Chlorine Total

DPD Rapid Liquid Method[1]

Method 10060

0.02 to 2.00 mg/L Cl_2

Pour-Thru Cell

Scope and application: For treated water. This product has not been evaluated to test for chlorine and chloramines in medical applications in the United States.

[1] 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.
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.
Prepare the indicator reagent before use. Refer to Prepare the reagents on page 4.
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.

Items to collect

Description	Quantity
DPD Indicator Powder, 24-g	varies
Total Chlorine Indicator Solution (refer to Prepare the reagents on page 4)	1 mL
Total Chlorine Buffer Solution	1 mL
Deionized water	varies
Mixing cylinder, graduated, 100-mL glass	1

Items to collect (continued)

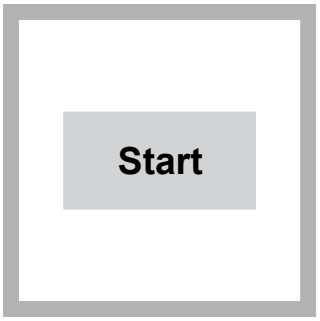
Description	Quantity
Dispenser, adjustable volume, 1.0–5.0 mL	2
Pour-Thru Module and Cell (Refer to instrument specific information)	1

Refer to Consumables and replacement parts on page 5 for order information.

Sample collection

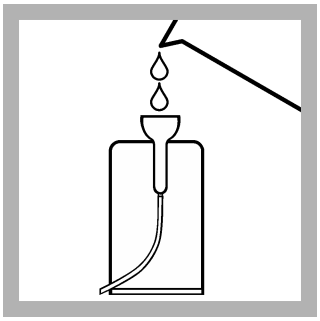
- Analyze the samples immediately. The samples cannot be preserved for later analysis.
- Chlorine is a strong oxidizing agent and is unstable in natural waters. Chlorine reacts quickly with various inorganic compounds and more slowly with organic compounds. Many factors, including reactant concentrations, 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.

Test procedure

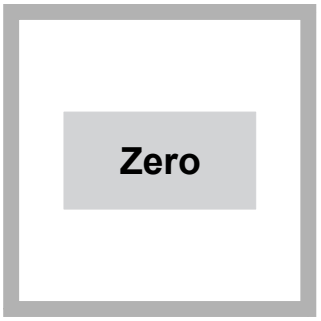


1. Start program **82 Chlorine F&T RL**. For information about sample cells, adapters or light shields, refer to Instrument-specific information on page 1.

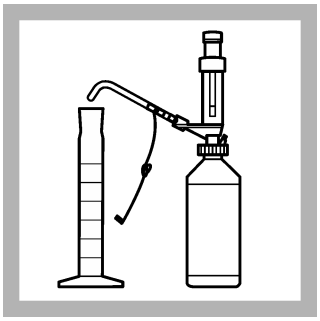
Note: *Although the program name can be different between instruments, the program number does not change.*



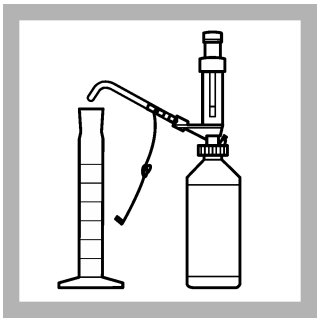
2. Pour 50 mL of sample into the Pour-Thru Cell.



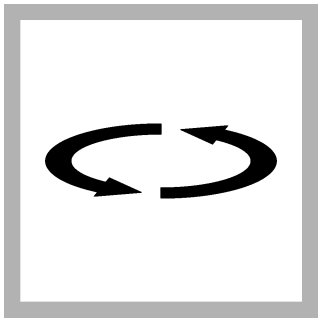
3. When the flow stops, push **ZERO**. The display shows 0.00 mg/L CL_2.



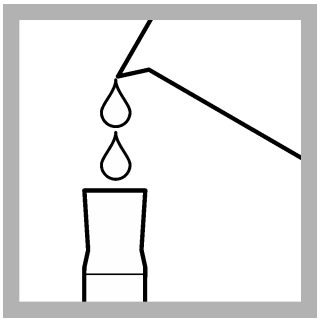
4. Use the bottle-top dispenser to add 1.0 mL of Total Chlorine Buffer Solution to a clean, dry 100-mL glass mixing cylinder.



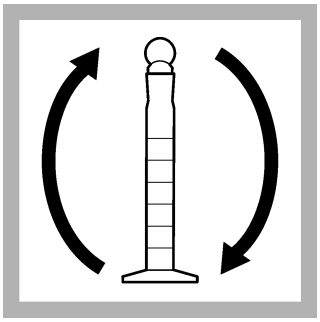
5. Use the bottle-top dispenser to add 1.0 mL of prepared Total Chlorine Indicator Solution to the same mixing cylinder.



