Chlorine, Free

DOC316.53.01256

USEPA[1] Indophenol Method

Method 10241

0.04 to 4.50 mg/L Cl_2

Powder Pillows

Scope and application: For the determination of residual free chlorine levels in the presence of manganese, chloramines and other oxidants that interfere with DPD colorimetric, DPD titrimetric and amperometric methods for free chlorine. For use in potable water, chlorinated drinking water, swimming pool water and treated wastewater effluent. This product has not been evaluated to test for chlorine and chloramines in medical applications in the United States.

[1] Hach Method 10241 is USEPA approved for the determination of free chlorine in drinking water, Federal Register Volume 81, Number 138 (Tuesday, July 19, 2016).

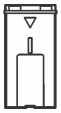
Test preparation

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
DR6000	—	The orientation key is toward the arrow on the universal cell adapter.	4864302 
DR5000	A23618	The orientation key is toward the user.	
DR3900	LZV846 (A)	The orientation key is away from the user.	
DR1900	9609900 or 9609800 (C)	The orientation key is toward the arrow on the adapter.	
DR/850, DR/890	—	The orientation key is at the 2 o'clock position.	
DR900	—	The orientation key is toward the user.	
DR3800 DR2800 DR2700	LZV585 (B)	The 1-cm path is aligned with the arrow on the adapter.	5940506 

Before starting

Install the instrument cap on the DR900 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.
This method uses the same program number as the indophenol monochloramine method.
The sample and reagent from one analysis can contaminate other analyses and interfere with the test results. Make sure to rinse the cells and caps several times with deionized water or with the sample water before each test.
Do not switch the caps of the sample cells between the blank and sample during the analysis.
Tap the sample cells lightly on a hard surface or slowly invert the cells to remove air bubbles from the cell walls.
Make sure to keep the cap on the sample cells when not in use to prevent contamination from ammonia.

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

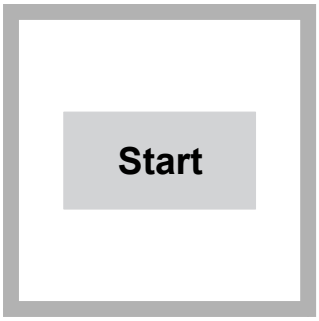
Description	Quantity
Freechlor F Reagent Solution	5 drops
Monochlor F reagent pillows	2
Sample cells (For information about sample cells, adapters or light shields, refer to Instrument-specific information on page 1.)	2

Refer to Consumables and replacement items on page 7 for order information.

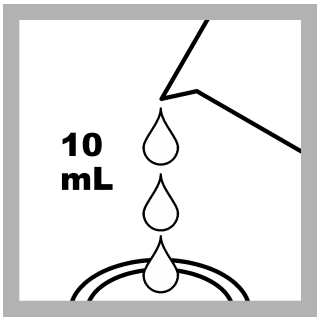
Sample collection

- 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.

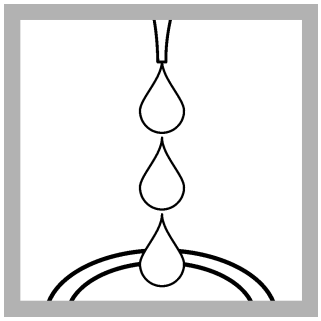
Test procedure



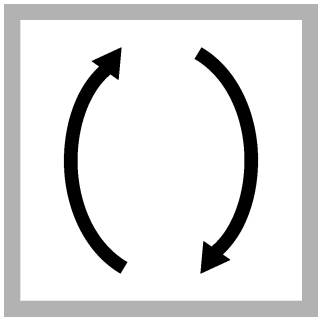
1. Start program **66, Monochloramine LR**. For information about sample cells, adapters or light shields, refer to Instrument-specific information on page 1.



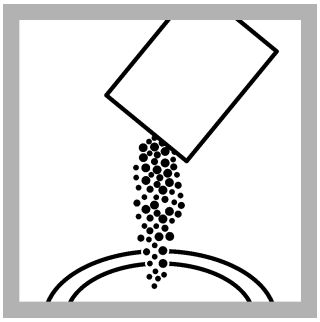
2. Fill two sample cells with 10 mL of sample. Label one cell as the sample. Label the other cell as the blank.



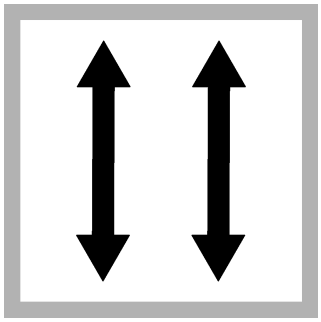
3. Add 5 drops of the Freechlor F Reagent to the sample.



