Chlorine Demand/Requirement

DOC316.53.01146

Method 10223

DPD Reagent[1]

Scope and application: To determine the chlorine demand and the chlorine requirement in drinking water production. To set up chlorine demand constants and historical background data studies on raw water quality. To determine the chlorine demand on distributed waters.

[1] Adapted from *Standard Methods for the Examination of Water and Wastewater*, Section 2350.

Test preparation

Before starting

Make sure to read all of the procedure steps before analysis starts.

Make sure to determine the magnitude of the chlorine demand in the sample and which chlorine method to use that will determine the chlorine residual.
The first time this method is used or when a new water source is analyzed, a screening test is necessary to determine an approximate chlorine demand level before a full chlorine demand test series is completed.

1. Add 0.5 mL and 1.0 mL of Chlorine Dosing Solution to a 125-mL water sample.
2. Use the contact time specified in the test plan and then analyze the chlorine residual.
3. Use the chlorine residual values to determine the specific dose requirements in the test plan. As a rule, use the HR DPD Chlorine Method (Method 10069) for raw water samples or where the chlorine residual is more than 2.0 mg/L chlorine. Use the LR DPD Chlorine Method (Method 8021) for low chlorine demand waters, such as treated waters or samples where the chlorine residual is less than 2.0 mg/L chlorine.

Complete a test plan to determine the number of sample doses, the concentration of chlorine dose additions and length of chlorine contact time. Refer to Test plan on page 5.

Prepare the sample containers, test bottles and labware before use. Refer to Prepare analysis labware on page 2.

Make sure that the sample temperature agrees with the temperature in the test plan before analysis.

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 PP, 10 mL or 25 mL	varies
Chlorine Dosing Solution ampules	varies
Sample bottles and caps	6
Bottle labels	6
pH meter	1
Thermometer	1
Pipet, TenSette, 0.1–1.0 mL and tips	1
Stir plate	1
Stir bar magnets	6
Spectrophotometer or colorimeter	1
Tweezers	1

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

Sample collection and storage

- Collect samples in clean glass or plastic bottles.
- Analyze the samples as soon as possible for best results.
- If immediate analysis is not possible, keep the samples at or below 6 °C (43 °F) for a maximum of 24 hours.
- Condition the sample to the test plan temperature before the test.

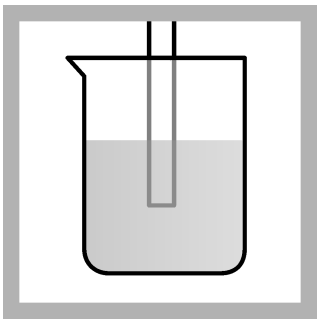
Prepare analysis labware

Pretreat the labware to remove any chlorine demand.

1. Add 1 mL of commercial bleach to 1 liter of water.

   As an alternative, add 2.0 mL of the Chlorine Dosing Solution to each bottle and fill to overflow with deionized water.
2. Soak the labware in this solution for a minimum of 1 hour.
3. Fully rinse the labware with deionized water.

Test procedure

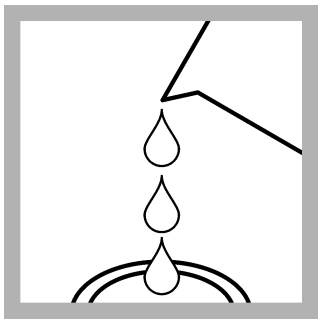


1. Measure and record the temperature and pH of the sample.

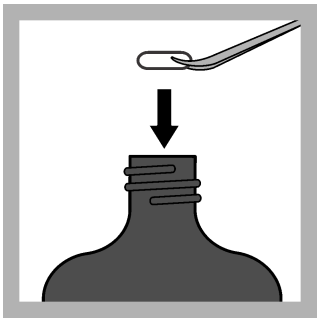
Make sure that the sample temperature agrees with the temperature in the test plan before analysis. If necessary, increase or decrease the temperature of the collected sample.

