Chlorine Demand/Requirement

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Method 10223

DPD Reagent [1]

Scope and Application: For determining the chlorine demand and the chlorine requirement in drinking water production. For establishing chlorine demand constants and establishing historical background data on raw water quality. For determining chlorine demand on distributed waters.

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

Test preparation

Before starting the test:

Important Note: *Read Getting started and all procedure steps before performing this test.*
Develop a chlorine demand plan to detail the number of sample doses, the concentration of chlorine dose additions and length of chlorine contact time. See *Chlorine demand test plan* and *Getting started*.
Precondition sample containers, test bottles and labware to be chlorine demand free. See *Treatment of analysis labware*.
Allow time for samples to equilibrate to the temperature indicated in the test plan before beginning the test.

Collect the following items:

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
Sample Cells, 10 mL 1-inch square or 1-cm/10 mL	2
Spectrophotometer or Colorimeter	1

DPD Reagent

1. Complete a *Chlorine demand test plan*.

Measure and record the temperature and pH of the sample water to be tested.

2. Prepare 6 chlorine demand-free bottles. Rinse each bottle with sample and fill each 118-mL bottle with approximately 100 mL of the sample to be tested.

Label the bottles 1 to 6.

3. Use tweezers or tongs to insert a stir bar magnet into each bottle. Set Bottle #1 on a stir plate and stir gently. A small vortex should be visible on the surface of the liquid.

Do not handle the stir bar with fingers. Bare fingers will add chlorine demand to the sample.

4. Open a Chlorine Dosing Solution Ampule. Using a TenSette Pipet, add 0.1 mL of the chlorine solution to Bottle #1 while stirring. Immerse the end of the pipet tip under the water to dispense the chlorine. Mixing while adding the chlorine is imperative to avoid highly localized areas of chlorine concentration.

5. Turn off the stirrer and fill the bottle until it overflows with sample. Cap and invert to mix. Record the start time and put the sample bottle in the dark or wrap with foil. Each 0.1 mL of chlorine dosing solution added will add approximately 1.0 mg/L Cl_2 to the sample.

6. Calculate the actual amount of chlorine added. See *Chlorine addition calculation* for the formula and an example.

The amounts of Dosing Solution added may be increased or decreased based on the expected organic level of the sample water and chlorine contact time.

Repeat steps 4–6

7. Repeat Steps 4–6 for bottles 2 through 6. Increase the amount of chlorine added in increments of 0.1 mL. See *Incremental addition of Cl2 dosing solution* and *Getting started*. Stagger the chlorine additions if the contact time is expected to be less than 30 minutes. This allows time to perform the chlorine analysis on each sample bottle at the specified contact time.

Method 8021
or
Method 10069

8. After the prescribed contact is completed, analyze the samples for Free Chlorine using DPD Free Chlorine Reagent. Use Method 8021 if the desired chlorine residual is below 2.0 mg/L Cl_2 or Method 10069 if residuals of greater than 2.0 mg/L Cl_2 are required. Follow the procedure supplied with the spectrophotometer or colorimeter being used.

DPD Reagent (continued)

9. Subtract the residual chlorine determined in Step 8 from the original amount of chlorine added to each bottle to determine the chlorine demand: *Cl_2 Demand = Cl_2 added concentration (mg/L) – Cl_2 residual measured concentration (mg/L)*.[1]

Report the chlorine demand according to the goals of the study.

Example: The sample dosed at 6.0 mg/L consumed 4.1 mg/L chlorine after 2 hours at 20 °C and pH 8.1.

10. Determine the chlorine requirement (chlorine dosage) needed to meet the operating goal: *Cl_2 Requirement = Cl_2 Demand + Cl_2 Residual Required*

Report the chlorine requirement according to the goals of the study.

Example: The sample required a dose of 3.0 mg/L chlorine to achieve a free chlorine residual of 1.1 mg/L chlorine after 2 hours at 20 °C and pH 8.1.

[1] Some bottles will have no residual chlorine if the chlorine demand exceeded the amount of chlorine added. Choose a bottle that has a chlorine residual to determine the demand. See *Chlorine demand results*.

Chlorine addition calculation

Use the following formula to calculate the concentration of the chlorine added in step 6.

$$\text{mg/L } Cl_2 = \frac{0.1 \text{ mL } \langle \text{volume of standard added} \rangle \times \text{ampule certificate value } \langle \text{ mg/L } Cl_2 \rangle}{125 \text{ mL}}$$

Example:

$$\text{mg/L } Cl_2 = \frac{0.1 \text{ mL} \times \text{certificate value of 1250 mg/L } Cl_2}{125 \text{ mL}}$$

mg/L Chlorine = **1.0**

Incremental reagent addition

Incremental addition of Cl2 dosing solution defines the incremental addition of a 1250 mg/L chlorine dosing solution.

