

## DPD Method<sup>1</sup>

**Method 10069**
**0.1 to 10.0 mg/L Cl<sub>2</sub> (HR)**
**Powder Pillows**

**Scope and application:** For determinations of higher levels of free chlorine (hypochlorous acid and hypochlorite ion) in drinking water, cooling water and industrial process waters. This product has not been evaluated to test for chlorine and chloramines in medical applications in the United States.

<sup>1</sup> 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 requirements that can change between instruments, such as adapter and sample cell 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                    | Adapter                | Sample cell orientation                                 | Sample cell  |
|-------------------------------|------------------------|---|--|
| DR 6000                       | —                      | The orientation key is toward the user.                 | 4864302<br>  |
| DR 5000                       | A23618                 | The orientation key is toward the user.                 |  |
| DR 3900                       | LZV846 (A)             | The orientation key is away from the user.              |  |
| DR 1900                       | 9609900 or 9609800 (C) | The orientation key is toward the arrow on the adapter. |  |
| DR 900                        | —                      | The orientation key is toward the user.                 |  |
| DR 3800<br>DR 2800<br>DR 2700 | LZV585 (B)             | The 1-cm path is aligned with the arrow on the adapter. | 5940506<br> |

### Before starting

Samples must be analyzed immediately after collection and cannot be preserved for later analysis.

Install the instrument cap on the DR 900 cell holder before ZERO or READ is pushed.

In bright light conditions (e.g., direct sunlight), close the cell compartment, if applicable, with the protective cover during measurements.

If the chlorine concentration is less than 2 mg/L, use Method 8021, program number 80.

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

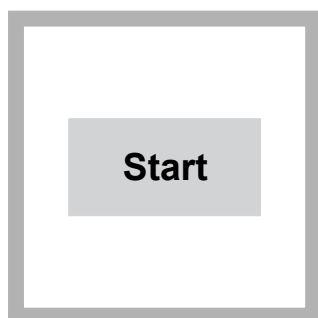
| Description   | Quantity |
|---|----------|
| DPD Free Chlorine Reagent Powder Pillows, 25-mL   | 1        |
| Sample cells (For information about sample cells, adapters or light shields, refer to <a href="#">Instrument-specific information</a> on page 1.) | 2        |

Refer to [Consumables and replacement items](#) on page 5 for order information.

## Sample collection

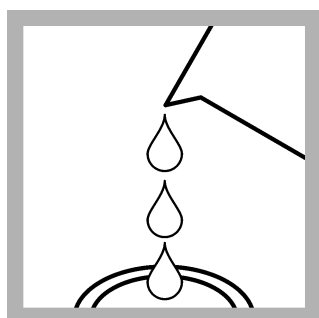
- Analyze the samples immediately. The samples cannot be preserved for later analysis.
- Chlorine is a strong oxidizing agent and is unstable in natural waters. Chlorine reacts quickly with various inorganic compounds and more slowly with organic compounds. Many factors, including reactant concentrations,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

## Powder pillow procedure

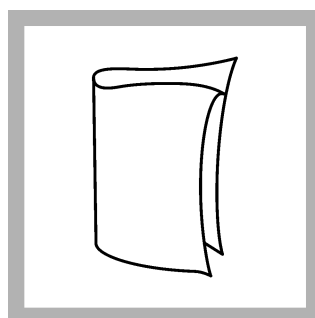


**1. Start program 88 Chlorine F&T HR.** For information about sample cells, adapters or light shields, refer to [Instrument-specific information](#) on page 1.

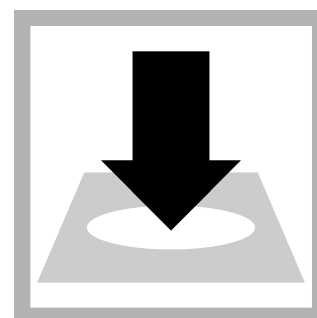
**Note:** Although the program name can be different between instruments, the program number does not change.



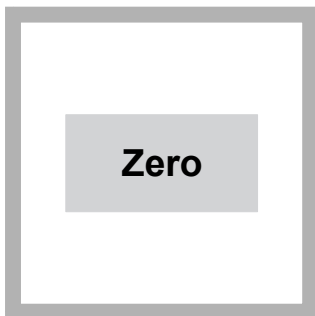
**2. Prepare the blank:** Fill a sample cell to the 5-mL mark with sample.