2. Prepare six chlorine demand-free bottles. Identify and put a label in bottles 1 through 6.

3. Rinse each bottle with sample.

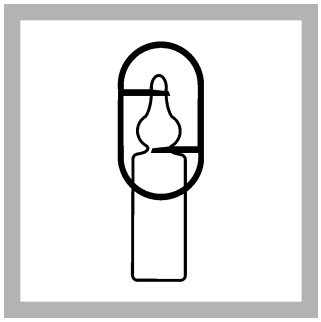


4. Fill each 118-mL bottle with approximately 100 mL of the collected sample.

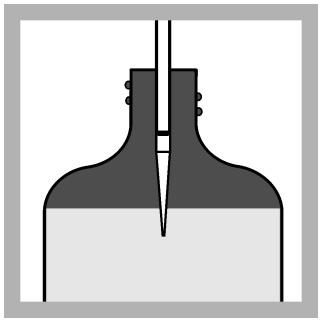


5. Use tweezers or tongs to put a stir bar magnet into each bottle. Do not touch the stir bar.

6. Put Bottle #1 on the stir plate. Set a low stir speed. A small vortex will show on the surface of the liquid.



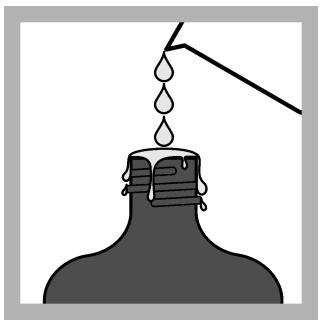
7. Use the ampule breaker to open a Chlorine Dosing Solution Ampule.



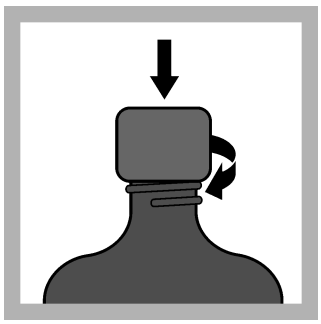
8. Use a TenSette Pipet to add 0.1 mL of the chlorine solution to Bottle #1 while stirring. Put the end of the pipet tip under the water to dispense the chlorine. To prevent highly localized areas of chlorine concentration is mandatory to stir the sample while the chlorine is added.

Each 0.1 mL of Chlorine Dosing Solution will add approximately 1.0 mg/L Cl_2 to the sample.

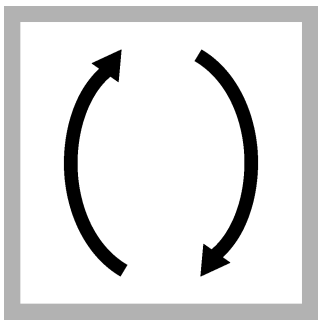
9. Set the stirrer to off.



10. Fill the bottle with sample until it overflows.

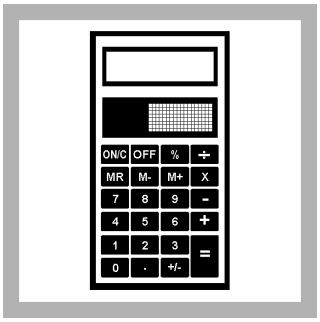


11. Put the cap on the bottle.



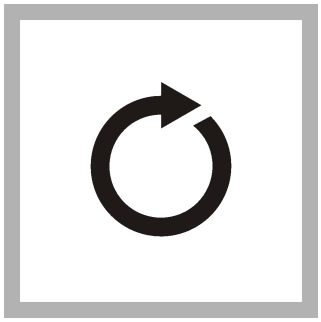
12. Invert to mix.

13. Put the sample bottle in a dark location or wrap with foil.



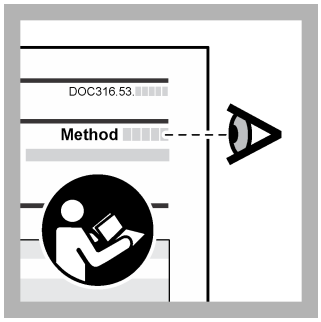
14. Calculate the actual amount of chlorine concentration. Refer to Chlorine addition calculation on page 5.