Table 97 Incremental addition of Cl_2 dosing solution

Bottle #	Cl_2 dosing solution added (mL)	Increases sample concentration (in mg/L Cl_2) by
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

Chlorine demand results

Select the sample bottle that most closely fits the following criteria to calculate the chlorine demand.

1. Residual chlorine measured is less than the chlorine dose added (0.03* mg/L).
2. Residual chlorine measured is greater than 0.03* mg/L.
3. Chlorine dose added is most similar to the dosage range expected in the field.

Criteria 1 and 2 ensure that the chlorine residual and demand are greater than the detection limit of the DPD method used for determining the chlorine residual. If no sample portion satisfies all criteria, repeat the test and adjust the chlorine doses accordingly.

Chlorine demand test plan

Chlorine demand test plans are developed for many purposes. The purpose should be well defined and documented. This will develop the specific details of the plan, with the goal of establishing reproducible test conditions to obtain reproducible data. This data is useful in characterizing and optimizing a water treatment operation. Purposes for developing a chlorine demand test plan might be:

Characterize the water system to establish a historical data baseline.
This baseline with chlorine demand date can be used to troubleshoot water quality problems, provide background information for new employees and can provide additional support for monitoring changes in water quality. The plan would include:

- The standard elements of temperature, water pH, chlorine dose rate and chlorine contact time.
- Additional specific details to allow other analysts to reproduce the plan.

Characterize the chlorine demand of an influent raw water source.
Data obtained to establish chlorine demand data for use in understanding the effects of water source changes, blending operations and seasonal weather variations. The plan would include:

- Source water description, sample location, time of year, specific or unusual weather events

* The minimum detection limit for DPD Chlorine Method 8021 when calculating the concentrations by difference (1.412 x 0.02 mg/L).

- Additional complementary tests to be run, such as TOC, turbidity or UV-254, in addition to the standard temperature, pH, chlorine dose rate and contact time.

Track the reduction in chlorine demand as water moves through the treatment process. Data obtained would be used to establish a baseline for monitoring the effects of treatment changes, seasonal water temperatures and overall changes in chlorine demand. The plan would include:

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

Getting started

Before starting this procedure, determine:

- The magnitude of the chlorine demand present in the water to be tested.
- Which chlorine method to use to determine chlorine residual.

First time users of this method or users evaluating a new water source should perform a screening test to determine an approximate chlorine demand level before performing a full chlorine demand test series.

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

Chlorine demand procedure modification

The chlorine demand procedure is an operationally defined procedure. The procedure is defined by the user and may be modified to meet the specific requirements of the sample or the process operation. Run chlorine demand studies under the range of conditions expected in the field. Use the basic test protocol while changing contact time, temperature, sample pH and chlorine concentrations. Total Chlorine or Monochloramine can be determined as required from the residual measured at the end of the prescribed contact time.

Use the following guidelines if modifications are made:

- Make smaller chlorine concentration additions by using a larger sample size. A 237-mL bottle (contains 250 mL when filled to overflowing) is available for low chlorine demand applications. Each 0.1 mL of chlorine dosing solution added will increase the chlorine concentration by approximately 0.5 mg/L. Substitute 250 mL for 125 mL in the above equation. 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 additions of chlorine. Use 0.2 mL, 0.4 mL, 0.6 mL, etc., to spike the bottles in steps 4 and 7 in the procedure.
- Wrap sample bottles made of clear colorless glass in foil to protect from light or kept in the dark during the contact time.
- Sample pH can be modified or standardized by adding a fixed amount of a pH buffer solution to each bottle. Prepare a reagent blank bottle using organic free water. Add the same amount of buffer to this blank, add a known amount of chlorine and carry the blank through the procedure. Add only enough buffer to give the desired pH. This will check the chlorine demand (if any) that was added by the buffer. Subtract the chlorine demand of the blank from the sample chlorine demand values.

- Chlorine demand tests that have an extended contact time will require temperature control if the sample temperature is significantly different from the analysis environment. Use a refrigerator, water bath or incubator as required. It is important to control and document these variables in order to be able to duplicate the chlorine demand procedure on future samples.