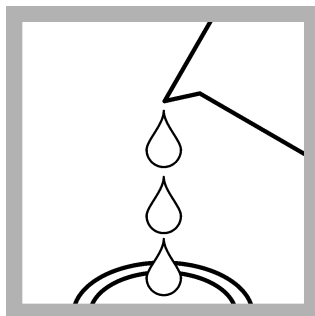
**3. Clean the blank sample cell.**



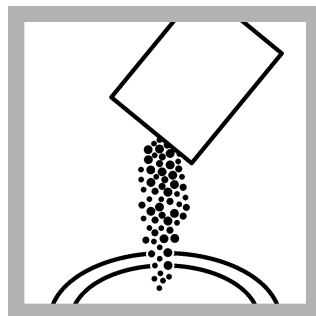
**4. Insert the blank into the cell holder.**



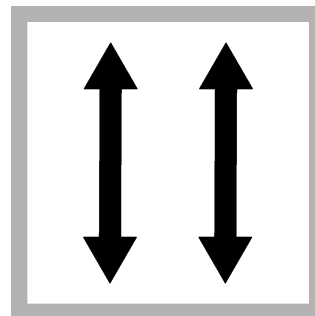
5. Push **ZERO**. The display shows 0.0 mg/L Cl<sub>2</sub>.



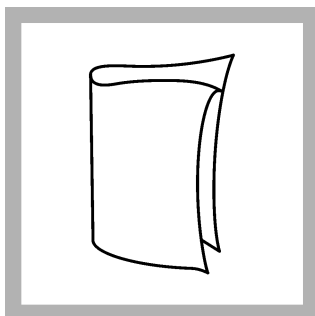
6. **Prepare the sample:** Fill a second sample cell to the 5-mL mark with sample.



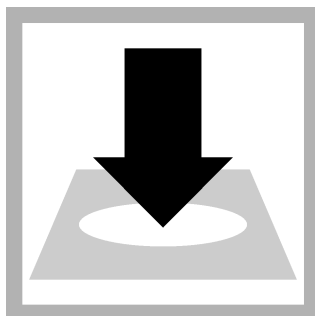
7. Add the contents of one DPD Free Chlorine Powder Pillow for 25-mL samples to the sample.



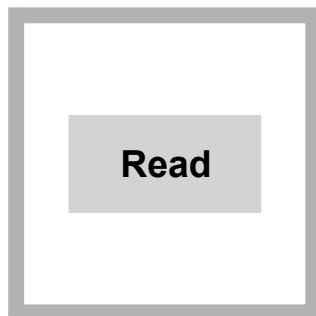
8. Put the stopper on the sample cell. Shake the sample cell for about 20 seconds to dissolve the reagent. A pink color shows if chlorine is in the sample.



9. Clean the sample cell.



10. Insert the prepared sample into the cell holder.



11. Push **READ**. Results show in mg/L Cl<sub>2</sub>.

## Interferences

| Interfering substance  | Interference level   |
|--|--|
| Acidity  | More than 150 mg/L CaCO <sub>3</sub> . The full color may not develop or the color may fade instantly. Adjust to pH 6–7 with 1 N Sodium Hydroxide. 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.   |
| Alkalinity   | More than 250 mg/L CaCO <sub>3</sub> . 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 <sub>2</sub>   | Positive interference at all levels  |
| Chlorine Dioxide, ClO <sub>2</sub>   | Positive interference at all levels  |
| Inorganic chloramines  | Positive interference at all levels  |
| Chloramines, organic   | May interfere  |
| Hardness   | No effect at less than 1000 mg/L as CaCO <sub>3</sub>  |
| Manganese, Oxidized (Mn <sup>4+</sup> , Mn <sup>7+</sup> ) or Chromium, Oxidized (Cr <sup>6+</sup> ) | Pre-treat the sample as follows: <ol style="list-style-type: none"> <li>1. Adjust the sample pH to 6–7.</li> <li>2. Add 3 drops of Potassium Iodide (30-g/L) to 10 mL of sample.</li> <li>3. Mix and wait 1 minute.</li> <li>4. Add 3 drops of Sodium Arsenite (5-g/L) and mix.</li> <li>5. Use the test procedure to measure the concentration of the treated sample.</li> <li>6. Subtract this result from the result without the treatment to obtain the correct chlorine concentration.</li> </ol> |

| Interfering substance                        | Interference level  |
|--|---|
| Ozone  | Positive interference at all levels   |
| Peroxides                                    | May interfere   |
| Highly buffered samples or extreme sample pH | Can prevent the correct pH adjustment of the sample by the reagents. Sample pre-treatment may be necessary. Adjust to pH 6–7 with acid (Sulfuric Acid, 1.000 N) or base (Sodium Hydroxide, 1.00 N). |

### Monochloramine interference

For conventional free chlorine disinfection (beyond the breakpoint), typical monochloramine concentrations are very low. If monochloramine is present in the sample, its interference in the free chlorine test depends on the sample temperature, relative amount of monochloramine to free chlorine and the time required to do the analysis. Typical interference levels of monochloramine as mg/L Cl<sub>2</sub> in the free chlorine test are shown in Table 2 (1 minute test time). Measure the monochloramine levels with method 10200 for Chloramine (Mono) and Free Ammonia.

