</td></tr>
</table>

[1] See *Optional reagents and apparatus*.

[2] Samples treated with sodium arsenite for interferences will be hazardous waste as regulated by the Federal RCRA for arsenic (D004). Refer to the current MSDS for safe handling and disposal instructions.

Sample collection, storage and preservation

- Analyze samples for chlorine immediately after collection. 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 chlorine in water.
- Avoid plastic containers. 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 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.
- A common error in testing for chlorine is not 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 head space (air) above the sample.

- Perform the chlorine analysis immediately.

Treating analysis labware

Glassware used in this test must be chlorine demand-free. Fill the mixing cylinder and sample container with a dilute solution of chlorine bleach prepared by adding 1 mL of commercial bleach to 1 liter of water. Soak in this solution at least one hour. After soaking, rinse thoroughly with deionized water and allow to dry before use.

Treat the Pour-Thru Cell similarly with dilute bleach and let stand for several minutes. Rinse several times with deionized water.

Cleaning the Pour-Thru cell

The Pour-Thru 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

Required for accuracy check:

- Low Range Chlorine Voluette® Ampule Standard Solution, 25 to 30-mg/L (25,000 to 30,000 µg/L) Cl_2
- TenSette® Pipet and Pipet Tips
- Ampule Breaker

Standard additions method (samples spike)

1. After reading test results, leave the sample cell (unspiked sample) in the instrument.
2. Select Options>More>Standard Additions from the instrument menu.
3. Default values for standard concentration, sample volume, and spike volumes can be accepted or edited. Enter the chlorine concentration from the ampule package. After values are accepted, the unspiked sample reading will appear in the top row. See the user manual for more information.
4. Snap the top off a Low Range Chlorine Voluette® Ampule Standard Solution, 25 to 30-mg/L (25,000 to 30,000 µg/L).
5. Prepare three sample spikes. Use the TenSette® Pipet to add 0.1, 0.2, and 0.3 mL of standard to three 50-mL samples, respectively. Swirl gently to mix.
6. Analyze each sample spike as described in the procedure above, starting with the 0.1 mL sample spike. Accept each standard additions reading by pressing **READ**. Each addition should reflect approximately 100% recovery.
7. After completing the sequence, press **GRAPH** to view the best-fit line through the standard additions data points, accounting for the matrix interferences. Press **IDEAL LINE** to view the relationship between the sample spikes and the “Ideal Line” of 100% recovery.

* See *Optional reagents and apparatus*.

Method performance

Program	Standard	Precision 95% Confidence Limits of Distribution	Sensitivity Concentration change per 0.010 Abs change	
			Portion of Curve	Concentration
86	295 µg/L Cl_2	290–300 µg/L Cl_2	Entire range	17 µg/L Cl_2

Summary of method

Several 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 required. The reproducible optics of the Pour-Thru Cell give more stable readings than is possible with movable sample cells, resulting in more stable measurements.

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 product. Sample color is compensated by zeroing the spectrophotometer on a filtered sample.

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. Test results are measured at 515 nm.

Consumables and replacement items

Required reagents

Description	Quantity/Test	Unit	Catalog number
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
Water deionized	varies	4 L	27256

Required apparatus

Description	Quantity	Unit	Catalog number
ULR Chlorine Apparatus Set, includes:	—	—	2595600
Membrane Filters, 3-micron, 25-mm	1	25/pkg	2594025
OriFlo™ Assembly	1	each	4966000
Beaker, 250-mL	1	each	50046H
Breaker, ampule	1	each	2484600
Cylinder, graduated mixing, 50-mL	1	each	189641
Pipet, TenSette®, 0.1 to 1.0 mL	1	each	1970001
Pipet Tips, for TenSette Pipet 1970001	2	50/pkg	2185696

Recommended standards

Description	Unit	Catalog number
Chlorine Standard Solution, Voluette® Ampule, 25–30 mg/L, 2-mL	20/pkg	2630020

Optional reagents and apparatus

Description	Unit	Catalog number
Forceps, flat square tips, 115 mm	each	1453700
Potassium Iodide, 30 g/L	100 mL MDB	34332
Sodium Arsenite, 5 g/L	100 mL	104732
Sulfuric Acid, 1 N 100 mL	100 mL MDB	127032
Sulfuric Acid, 5.25 N	1000 mL	244953

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