Chlorine, Free

DOC316.53.01024

DPD Method[1] **Method 10102**

0.09 to 5.00 mg/L Cl_2 **Test 'N Tube™ Vials**

Scope and application: For testing higher levels of free chlorine (hypochlorous acid and hypochlorite ion) in drinking water, cooling water and industrial process 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 adapter and light shield requirements for the instruments that use them.

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

Table 1 Instrument-specific information for test tubes

Instrument	Adapters	Light shield
DR 6000, DR 5000	—	—
DR 3900	—	LZV849
DR 3800, DR 2800, DR 2700	—	LZV646
DR 1900	9609900 (D[1])	—
DR 900	4846400	Cover supplied with the instrument

[1] The D adapter is not available with all instrument versions.

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.
DR 3900, DR 3800, DR 2800 and DR 2700: Install the light shield in Cell Compartment #2 before this test is started.
For the best results, measure the reagent blank value for each new lot of reagent. Replace the sample with deionized water in the test procedure to determine the reagent blank value. Subtract the reagent blank value from the sample results automatically with the reagent blank adjust option.
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

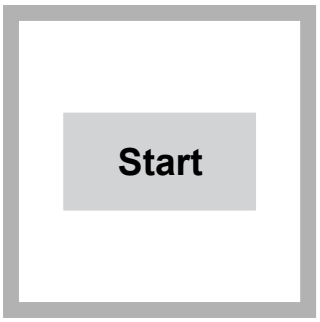
Description	Quantity
Light shield (For information about sample cells, adapters or light shields, refer to Instrument-specific information on page 1.)	1
Test 'N Tube™ DPD Free Chlorine Reagent	1
Wipes, disposable	varies

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

Sample collection

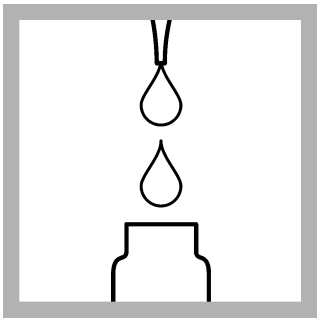
- Analyze the samples immediately. The samples cannot be preserved for later analysis.
- Chlorine is a strong oxidizing agent and is unstable in natural waters. Chlorine reacts quickly with various inorganic compounds and more slowly with organic compounds. Many factors, including reactant concentrations,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

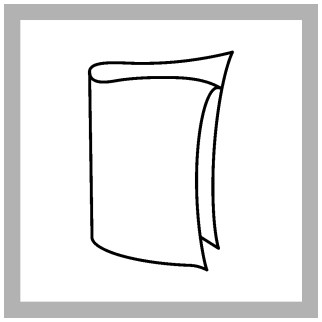


1. Start program **89 Chlorine F&T TNT**. For information about sample cells, adapters or light shields, refer to Instrument-specific information on page 1.

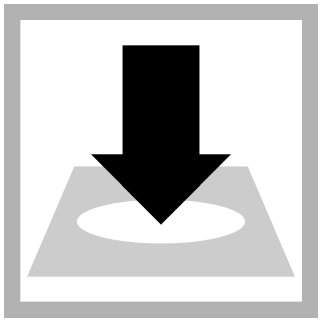
Note: *Although the program name can be different between instruments, the program number does not change.*



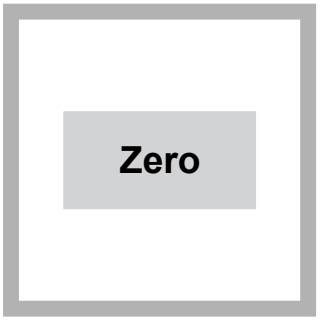
2. Prepare the blank: Fill an empty Test 'N Tube vial to the top of the label with sample.



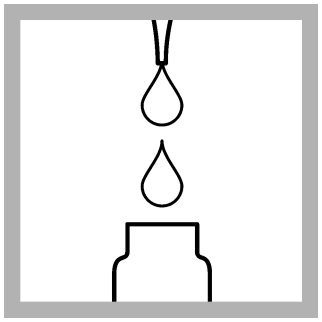
3. Clean the blank vial.



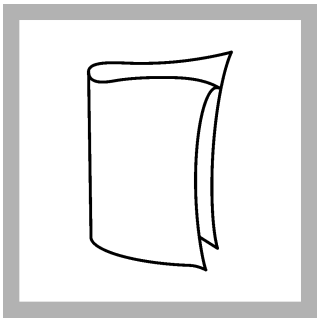
4. Insert the blank vial into the 16-mm cell holder.



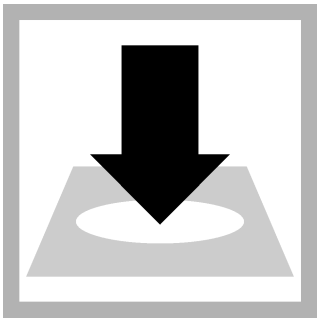
5. Push **ZERO**. The display shows 0.00 mg/L Cl_2.



6. Prepare the sample: Remove the cap from a Free Chlorine DPD Test 'N Tube. Fill the vial to the top of the label with sample.



7. Clean the sample vial.



8. Insert the sample vial into the 16-mm cell holder.

9. Push **READ**. Results show in mg/L Cl_2.

Interferences

Interfering substance	Interference level
Acidity	More than 150 mg/L $CaCO_3$. 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 $CaCO_3$. 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	Positive interference at all levels
Chlorine Dioxide, ClO_2	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 $CaCO_3$
Manganese, Oxidized (Mn^{4+}, Mn^{7+}) or Chromium, Oxidized (Cr^{6+})	Pre-treat the sample as follows: **1.** Adjust the sample pH to 6–7. **2.** Add 3 drops of Potassium Iodide (30-g/L) to 10 mL of sample. **3.** Mix and wait 1 minute. **4.** Add 3 drops of Sodium Arsenite (5-g/L) and mix. **5.** Use the test procedure to measure the concentration of the treated sample. **6.** Subtract this result from the result without the treatment to obtain the correct chlorine concentration.

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_2 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_2Cl (as Cl_2)	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

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 10-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
89	2.68 mg/L Cl_2	2.63–2.73 mg/L Cl_2	0.03 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, 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.
Test 'N Tube™ DPD Free Chlorine Reagent	1	50/pkg	2105545

Recommended standards and apparatus

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
Chlorine Standard Solution, 2-mL PourRite® Ampules, 25–30 mg/L	20/pkg	2630020
Ampule Breaker, 2-mL PourRite® Ampules	each	2484600
Ampule Breaker, 10-mL Voluette® Ampules	each	2196800

Optional reagents and apparatus

Description	Unit	Item no.
Paper, pH, 0–14 pH range	100/pkg	2601300
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
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
Test tube rack, stainless steel	each	1864100
Thermometer, non-mercury, –10 to +225 °C	each	2635700
Wipes, disposable	280/pkg	2097000

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