Treatment of analysis labware

Glassware used in this test must be chlorine demand-free. Treat all glassware with a dilute solution of chlorine bleach prepared by adding 0.5 mL of commercial bleach to 1 liter of water. Alternatively, the sample bottles may be treated by adding 2.0 mL of the Chlorine Dosing Solution to each 125-mL bottle and filling to overflowing with deionized water. Soak glassware in this solution for at least one hour. After soaking, rinse the glassware with copious amounts of chlorine demand-free water before filling with sample.

Sampling and storage

Most reliable results are obtained on fresh low solid samples that are analyzed immediately. Samples may be stored up to 24 hours at 4 °C. Warm the samples to the required temperature before running the chlorine demand test.

Summary of method

The chlorine demand of a water sample is defined as the difference between the concentration of chlorine added to the sample and the concentration of the chlorine residual remaining at the end of a predetermined contact time. The chlorine demand is a function of chlorine concentration, sample temperature, contact time and sample pH.

The chlorine requirement is the amount of chlorine required to achieve a predetermined chlorine residual at a prescribed 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 such as 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 general 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 present such as ferrous, manganous, nitrite, sulfide and sulfite ions. Ammonia present in the water also consumes chlorine to form chloramines.

Chlorine demand is significantly impacted by the physical and chemical characteristics of the water sample. Chlorine demand studies ran at 10 °C will be considerably different than studies ran at 20 °C. It is imperative that the sample temperature, pH and chlorine dose be accurately measured and recorded. It is difficult to extrapolate chlorine demand data from one water source to another. Demand studies need to be performed directly on the water source of interest. This provides the information required to establish chlorine demand constants, to provide usable historical data and to provide the test requirements for making repeatable and meaningful chlorine demand measurements.

Consumables and replacement items

Required reagents

Description	Catalog number
DPD Free Chlorine Reagent Powder Pillows, 10 mL	2105569
OR	—
DPD Free Chlorine Reagent Powder Pillows, 25 mL	1407099
Chlorine Dosing Solution Ampules, 1190–1310 mg/L as Cl_2, 10-mL ampules, 16/pkg	2504810

Required Apparatus

Description	Catalog number
Bottles, Amber Glass, 118-mL 6/pkg	714424
Caps, Black, PP Teflon liner, 12/pkg	2401812

Optional reagents and apparatus

Description	Catalog number
Ampule Breaker, for Voluette Ampules	2196800
Bottles, Amber Glass, 237 mL, 6/pkg	714441
Bottles, Amber Glass, 1000 mL, 6/pkg	714463
Buffer Powder Pillows, pH 6.86, 15/pkg	1409895
Buffer Powder Pillows, pH 8.00, 15/pkg	1407995
Buffer Powder Pillows, pH 8.3, 15/pkg	89868
Buffer Solution, pH 7.0, demand-free, 500 mL	2155353
Caps, for 714441 Bottles, 6/pkg	2166706
Caps, for 714463 Bottles, 6/pkg	2371026
Chlorine Standard Solution Ampules, 10 mL, 50–75 mg/L as Cl_2, 16/pkg	1426810
DPD Free Chlorine AccuVacs, 25/pkg	2502025
DPD Free Chlorine SwifTest Dispenser with reagents	2802300
DPD Total Chlorine Reagent Powder Pillows, 25 mL	1406499
DPD Total Chlorine Reagent PP, 10 mL	2105969
DPD Total Chlorine SwifTest Dispenser with reagents	2802400
Graduated Cylinder, plastic, 100 mL	108142
Incubator, Model 205, 110 V, 0 to 40 °C	2616200
Labels, PolyPaper, 1.5 x 3 inches, 120/pkg	2091502
Monochlor F Reagent Powder Pillows, 10 mL	2802299

Optional reagents and apparatus (continued)

Description	Catalog number
Sens***ion*** 2 Portable pH/ISE Meter, with electrode	5172510
Sodium Hydroxide Standard Solution, 0.100N, 500 mL	19153
Standard Methods Handbook	2270800
Stir Bar, Teflon-coated, 2.22 cm x 0.48 cm	4531500
Stir Plate, 120 V, 4.25 x 4.25 inches	2881200
Sulfuric Acid Std. Solution, 0.100 N, 500 mL	20253
TenSette Pipet, 0.1 - 1.0 mL	1970001
Tips for TenSette Pipet, 0.1-1.0 mL, 50/pkg	2185696
Thermometer, Double Scale, –20 to 110 °C (0–230 °F)	2095911
Tweezers	1428200
Water, Organic-Free 500 mL	2641549

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