

chlorine, free

DPD-2 method¹

0.06 to 2.00 mg/L Cl₂

powder pillows

scope and application: For testing free chlorine (hypochlorous acid and hypochlorite ion) in water, treated waters, estuary and seawater.

¹ Adapted from Standard Methods for the Examination of Water and Wastewater.




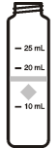
test preparation

instrument specific information

Table 1 shows the sample cell and cell orientation requirements for the SUEZ instruments that can use this Analytical Procedure (AP).

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

Table 1 Instrument-specific information

Instrument	Sample cell orientation	Sample cell
DR 2800 DR 1900	The fill line is to the right.	L2793.0002 
DR 900	The fill lines and diamond mark are toward the display.	L1976 

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before starting

After the reagent is added, a pink color will develop if chlorine is present.
Accuracy is not affected by undissolved reagent powder.
Dilute the sample if the sample initially becomes dark pink, then immediately goes clear after the reagent addition.
If the test result is over-range, dilute the sample with a known volume of high quality, chlorine demand-free water and repeat the test. Some loss of chlorine may occur due to the dilution. Multiply the result by the dilution factor.
Samples must be analyzed immediately after collection and cannot be preserved for later analysis.
Collect the sample in a glass container. Chlorine can react with plastic containers. Refer to Sample collection on page 2.
Do not use the same sample cells for free and total chlorine. If trace iodide from the total chlorine reagent is carried over into the free chlorine determination, monochloramine will interfere. It is best to use separate, dedicated sample cells for free and total chlorine measurements.
The sample temperature must be 20–25 °C (68–77 °F) for accurate results.
Install the instrument cap on the DR 900 cell holder before ZERO or READ is pushed.
Refer to the instrument user manual for timer operation instructions.
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.
Clean the external surface of the sample cells before insertion into the instrument cell holder. Use a damp towel and then a dry towel to remove fingerprints or other marks.
Highly buffered samples or extreme pH may exceed the buffering capacity of the reagent and require sample pre-treatment.
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.
Results that are not within the working range of this procedure are not valid.

sample collection

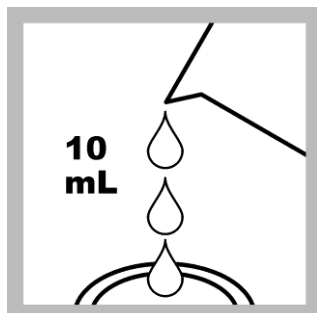
- Analyze the samples immediately. The samples cannot be preserved for later analysis.
- Chlorine is a strong oxidizing agent and is unstable in natural waters. Chlorine reacts quickly with various inorganic compounds and more slowly with organic compounds. Many factors, including reactant concentrations,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

Procedure

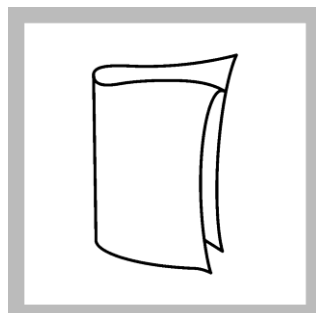


1. Start program **80 Chlorine F&T PP**. For information about sample cells, adapters or light shields, refer to Instrument specific information on page 1.

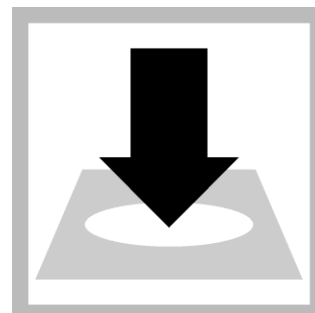
Note: Although the program name can be different between instruments, the program number does not change.



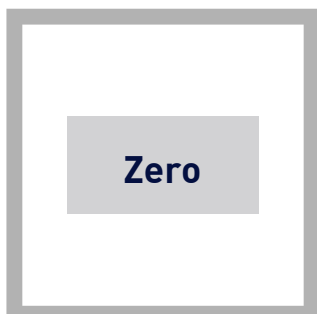
2. **Prepare the blank:** Fill the sample cell with 10 mL of sample.



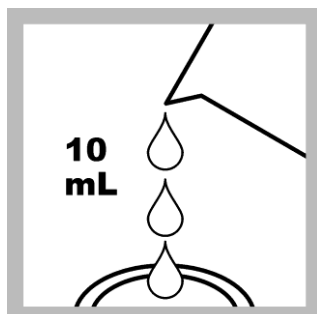
3. Clean the blank sample cell.



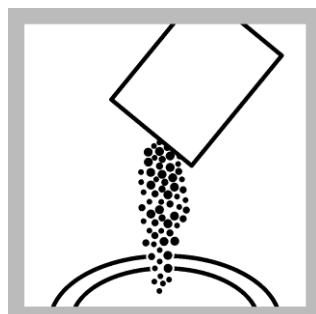
4. Insert the blank into the cell holder.