Increase or decrease the quantity of Chlorine Dosing Solution based on the estimate organic level of the sample water and chlorine contact time.

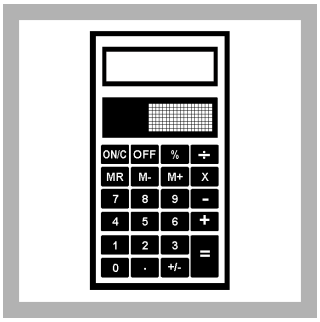


15. Do steps 8–14 again for the remaining bottles. Increase the dose of Chlorine Dosing Solution in increments of 0.1 mL. Refer to Incremental reagent dose on page 5.

If the contact time is less than 30 minutes, add the chlorine dosing solution to bottles 2–6 in successive order. Make sure to have sufficient time for complete analysis of each bottle at the specified contact time.

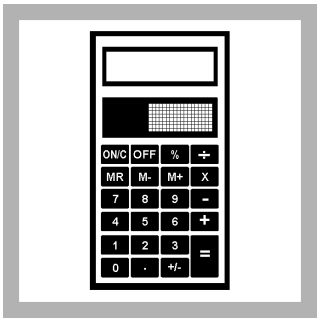


16. After the specified contact time, analyze the samples for residual Free Chlorine. Use the DPD Free Chlorine Reagent procedure (Method 8021 or Method 10069). Follow the chlorine procedure supplied with the spectrophotometer that is used.



17. Subtract the residual chlorine (step 16) from the quantity of chlorine that was added to each bottle (step 8) to determine the chlorine demand: Cl_2 Demand = Cl_2 added concentration (mg/L) – Cl_2 residual measured concentration (mg/L)[1].

Make a report of the chlorine demand based on the test plan (e.g., the sample dosed at 6.0 mg/L consumed 4.1 mg/L chlorine after 2 hours at 20 °C (68 °F) and pH 8.1).



18. Determine the chlorine requirement (chlorine dosage) that is necessary to agree with the operating objective: *Cl_2 Requirement = Cl_2 Demand + Cl_2 Residual Required.*

Make a report of the chlorine demand based on the the test plan (e.g., the sample required a dose of 3.0 mg/L chlorine to get a free chlorine residual of 1.1 mg/L chlorine after 2 hours at 20 °C (68 °F) and pH 8.1).

[1] Some bottles will have no residual chlorine if the chlorine demand is more than the quantity of chlorine added. Select a bottle that has a chlorine residual to determine the demand. Refer to Test results on page 5.

Test results

Select the sample bottle that most approximately agrees the most with the criteria that follows to calculate the chlorine demand.

Criteria 1—Residual chlorine measured is less than the chlorine dose added (0.03[2] mg/L).

Criteria 2—Residual chlorine measured is more than 0.03 mg/L

Criteria 3—Chlorine dose added is most similar to the dosage range estimated in the field.

Criteria 1 and 2 make sure that the chlorine residual and demand are more than the detection limit of the DPD method used to determine the chlorine residual. If no sample bottle agrees to all criteria, repeat the test and adjust the chlorine doses accordingly.

Chlorine addition calculation

Use the following formula to calculate the concentration of the chlorine added to each bottle.

mg/L CL_2 = Volume of standard added × ampule certificate value ÷ 125 mL

Example:

mg/L Cl_2 = 0.1 mL × certificate value of 1250 mg/L Cl_2 ÷ 125 mL = 1.0 mg/L Chlorine

Incremental reagent dose

Table 1 shows the incremental dose of a 1250-mg/L Chlorine Dosing Solution.