4. Put the stopper on the sample cell. Invert to mix.

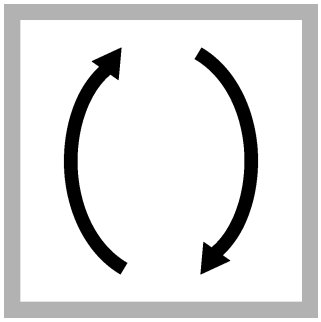


5. Add the contents of one Monochlor F Reagent Powder Pillow to each sample cell.

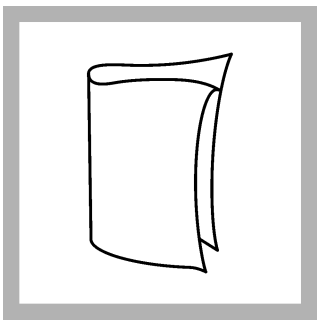


6. Close the sample cells. Shake the sample cells for approximately **20 seconds** to dissolve the reagent. A green color shows if free chlorine is in the sample.

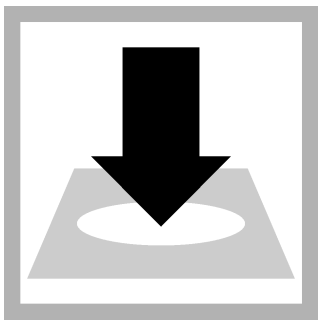
7. Start the instrument timer. A 5-minute reaction time starts. Adjust the reaction time for the sample temperature. Refer to Color development time on page 3.



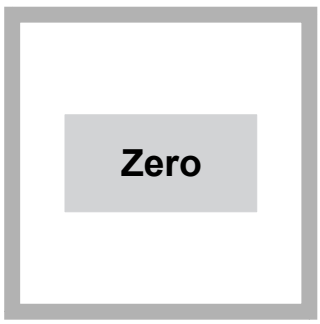
8. When the timer expires, invert the blank to mix.



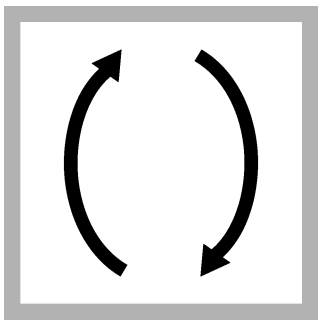
9. Clean the blank sample cell.



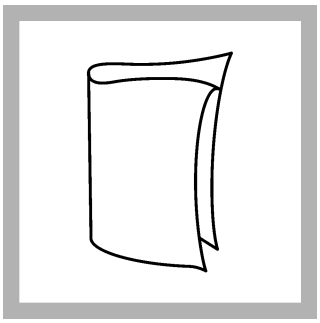
10. Insert the blank into the cell holder.



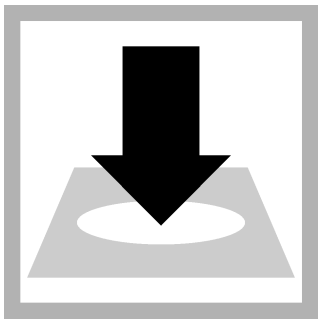
11. Push **ZERO**. The display shows 0.00 mg/L Cl_2.



12. Invert the prepared sample to mix.



13. Clean the prepared sample cell.



14. Insert the prepared sample into the cell holder.

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

Color development time

Test results are strongly influenced by the sample temperature. The reaction times in the procedure are for samples at 18–20 ºC (64–68 ºF). Adjust the reaction times for the sample temperature as shown in Table 2. The color is stable for a maximum of 15 minutes after the specified development time.

If the sample temperature is less than 10 °C (50 °F), especially if the sample is measured outdoors in cold weather, measure the prepared sample again 5 to 10 minutes after the development time given in Table 2. Measure the prepared sample again to make sure that the reaction has completed. The colorimetric reaction has completed if the results do not increase by more than 10% within 10 minutes of the development time.

Table 2 Color development time

Sample temperature (°C)	Sample temperature (°F)	Development time (minutes)
5	41	10
7	45	9
9	47	8
10	50	8
12	54	7
14	57	7
16	61	6
18	64	5
20	68	5
23	73	2.5
25	77	2
> 25	> 77	2

Interferences

Table 3 shows the substances that were tested for interference and do not interfere at or below the levels that are shown. Table 4 shows a list of interfering substances and interference levels.