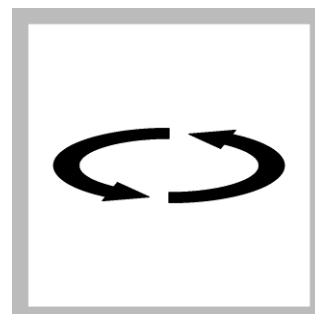
5. Push **ZERO**. The display shows 0.00 mg/L Cl₂.



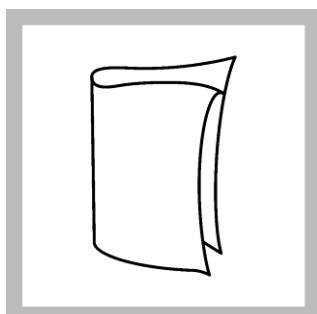
6. **Prepare the sample:** Fill a second sample cell with 10 mL of sample.



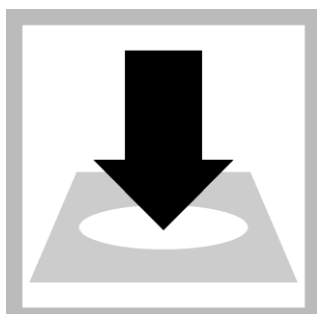
7. Add the contents of one DPD-2 Free Chlorine powder pillow to the sample cell.



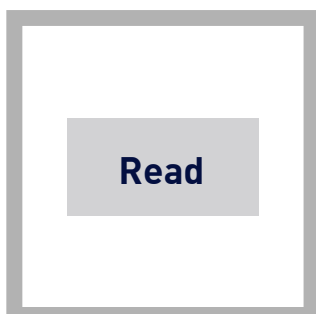
8. Immediately swirl the sample cell for 20 seconds to mix. A pink color shows if chlorine is present. Go to the next step immediately



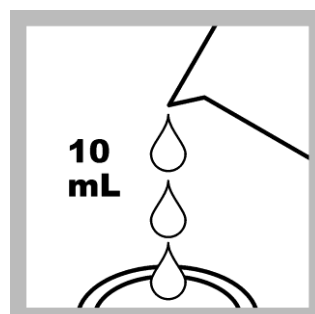
9. Clean the prepared sample cell.



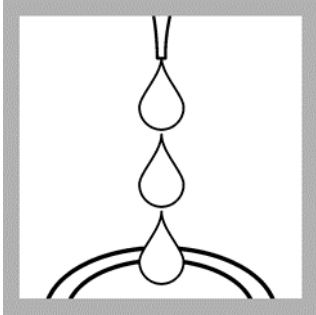
10. Insert the prepared sample into the cell holder.



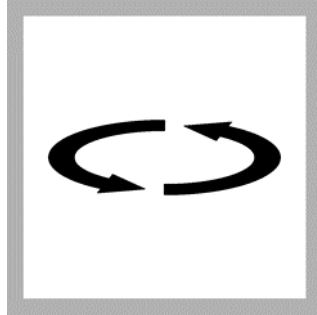
11. Exactly 30 seconds after the DPD-2 reagent is added, push **READ**. Results show in mg/L Cl₂.



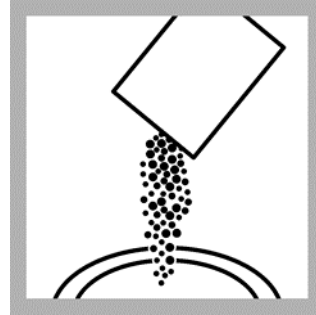
12. **Matrix correction sample:** Fill a third sample cell with 10 mL of sample.



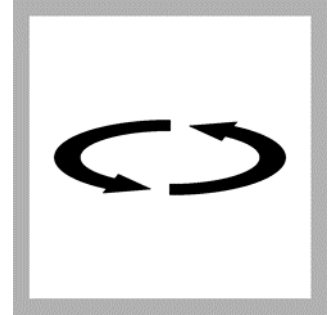
13. Add 0.5 mL of Free Chlorine Arsenite Reagent.



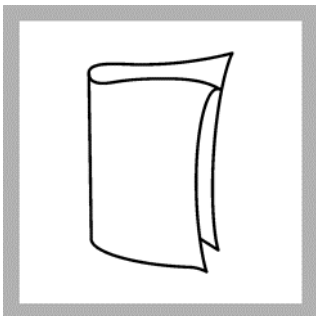
14. Swirl to mix. Wait 1 minute.



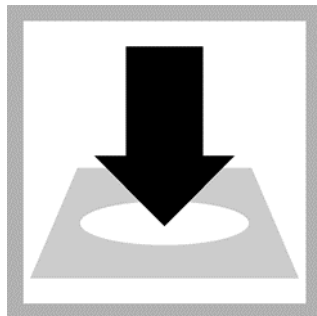
15. One minute after the arsenite reagent is added, add the contents of one DPD-2 Free Chlorine Powder Pillow to the correction sample.



