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Standard Practice for
Estimation of Chlorine Requirement or Demand of Water, or Both[1]

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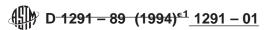ϵ¹ ~~NOTE—Section 12, Keywords, was added editorially in April 1994.~~

1. Scope

1.1 This practice provides a means of estimating the quantity of chlorine required to be added to a unit volume of water to accomplish a predetermined treatment objective or to completely react with all chlorine reactable substances in the water, or both.

1.2 Temperature, pH, and initial chlorine dosage are all variables in estimating the optimum chlorination practice. The effects of these variables can be evaluated using this practice.

1.3 Chlorine residual is determined using Test Method D 1253.

1.4 This practice is applicable to all types of water in which the stated treatment objective can be evaluated or residual chlorine can be measured, or both.

1.5 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.* For a specific hazard statement, see Note 1.

2. Referenced Documents

2.1 *ASTM Standards:*

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[1] This practice is under the jurisdiction of ASTM Committee D~~=~~19 on Water and is the direct responsibility of Subcommittee ~~D19.11~~ D19.03 on ~~Sampling of Water for Power Generation~~ ~~and~~ ~~Process Use.~~ Water-Formed Deposits, Surveillance of Water, and Flow Measurement of Water.

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D 1129 Terminology Relating to Water[2]
D 1193 Specification for Reagent Water[2]
D 1253 Test Method for Residual Chlorine in Water[2]
D 1293 Test Methods for pH of Water[2]
D 3370 Practices for Sampling Water from Closed Conduits[2]

3. Terminology

3.1 *Definitions of Terms Specific to This Standard:*

3.1.1 *chlorine demand*—the amount of chlorine that must be added to a unit volume of water under specified conditions of pH, temperature, and contact time to completely react with all chlorine-reactable substances in the water. It is defined as the difference between the amount of chlorine applied and the amount of free chlorine remaining at the end of the contact period.

3.1.2 *chlorine requirement*—the amount of chlorine that must be added to a unit volume of water under specified conditions of pH, temperature, and contact time to achieve the objectives of chlorination.

3.2 *Definitions*—For definitions relating to this practice, see Terminology D 1129.

4. Summary of Practice

4.1 Known amounts of chlorine are added to a series of 500 mL aliquots of sample. The treated sample aliquots are permitted to stand for a specified contact time (or a variety of different specified contact times) under specified conditions of pH and temperature. At the end of the contact time, the sample aliquots are either analyzed for chlorine content by Test Method D 1253 or subjected to whatever evaluative technique is required to establish accomplishment of the treatment objective, or both.

5. Significance and Use

5.1 Chlorine is added to potable water, waste water, and industrial water for a variety of purposes. Some of these purposes are:

5.1.1 To eliminate or reduce the growth of microorganisms in water,

5.1.2 To destroy or modify decomposable organic substances so as to reduce the biochemical oxygen demand of the water,

5.1.3 To eliminate or reduce taste, odors, and color in the water,

5.1.4 To separate grease in waste water by eliminating the protective colloidal effect of proteins present, and

5.1.5 To destroy or modify substances in the waste water that react directly by oxidation, such as ammonia, cyanates, cyanides, ferrous iron, nitrites, phenol, phosphorus, sulfides, sulfites, thiocyanates, and other oxidizable constituents.

5.2 It is important to avoid over-chlorination in order to minimize chemical consumption, meet restrictions specified by regulatory agencies, and minimize equipment degradation.

6. Apparatus

6.1 All of the apparatus listed in Test Methods D 1293 and D 1253 may be required. Any other apparatus necessary to carry out the final evaluation of the effects of chlorination will be required.
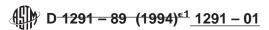
7. Reagents and Materials

7.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. [3] Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

7.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water conforming to Specification D 1193, Type III, which has been rendered chlorine demand-free. Chlorine demand can be removed by treating with excess chlorine and allowing this treated solution to stand in sunlight for several hours to destroy the chlorine residuals. Test Method D 1253 may be used to assure complete destruction of these residuals.

7.3 *Acetic Acid Solution* (1 + 1)—Mix equal volumes of glacial acetic acid and water.

7.4 *Calcium Hydroxide Solution* (10.7 g/L)—Weigh 10.7 g of 100 % hydrated lime, $Ca(OH)_2$, and suspend in water. Dilute the suspension to 1 L. Shake well each time before using.

7.5 *Chlorine Solution, Standard*—Prepare one of the standard solutions described in 7.5.1 and 7.5.2; standardize as described in 7.5.3.

7.5.1 *Chlorine Water*—Pass chlorine gas through reagent water until the solution contains from 0.5 to 10.0 mg/L Cl_2.

NOTE 1—**Warning:** Use a slow rate of addition and carry out the operation under a hood. Store in a glass stoppered amber bottle and standardize daily before use.

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[2] *Annual Book of ASTM Standards*, Vol 11.01.
[3] *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmaceutical Convention, Inc. (USPC), Rockville, MD.