**Table 2 Monochloramine interference at different sample temperatures**

| NH <sub>2</sub> Cl (as Cl <sub>2</sub> ) | 5 °C (41 °F) | 10 °C (50 °F) | 20 °C (68 °F) | 30 °C (83 °F) |
|--|--------------|---------------|---------------|---------------|
| 1.2 mg/L                                 | 0.15         | 0.19          | 0.30          | 0.29          |
| 2.2 mg/L                                 | 0.35         | 0.38          | 0.55          | 0.61          |
| 3.2 mg/L                                 | 0.38         | 0.56          | 0.69          | 0.73          |

### 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 Standard Solution, 2-mL PourRite® Ampule, 50–75 mg/L (use mg/L on label)
- Breaker, PourRite Ampules
- Pipet, TenSette®, 0.1–1.0 mL and tips
- Mixing cylinders, 10-mL (3)

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 mL, 0.2 mL and 0.3 mL of the standard solution, respectively, to three 5-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 |
|---------|--------------------------|-------------------------------------|--|
| 88      | 5.4 mg/L Cl <sub>2</sub> | 5.3–5.5 mg/L Cl <sub>2</sub>        | 0.04 mg/L Cl <sub>2</sub>                                |

## Summary of method

The range of analysis using the DPD method for free chlorine can be extended by adding more indicator in proportion to sample volume. Thus, a larger fill powder pillow of DPD Free Chlorine Reagent is added to a 5-mL sample portion. 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, the intensity of which is proportional to the chlorine concentration. The measurement wavelength is 530 nm for spectrophotometers or 520 nm for colorimeters.

## Consumables and replacement items

### Required reagents

| Description                                    | Quantity/Test | Unit    | Item no. |
|--|---------------|---------|----------|
| DPD Free Chlorine Reagent Powder Pillow, 25-mL | 1             | 100/pkg | 1407099  |

### Recommended standards and apparatus

| Description  | Unit   | Item no. |
|--|--------|----------|
| Ampule Breaker, 2-mL PourRite <sup>®</sup> Ampules                         | each   | 2484600  |
| Ampule Breaker, 10-mL Voluette <sup>®</sup> Ampules                        | each   | 2196800  |
| Chlorine Standard Solution, 2-mL PourRite <sup>®</sup> Ampules, 50–75 mg/L | 20/pkg | 1426820  |
| Chlorine Standard Solution, 2-mL PourRite <sup>®</sup> Ampules, 25–30 mg/L | 20/pkg | 2630020  |
| Chlorine Standard Solution, 10-mL Voluette <sup>®</sup> Ampule, 50–75 mg/L | 16/pkg | 1426810  |
| SpecCheck <sup>™</sup> Gel Secondary Standard Kit, Chlorine DPD, 0–10 mg/L | 4/pkg  | 2893300  |

### Optional reagents and apparatus

| Description  | Unit       | Item no. |
|--|------------|----------|
| Mixing cylinder, graduated, 25-mL                      | each       | 2088640  |
| DPD Free Chlorine Reagent Powder Pillows, 10-mL        | 1000/pkg   | 2105528  |
| DPD Free Chlorine Reagent Powder Pillows, 10-mL        | 300/pkg    | 2105503  |
| Paper, pH, 0–14 pH range                               | 100/pkg    | 2601300  |
| Pipet, TenSette <sup>®</sup> , 0.1–1.0 mL              | each       | 1970001  |
| Pipet tips for TenSette <sup>®</sup> Pipet, 0.1–1.0 mL | 50/pkg     | 2185696  |
| Pipet tips for TenSette <sup>®</sup> Pipet, 0.1–1.0 mL | 1000/pkg   | 2185628  |
| Potassium Iodide, 30-g/L                               | 100 mL     | 34332    |
| Sodium Arsenite, 5-g/L                                 | 100 mL     | 104732   |
| Sodium Hydroxide Standard Solution, 1.0 N              | 100 mL MDB | 104532   |
| Sulfuric Acid Standard Solution, 1 N                   | 100 mL MDB | 127032   |

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**Optional reagents and apparatus (continued)**

| <b>Description</b>                       | <b>Unit</b> | <b>Item no.</b> |
|--|-------------|-----------------|
| Test tube rack, stainless steel          | each        | 1864100         |
| Thermometer, non-mercury, -10 to +225 °C | each        | 2635700         |



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