Table 3 Non-interfering substances

Substance	Interference level
Alanine	1 mg/L N
Aluminum	10 mg/L Al
Bromide	100 mg/L Br^-
Bromine	15 mg/L Br_2
Calcium	1000 mg/L as $CaCO_3$
Chloride	18,000 mg/L Cl^-
Chlorine Dioxide	5 mg/L ClO_2
Chromium (III)	5 mg/L Cr^{3+}
Copper	10 mg/L Cu
Cyanide	10 mg/L CN^-
Dichloramine	10 mg/L as Cl_2
Fluoride	5 mg/L F^-
Glycine	1 mg/L N
Iodine	4 mg/L I_2
Iron (II)	10 mg/L Fe^{2+}
Iron (III)	10 mg/L Fe^{3+}
Lead	10 mg/L Pb
Manganese (+7)	3 mg/L MnO_4^-
Nitrate	100 mg/L N
Nitrite	50 mg/L N

Table 3 Non-interfering substances (continued)

Substance	Interference level
Oxone®[1] (potassium peroxomonopersulfate)	30 mg/L
Phosphate	100 mg/L PO_4^{3-}
Silica	100 mg/L SiO_2
Sulfate	2600 mg/L SO_4^{2-}
Tyrosine	1 mg/L N
Urea	10 mg/L N
Zinc	5 mg/L Zn

Table 4 Interfering substances

Interfering substance	Interference level
Ozone[2]	> 1 mg/L O_3
Sulfide[2]	> 0.5 mg/L S^{2-}

Test applications

Finished chlorinated drinking waters and distributions systems

Finished waters contain free chlorine and various levels of organic chloramines and inorganic contaminants. The reaction of free chlorine with easily oxidizable species is thought to be complete and the remaining free chlorine is in a steady-state equilibrium. Replicate analyses for free chlorine on this type of water should give equivalent results. It is especially important when testing water where free chlorine residual levels are low to obey all precautions that refer to sample cell cleanliness, water temperature and sampling techniques.

At breakpoint

These waters can contain a mixture of free chlorine, chloramines and nuisance residuals depending on water temperature, mixing efficiencies, sampling location and distance beyond the theoretical breakpoint. The water can be in a state of "dynamic equilibrium" and the chemical speciation can change quickly, especially if at or near the breakpoint. The chemical speciation can change dynamically in both the blank cell and the sample cell. Start the analysis immediately on these types of samples. Test results can be difficult to reproduce on duplicate samples because of the dynamics of the water. Test results are best used to identify free chlorine trends and to monitor changes because of different mixing efficiencies, sampling locations, temperature changes, increased chlorine feed rates, and so forth.

In chloramination kinetic studies

These waters will contain a mixture of free chlorine and chloramines depending on water temperature, mixing efficiencies, sampling locations, feed rates for chlorine and ammonia and contact time. The water is in a state of "dynamic equilibrium" and the chemical speciation can change quickly depending on water conditions. The chemical speciation can change dynamically in both the blank cell and the sample cell. Start the analysis immediately on these types of samples. Test results can be difficult to reproduce on duplicate samples because of the dynamics of the water. Test results are best used to identify free chlorine trends and to monitor changes based on changes in mixing efficiencies, sampling locations, water temperature changes, increased chlorine feed rates, and so forth.

[1] Oxone is a registered trademark of E.I. du Pont de Nemours & Co., Inc.
[2] This compound does not normally exist with free chlorine.

With other oxidants

Other oxidants can include Oxone, permanganate, chlorine dioxide, bromine and iodine. It is assumed that the free chlorine residual has stabilized in the presence of the other oxidants. Replicate analyses for free chlorine on this type of water is expected to give equivalent results. The levels of alternate oxidants that can be present without interference have been tested only in laboratory bench studies (refer to Table 3 on page 4). Field data for free chlorine in the presence of these oxidants is not available.

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, 25–30 mg/L (use concentration on label)
- Ampule 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
66	3.51 mg/L Cl_2	3.47–3.55 mg/L Cl_2	0.04 mg/L Cl_2

Summary of method

An ammonia solution at a pH of 8.3 is added to a sample that contains free chlorine. The free chlorine is immediately converted into monochloramine (NH_2Cl). In the presence of a cyanoferrate catalyst, the monochloramine reacts with a substituted phenol to form an intermediate monoimine compound. The intermediate couples with excess substituted phenol to form a green indophenol compound, which is proportional to the amount of free chlorine in the sample. A sample blank that contains Monochlor F Reagent corrects for background color from the reagent and sample. The measurement wavelength is 655 nm for spectrophotometers or 610 nm for colorimeters.

Consumables and replacement items

Required reagents

Description	Quantity/Test	Unit	Item no.
Freechlor F Reagent Solution	5 drops	50-mL SCDB	2964926
Monochlor F Reagent Pillows	2	100/pkg	2802299

Recommended standards

Description	Unit	Item no.
Chlorine Standard Solution, 2-mL PourRite® Ampules, 50–75 mg/L	20/pkg	1426820
Chlorine Standard Solution, 10-mL Voluette® Ampule, 50–75 mg/L	16/pkg	1426810
Chlorine Standard Solution, 2-mL PourRite® Ampule, 25-30 mg/L	20/pkg	2630020

Optional reagents and apparatus

Description	Unit	Item no.
PourRite® Ampule Breaker, 2 mL	each	2484600
Ampule Breaker, 10-mL Voluette® Ampules	each	2196800
Pipet, TenSette®, 0.1–1.0 mL	each	1970001
Pipet tips for TenSette® Pipet, 0.1–1.0 mL	50/pkg	2185696

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