# Chlorine, Free

DOC316.53.01026

## DPD Rapid Liquid Method[1]

**Method 10059**

**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 |
| Free Chlorine Indicator Solution bottle with bottle-top dispenser (refer to Prepare the reagents on page 4) | 1 mL |
| Free Chlorine Buffer Solution bottle with bottle-top dispenser | 1 mL |
| Mixing cylinder, graduated, 100-mL glass | 1 |
| Dispenser, adjustable volume, 1.0–5.0 mL | 2 |

## Items to collect (continued)

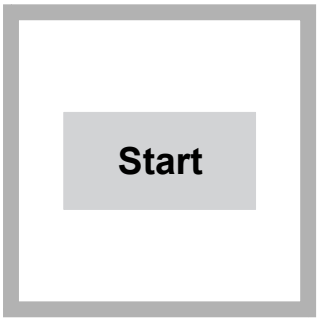
| Description | Quantity |
|---|---|
| Pour-Thru Module and Cell (For information about sample cells, adapters or light shields, refer to Instrument-specific information on page 1.) | 1 |
| Water, deionized | varies |

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

## Sample collection

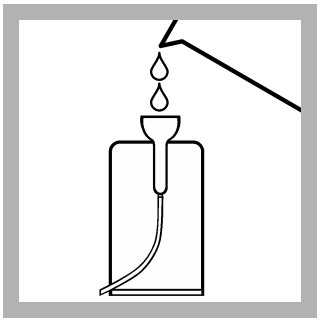
- Analyze the samples immediately. The samples cannot be preserved for later analysis.
- Chlorine is a strong oxidizing agent and is unstable in natural waters. Chlorine reacts quickly with various inorganic compounds and more slowly with organic compounds. Many factors, including reactant concentrations,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

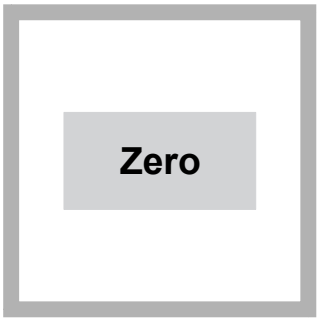



**1.** Start program **82 Chlorine F&T RL**. For information about sample cells, adapters or light shields, refer to Instrument-specific information on page 1.

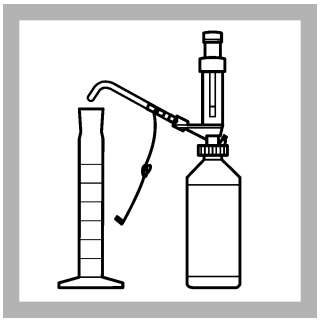
***Note:*** *Although the program name can be different between instruments, the program number does not change.*



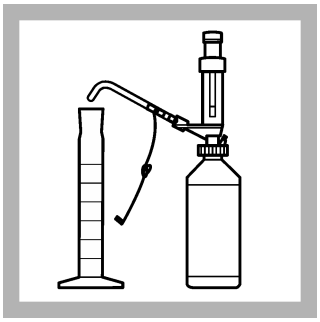
**2.** Pour 50 mL of sample into the Pour-Thru Cell.



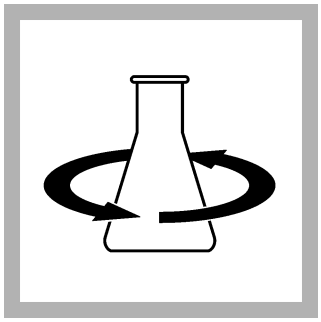

**3.** When the flow stops, push **ZERO**. The display shows 0.00 mg/L $CL_2$.



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

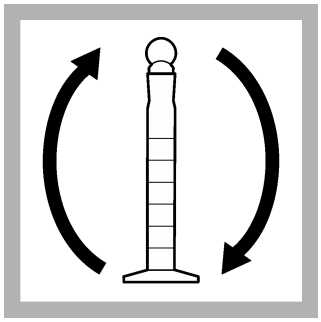


**5.** Use the bottle-top dispenser to add 1.0 mL of prepared Free Chlorine Indicator Solution to the same mixing cylinder.

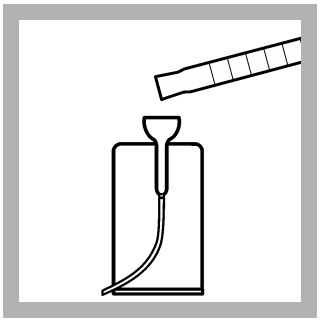


**6.** Swirl to mix. Immediately continue to the next step.

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

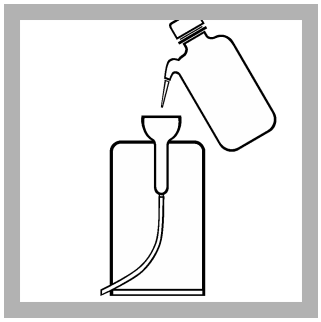


**8.** Put the stopper on the mixing cylinder. Lightly invert twice to mix. Continue immediately to the next step.



**9.** 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; approximately half of the sample can be discarded.


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



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

## Interferences

| Interfering substance | Interference level |
|---|---|
| Alkalinity | More than 400 mg/L $CaCO_3$. The full color may not develop or the color may fade instantly. Adjust to pH 6–7 with 1 N Sulfuric Acid. Measure the amount to add on a separate sample aliquot, then add the same amount to the sample that is tested. Correct the test result for the dilution from the volume addition. |
| Bromine, $Br_2$ | Interferes at all levels. |
| Hardness | Levels below 1000 mg/L as $CaCO_3$ do not interfere. |
| Iodine, $I_2$ | Interferes at all levels. |
| Manganese, oxidized ($Mn^{4+}$, $Mn^{7+}$) or Chromium, oxidized ($Cr^{6+}$) | **1.** Adjust sample pH to 6-7 with 1.000 N Sulfuric Acid.<br>**2.** Add 9 drops Potassium Iodide (30 g/L) to an 80-mL sample.<br>**3.** Mix and wait for 1 minute.<br>**4.** Add 9 drops Sodium Arsenite[1] (5 g/L) and mix.<br>**5.** Analyze the treated sample as described in the procedure above.<br>**6.** Subtract the result of this test from the original analysis to obtain the correct concentration. |

| Interfering substance | Interference level |
|---|---|
| Monochloramine ($NH_2Cl$) | Samples that contain monochloramine cause a gradual drift to higher chlorine readings. When read within 1 minute of reagent addition, 3.0 mg/L monochloramine will cause an increase of less than 0.1 mg/L in the free chlorine reading. |
| 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 Free 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 Free 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 solution 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<br>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 in the sample as hypochlorous acid or hypochlorite ion (free chlorine or free available chlorine) immediately reacts with DPD (N,N-diethyl-p-phenylenediamine) indicator to form a pink color which is proportional to the chlorine concentration. The measurement wavelength is 530 nm.

## Consumables and replacement items

### Required reagents

| Description | Quantity/test | Unit | Item no. |
|---|---|---|---|
| Rapid Liquid Free Chlorine Reagent Set, includes: | | | 2556900 |
| DPD Indicator Powder, 24-g | 1 | varies | 2297255 |
| Free Chlorine Indicator Solution | 1 mL | 473 mL | 2314011 |
| Free Chlorine Buffer Solution | 1 mL | 473 mL | 2314111 |

### 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 |

### 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 |

## 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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