Table 1 Incremental dose of Cl_2 Dosing Solution

Bottle #	Cl_2 Dosing Solution (mL)	Cl_2 concentration increment (in mg/L)
1	0.1	1.0
2	0.2	2.0
3	0.3	3.0
4	0.4	4.0
5	0.5	5.0
6	0.6	6.0

Test plan

Test plans are made for different functions. Fully define and document the test plan because the specified details and objectives of the plan create reproducible test conditions to receive reproducible data. This data is useful in characterizing and optimizing a water treatment operation. The functions of a test plan can be:

1. **Identify the water system to setup a historical baseline.**
   This baseline with a chlorine demand date is used to troubleshoot water quality problems, give background information for new employees and supply additional support to monitor changes in water quality. The plan includes:
   - The standard elements of temperature, water pH, chlorine dose rate and chlorine contact time.
   - Additional specific details to let other analysts reproduce the plan.
2. **Calculate the chlorine demand of an influent raw water source.**
   Data obtained is used to analyze the effects of water source changes, blending operations and seasonal weather variations. The plan includes:
   - Source water description, sample location, time of year, specified or unusual weather events.

[2] The minimum detection limit for DPD Chlorine Method 8021 when the concentration is measured by the difference (1.412 x 0.02 mg/L).

- Additional complementary tests (plus the standard temperature, pH, chlorine dose rate and contact time). For example: TOC, turbidity or UV-254.

3. **Monitor the reduction in chlorine demand as water moves through the treatment process.**
   Data is used to set up a baseline to monitor the effects of treatment changes, seasonal water temperatures and overall changes in chlorine demand. The plan includes:

   - Specific sampling locations
   - Treatment practices in use and flow rates

Chlorine demand procedure modification

The chlorine demand procedure is an operationally-defined procedure. The procedure is user-defined and can be modified for specified requirements of the sample or the process operation. Complete chlorine demand studies with the range of conditions that are estimated for the field. Use the basic test protocol if the contact time, temperature, sample pH and chlorine concentrations are changed. Total Chlorine or Monochloramine is determined as required from the residual chlorine that was measured at the end of the specified contact time.

If modifications are made, use the guidelines that follow.

- Use a larger sample size to make smaller chlorine concentration. A 237-mL bottle (contains 250 mL when filled to overflow) is available for low chlorine demand applications. Each 0.1 mL of Chlorine Dosing Solution dose will increase the chlorine concentration by approximately 0.5 mg/L. For the chlorine addition equation, replace the 250 mL with 125 mL, refer to Chlorine addition calculation on page 5. A lower concentration Chlorine Standard Solution, 50–75 mg/L as Cl_2 is also available for testing low chlorine demand waters.
- High chlorine demand waters require larger chlorine doses. Add 0.2 mL, 0.4 mL, 0.6 mL, 0.8 mL, 1.0 mL and 1.2 mL Chlorine Dosing Solution in the test procedure for high chlorine demand waters.
- Use foil as a light protection for sample bottles made of clear colorless glass. If foil is not used, make sure to keep the sample bottles in a dark location during the contact time.
- Add a fixed amount of a pH buffer solution to each bottle to change the sample pH. Use organic-free water to prepare a reagent blank bottle. Add the same amount of buffer to the blank bottle and complete the test procedure on it. Add a sufficient quantity of buffer to give the necessary pH. Use the blank bottle to determine the chlorine demand that the buffer adds to the sample. Subtract the chlorine demand of the blank from the sample chlorine demand values.
- If the sample temperature is very different from the analysis location, test plan with an extended contact time will require temperature control. If necessary, use a refrigerator, water bath or incubator. It is important to control and document these variables to correctly duplicate the chlorine demand procedure on future samples.

Summary of method

The chlorine demand of a water sample is the difference between the concentration of chlorine added to the sample and the concentration of the chlorine residual that remains at the end of a specified contact time. The chlorine demand is a function of chlorine concentration, sample temperature, contact time and sample pH.

The chlorine requirement is the quantity of chlorine required to get a pre-determined chlorine residual at a specified contact time, pH and temperature.