7.5.2 *Sodium Hypochlorite Solution, Standard*—Dilute a commercial sodium hypochlorite or bleach solution containing 10 to 100 g of available chlorine per litre with water to provide a solution containing from 0.5 to 10 mg available chlorine per millilitre, depending upon the maximum expected chlorine requirement for the sample. This solution must be standardized before use.

7.5.3 Standardize the chlorine water or sodium hypochlorite solution, standard, as follows:

7.5.3.1 Transfer 10 mL of the solution to be standardized to a porcelain dish.

7.5.3.2 Add 10 mL of acetic acid (1 + 1) (see 7.3) and 10 mL of potassium iodide solution (see 7.8).

7.5.3.3 Titrate with sodium thiosulfate solution (0.10 *N*) (see 7.11) until the yellow color of the liberated iodine is almost discharged.

7.5.3.4 Add 1 mL of starch indicator solution (see 7.12) and continue the titration to a colorless endpoint.

7.5.3.5 Calculate the concentration of available chlorine as follows:

$$\text{Available chlorine, mg/mL} = \frac{A \times B \times 35.45}{C}$$

where:
A = sodium thiosulfate solution, standard, mL,
B = normality of sodium thiosulfate solution, standard, and
C = chlorine solution titrated, mL.

7.6 *Hydrochloric Acid* (1 + 1)—Mix equal volumes of concentrated HCl (sp gr 1.19) and water.

7.7 *Potassium Dichromate Solution* (0.100 *N*)—Dissolve 4.904 g of anhydrous potassium dichromate ($K_2Cr_2O_7$) of primary standard quality in water and dilute to 1000 mL in a volumetric flask.

7.8 *Potassium Iodide Solution* (50 g/L)—Dissolve 50 g of potassium iodide (KI) in 1 L of freshly boiled and cooled water. Add 1 g of sodium bicarbonate ($NaHCO_3$) to stabilize the solution. Store in an amber bottle and avoid direct exposure to sunlight.

7.9 *Sodium Hydroxide Solution* (10 g/L)—Dissolve 10 g of sodium hydroxide (NaOH) in water and dilute to 1 L.

Note 2—**Caution:** Heat is generated when dissolving sodium hydroxide in water.

7.10 *Sodium Thiosulfate Solution, Standard* (0.10 *N*)—Transfer 25 g of sodium thiosulfate pentahydrate ($Na_2S_2O_3 \cdot 5H_2O$) to a 1-L volumetric flask containing about 800 mL water. Dissolve the compound in the water by shaking and periodic inversion. Add 1 g of sodium carbonate (Na_2CO_3) and dissolve. Dilute the solution to 1 L with water.

7.10.1 Standardize the sodium thiosulfate solution: Add 70 mL of water to a porcelain dish, and add, with constant stirring, 1 mL of concentrated sulfuric acid (H_2SO_4), 10.0 mL of 0.100 *N* $K_2Cr_2O_7$, and 20 mL of potassium iodide solution (see 7.8). Permit the reaction mixture to stand in the dark for about six minutes. Then titrate with the sodium thiosulfate solution until the yellow color of the liberated iodine is almost discharged. Add 1 mL of starch indicator solution (see 7.12) and continue the titration to a colorless endpoint.

7.10.1.1 The normality can be calculated as:

$$\text{Normality, } Na_2S_2O_3 = \frac{1}{Na_2S_2O_3 \text{ required in titration, mL}}$$

7.10.1.2 Perform this standardization in triplicate and average the results.

7.11 *Starch Indicator Solution*—Make a paste of 1 g of soluble starch and mix into 1 L of boiling water. Then, add 20 g of potassium hydroxide (KOH), mix thoroughly, and allow to stand for 2 h. Add 6 mL of glacial acetic acid (99.5 %). Mix thoroughly and then add sufficient HCl (sp gr 1.19) to adjust the pH value of the solution to 4.0. Store in a glass-stoppered bottle. Starch solution prepared in this manner will remain chemically stable for 1 year.

7.12 *Sulfuric Acid* (sp gr 1.84)—Concentrated sulfuric acid (H_2SO_4).

8. Sampling

8.1 Collect the sample in accordance with Practices D 3370.

8.2 Conduct the test immediately following collection of the samples.

9. Procedure

Note 3—The area used for the test must not be in direct sunlight; tests should be run at the same temperature at which chlorination will be carried out. The temperature of the water just prior to, or immediately after, chlorination must not exceed 50°C.

9.1 Transfer 500 mL portions of sample to separate 1000 mL beakers.

Note 4—The number of aliquots required to determine chlorine requirement or demand is left to the judgment of the analyst. It will depend upon the degree of familiarity that the analyst has with the water being tested as well as other variables.

Note 5—One of two different sources of chlorine can be used in the chlorine addition, either chlorine water or sodium hypochlorite solution. In general, the type of chlorine that is used in the process should be used in the test. Chlorine water will tend to lower the pH of the water while sodium hypochlorite solution will tend to raise the pH.