6. Swirl to mix.
Continue to the next step immediately.

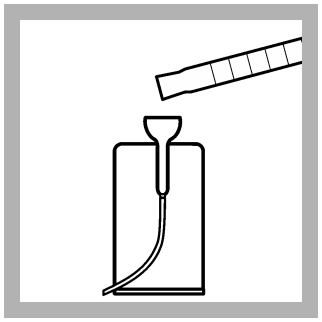


7. Carefully fill the same mixing cylinder to the 80-mL mark with sample.



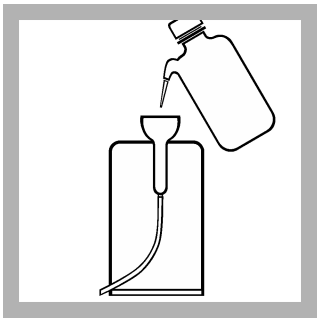
8. Put the stopper on the mixing cylinder. Invert the mixing cylinder carefully several times to mix.
Continue to the next step immediately.

9. Start the instrument timer. A 2-minute reaction time starts.
Complete the next two steps within 2 minutes after the timer expires.



10. When the timer expires, fill the funnel of the Pour-Thru Cell with the reacted sample from the mixing cylinder. It is not necessary to pour all of the sample into the Pour-Thru Cell; discard approximately half of the sample.

11. When the flow stops, push **READ**. Results show in mg/L CL_2.



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

Interferences

Interfering substance	Interference level
Alkalinity	More than 700 mg/L $CaCO_3$. May not develop full color or color may fade instantly. Neutralize to pH 6-7 with 1 N Sulfuric Acid. Find amount to be added on separate sample aliquot, then add the same quantity to the sample being tested. Correct for volume addition.
Bromine, Br_2	Interferes at all levels.
Hardness	Levels below 1000 mg/L as $CaCO_3$ will not interfere.
Hexavalent Chromium	Levels more than 1 mg/L will cause a positive interference.
Iodine, I_2	Interferes at all levels.

Interfering substance	Interference level
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 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 get the correct concentration.
Ozone	Interferes at all levels.

[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 the reagents

Prepare the Total Chlorine Indicator Solution before use as follows.

1. Use a powder funnel and add the contents of one 24 g bottle of DPD Powder to one 473-mL bottle of Total Chlorine Indicator Solution.
2. Invert several times and swirl until the powder is completely dissolved.
3. A pale pink color can develop, but should not have an effect on the results.
4. This solution gives accurate results for at least 1 month after mixing when kept in storage at 20–25 °C (68–77 °F).
5. Write the date of preparation on the Indicator Solution Bottle.
6. Discard any remaining solution after 1 month.
7. Use of this reagent after 1 month can result in high reagent blanks and low values at high concentration.
8. Do not mix fresh reagent with previously prepared reagent.

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:

- Chlorine Voluette® Ampule Standard Solution, 50 to 75-mg/L Cl_2 (use concentration on label)
- TenSette® Pipet and 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 0.3, 0.6 and 0.9 mL of the standard solution, respectively, to three 80-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
82	1.18 mg/L Cl_2	1.17–1.19 mg/L Cl_2	0.02 mg/L Cl_2

Summary of Method

Chlorine can be in water as free available chlorine and as combined available chlorine. Both forms can be in the same water and can be determined together as the total available chlorine. Free chlorine is available as hypochlorous acid and/or hypochlorite ion. Combined chlorine exists as monochloramine, dichloramine, nitrogen trichloride and other chloro derivatives. The combined chlorine oxidizes iodide in the reagent to iodine. The iodine and free chlorine in the sample react with the DPD (N,N-diethyl- p-phenylenediamine) indicator to form a pink color, which is proportional to the total chlorine concentration. To determine the concentration of combined chlorine, complete a free chlorine test and a total chlorine test. Subtract the free chlorine results from the results of the total chlorine test to obtain combined chlorine. The measurement wavelength is 530 nm.

Consumables and replacement parts

Required reagents

Description	Quantity/test	Unit	Item no.
Rapid Liquid Total Chlorine Reagent Set, includes:			2557000
DPD Indicator Powder, 24-g	1	varies	2297255
Total Chlorine Indicator Solution	1 mL	473 mL	2263411
Total Chlorine Buffer Solution	1 mL	473 mL	2263511

Recommended standards

Description	Unit	Item no.
Chlorine Standard Solution, 10-mL Voluette® Ampule, 50-75 mg/L	16/pkg	1426810
Chlorine Standard Solution, 2-mL PourRite® Ampules, 50–75 mg/L	20/pkg	1426820

Required apparatus

Description	Quantity/test	Unit	Item no.
Mixing cylinder, graduated, 100-mL glass	1	each	2636342
Dispenser, adjustable volume, 1.0–5.0 mL	2	each	2563137
Funnel, powder	1	each	2264467

Optional reagents and apparatus

Description	Unit	Item no.
Water, deionized	4 L	27256
Pipet, TenSette®, 0.1–1.0 mL	each	1970001
Pipet tips for TenSette® Pipet, 0.1–1.0 mL	50/pkg	2185696
Pipet tips for TenSette® Pipet, 0.1–1.0 mL	1000/pkg	2185628
Potassium Iodide, 30-g/L	100 mL	34332
Ampule Breaker, 2-mL PourRite® Ampules	each	2484600
Sodium Arsenite, 5-g/L	100 mL	104732
Sulfuric Acid Standard Solution, 1 N	100 mL MDB	127032
Sulfuric Acid, 5.25 N	1000 mL	244953
Ampule Breaker, 10-mL Voluette® Ampules	each	2196800

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