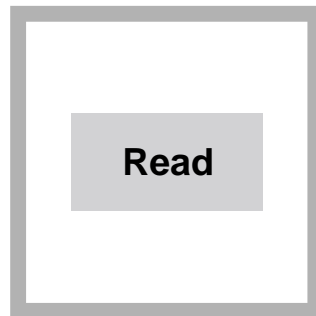
16. Swirl vigorously to dissolve the powder.



17. Immediately clean the correction sample.



18. Insert the correction sample into the cell holder.



19. Exactly 30 seconds after the powder pillow is added, push **READ**. Results show in mg/L Cl₂. The free chlorine in the sample is equal to the reading in step 11 minus the reading in step 19.

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. Neutralize to pH 6–7 with 1 N Sodium Hydroxide. Measure the amount to be added on a separate sample aliquot, then add the same amount to the sample that is tested. Correct the test result for the dilution caused by the volume addition.
Alkalinity	More than 250 mg/L CaCO ₃ . The full color may not develop or the color may fade immediately. Neutralize 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 caused by the volume addition.
Bromine	Causes positive interference
Chlorine Dioxide	Causes positive interference
Chloramines, organic	May cause positive interference
Hardness	No effect at less than 1000 mg/L as CaCO ₃
Iodine	Causes positive interference
Manganese, Oxidized (Mn ⁴⁺ , Mn ⁷⁺) or Chromium, Oxidized (Cr ⁶⁺)	The use of the matrix correction sample in this test procedure corrects for manganese and chromium positive interferences.
Monochloramine	Causes a gradual drift to higher readings. When read within 1 minute after reagent addition, 3 mg/L monochloramine causes less than a 0.1 mg/L increase in the reading.
Ozone	Causes positive interference
Peroxides	May cause positive interference
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 N) or base (Sodium Hydroxide, 1 N). Correct the test result for the dilution caused by the volume additions.

pollution prevention and waste management

If sodium arsenite was added to the sample for manganese or chromium interferences, the reacted samples will contain arsenic and may require special disposal consideration. Dispose of reacted solutions according to local, state and federal regulations.

accuracy check

standard additions method (sample spike)

1. Open a Chlorine Standard Solution Ampule.
2. Prepare three spiked samples:
 - a. Use a pipet to add 0.1 mL, 0.2 mL and 0.3 mL of the standard solution, respectively, to three 25-mL portions of fresh sample.
 - b. Swirl gently to mix.
3. Use the test procedure to measure the concentration of 10 mL of each of the spiked samples. Start with the smallest sample spike. Measure each of the spiked samples in the instrument.
4. Compare the expected result to the actual result. Each 0.1 mL of standard solution causes an incremental increase in chlorine. The exact increase depends on the concentration in the ampule. Refer to the certificate that is supplied with the ampule for this value.

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
80	1.25 mg/L Cl ₂	1.23–1.27 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, the intensity of which is proportional to the chlorine concentration. The Free Chlorine Arsenite Reagent reduces the free chlorine, allowing the method to measure and correct for matrix interferences. The measurement wavelength is 530 nm for spectrophotometers or 520 nm for colorimeters.

lab supply code numbers

Required reagents*

Description	Quantity/test	Unit	Code
Free Chlorine Arsenite Reagent	0.5 mL	120 mL	L2095.0120
DPD-2 Free Chlorine Reagent Powder Pillow, 10-mL	2	100/pkg	L2385

* Review the Safety Data Sheets (MSDS/SDS) for the chemicals that are used. Use any recommended personal protective equipment.

Spectrophotometers and colorimeters (select one)

Description	Quantity/Test	Unit	Code
DR 1900 Spectrophotometer with accessories	1	each	L1901
Sample cells, 10-mL square, matched pair	2	2/pkg	L2793.0002
DR 900 Colorimeter with accessories	1	each	L901
Sample cells, 10-20-25-mL, with cap	2	6/pkg	L1976

Optional reagents and apparatus

Description	Unit	Code
Chlorine Standard Solution, 10-mL Voluette® Ampule, 50–75 mg/L	16/pkg	L1219
Pipetter, adjustable volume, 1.00–10.00 mL	each	L1089
Tips for L1089 Pipetter, 10-mL	200/pkg	L20002
Pipetter, Socorex Calibra 822.1000, 100–1000 µL (EMEA only)	each	L8034
Pipetter, Socorex Calibra 832.10, 1.0–10.0 mL (EMEA only)	each	L8035
Tips for L8035 Pipetter, Socorex 312.10, 10-mL (EMEA only)	100/pkg	L8036
Tips for L8034 Pipetter, Socorex 319.1000B, 1000-µL (EMEA only)	250/pkg	L8037
Sodium Hydroxide Solution, 1 N	1000 mL	L255.1000
Sulfuric Acid Solution, 1 N	1000 mL	L283.1000
Timer, digital	each	L1941
Water, deionized	4000 mL	L243.4000