Chlorine demand is caused by a complex set of reactions. Chlorine reacts with dissolved or suspended organic materials in the water to form stable chlorinated organic compounds (e.g., trihalomethanes, haloacetic acids or other chlorinated organic compounds). Some of these compounds (trihalomethanes) are referred to as disinfection by-product (DBPs) and are regulated under the Disinfection/Disinfection By-Products Rule. Other chlorinated organics contribute to taste and odor problems. As a rule, the

lower the chlorine demand the lower the amounts of DBPs formed and less taste and odor problems occur. Chlorine also is reduced by inorganic reductants that contains the water (e.g., ferrous, manganous, nitrite, sulfide and sulfite ions). The ammonia that contains the water also consumes chlorine to form chloramines.

The physical and chemical properties of the water sample have a high effect on chlorine demand. Chlorine demand studies at 10 °C will be very different than studies at 20 °C. It is mandatory that the sample temperature, pH and chlorine dose are accurately measured and recorded. It is difficult to extrapolate chlorine demand data from one water source to another. Must complete chlorine demand studies directly on the water source of interest. The chlorine demand studies gives the information required to set up chlorine demand constants, to provide usable historical data and to provide the test requirements to make repeatable and meaningful chlorine demand measurements.

Consumables and replacement items

Required reagents

Description	Quantity/test	Unit	Item no.
Chlorine Dosing Solution Ampules, 1190–1310 mg/L as Cl2, 10-mL ampules,	varies	16/pkg	2504810
DPD Free Chlorine Reagent Powder Pillows, 10 mL	1 pillow	100/pkg	2105569
OR			
DPD Free Chlorine Reagent Powder Pillows, 25 mL	1 pillow	100/pkg	1407099

Required apparatus

Description	Quantity/test	Unit	Item no.
Bottles, amber glass, 118 mL	6	6/pkg	714424
Cap, with inert Teflon™ liner, for mixing bottle	varies	12/pkg	2401812

Optional reagents and apparatus

Description	Unit	Item no.
Ampule Breaker, 10-mL Voluette® Ampules	each	2196800
Bottles, amber glass, 237 mL	6/pkg	714441
Bottles, amber glass, 1000 mL	6/pkg	714463
Buffer, pH 6.86	15/pkg	1409895
Buffer, pH 8.0	15/pkg	1407995
Buffer, pH 8.3	25/pkg	89868
Buffer solution, pH 7.0, demand-free	1 L	2155353
Caps, for 237-mL amber glass bottles	6/pkg	2166706
Cap with Teflon™/PE line, for 1000-mL amber glass bottles	6/pkg	2371006
Chlorine Standard Solution, 10-mL Voluette® Ampule, 50–75 mg/L	16/pkg	1426810
DPD Free Chlorine AccuVacs®	25/pkg	2502025
SwifTest™ dispenser for free chlorine[3]	each	2802300
DPD Total Chlorine Reagent Powder Pillows, 25 mL	100/pkg	1406499
DPD Total Chlorine Reagent Powder Pillows, 10 mL	100/pkg	2105669

[3] Includes one vial of 2105560 for 250 tests.

Optional reagents and apparatus (continued)

Description	Unit	Item no.
SwifTest™ dispenser for total chlorine [4]	each	2802400
Graduated cylinder, plastic	100 mL	108142
Incubator, BOD, compact, model 205, 220/240 Vac	each	2616202
Monochlor F Reagent Powder Pillows	100/pkg	2802299
HQ11d portable meter kit with PHC101 pH electrode	each	HQ11D53101000
Sodium Hydroxide Standard Solution, 0.100 N	500 mL	19153
Standard Methods for the Examination of Water and Wastewater (current edition)	each	2270800
Stir bar, magnetic, 2.2 x 0.5 cm (7/8 x 3/16 in.)	each	4531500
Stirrer, magnetic	each	2881200
Sulfuric Acid Std. Solution, 0.100 N	500 mL	20253
Pipet, TenSette®, 0.1–1.0 mL	each	1970001
Pipet tips for TenSette® Pipet, 0.1–1.0 mL	50/pkg	2185696
Thermometer, enviro-safe, non-mercury, -20 to 110°C (0 to 230 °F)	each	2635702
Tweezers, plastic	each	1428200
Water, organic-free	500 mL	2641549

[4] Includes one vial of 2105660 for 250 tests.

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