9.2 If chlorine water is used for chlorination, add the estimated *maximum* amount of chlorine (as chlorine water) to one of the

sample aliquots. If sodium hypochlorite solution is used for chlorination, add the estimated *minimum* amount of chlorine (as sodium hypochlorite solution). Immediately measure the pH of the sample aliquot by Test Method D 1293. If the pH is not below the lower limit of the desired pH range, continue with 9.3. If the pH does fall below the lower limit of the desired range, add sodium hydroxide solution dropwise with continual stirring to bring the pH up to approximately the midpoint of the pH range, noting the amount of sodium hydroxide solution required. Then, discard this solution and transfer another 500 mL aliquot of sample to a 1-L beaker to replace it. Add the same amount of sodium hydroxide solution as was required for pH adjustment of the first sample aliquot to all of the sample aliquots. Proceed to 9.3.

9.3 If the estimated maximum amount of chlorine was added to the first sample aliquot, add incrementally smaller amounts of chlorine to each of the other sample aliquots, with the estimated minimum amount of chlorine being added to the last sample aliquot. If the estimated minimum amount of chlorine was added to the first sample aliquot, add incrementally greater amounts of chlorine to each of the other sample aliquots with the estimated maximum amount of chlorine being added to the last sample aliquot. Stir each sample aliquot gently after addition of chlorine. Proceed to 9.4.

9.4 Measure the pH of each sample aliquot by following Test Method D 1293.

9.5 If the pH is higher than the desired pH range, carefully adjust the pH downward by adding, with constant gentle stirring, hydrochloric acid (1 + 1) dropwise until the pH reaches the upper limit of the desired range.

Note 6—Care must be taken during the addition of HCl (1 + 1) to make sure that the pH is not lowered too rapidly and that the lower limit of the desired pH range is not exceeded. A rapid reaction (which itself lowers the pH) may ensue if the pH is taken too low.

9.6 Permit each portion of sample to stand for the desired contact time.

Note 7—Depending upon the application, a single contact time or a series of different contact times may be used for each sample aliquot. This is left to the judgment of the analyst.

9.7 To estimate chlorine requirement, perform whatever test is necessary on all of the sample aliquots at the end of the desired contact time to determine whether the objectives of chlorination have been met. If it is desired to maintain a certain concentration of residual available chlorine, perform the chlorine determination by Test Method D 1253.

9.8 To estimate chlorine demand, determine residual-free chlorine on all of the sample aliquots at the end of the desired contact time by Test Method D 1253.

10. Calculation

10.1 Calculate the chlorine dosage in milligrams per litre for each treated sample solution using Eq 1:

$$\text{Chlorine dosage, mg/L} = 2AB$$

(1)

where:
A = chlorinating solution added to each sample aliquot, mL, and
B = available chlorine per millilitre of chlorinating solution, mg (see 7.5.3).

10.2 Chlorine demand is estimated using Eq 2:

$$\text{Chlorine demand, mg/L} = C - D$$

(2)

where:
C = chlorine dosage, mg/L, and
D = free chlorine remaining at the end of contact time, mg/L.

Note 8—To calculate chlorine consumed, see Appendix X1.

11. Precision and Bias

11.1 *Precision*—Due to the many variables involved in—The estimation of chlorine requirement or demand, or both, it is impossible to measure the precision of the a practice. However, some idea of For measuring chlorine values, this practice refers the precision user to be expected may be obtained from Test Method D 1253. A statement for the precision and biats of chlorine measurepment is lorcated in the Test Method D 1253.

12. Keywords

12.1 chlorine; disinfection; drinking water; residual chlorine; water treatment

APPENDIX

(Nonmandatory Information)

X1. CALCULATION OF CHLORINE CONSUMED

X1.1 Calculate the chlorine consumed for each sample aliquot at each contact time using Eq X1.1:

$$\text{Chlorine consumed, mg/L} = \text{Chlorine dosage, mg/L}$$
$$- \text{Chlorine residual, mg/L}$$

$$(\text{X1.1})$$

X1.2 To determine the total amount of chlorine that would be consumed in a system over a period of time, plot the data as follows:

X1.2.1 On log-log graph paper, plot for a given sample aliquot the chlorine consumed versus the contact time in hours. Fit the best curve through the points. Determine the value of the chlorine consumed at the intercept of the line with the coordinate corresponding to a contact time of 1 h. Designate the value of this intercept as K. Determine the slope of the line and designate as n.

NOTE X1.1—Times in units other than hours may be appropriate for certain applications. K should be determined at unit rate. The value for n at a given temperature will vary with the characteristics of the water.

X1.2.2 The straight lines for each chlorine dose are of the general form described by Eq X1.2:

$$D = Kt^{n}$$

$$(\text{X1.2})$$

where:
D = chlorine consumed, mg/L,
t = contact time, h,
K = chlorine consumed after 1 h, mg/L, and
n = slope of curve.

X1.2.3 The chlorine consumed can be interpolated between test values by use of the above expression.

X1.2.4 Where a number of chlorine doses are tested at a given temperature and pH, the values of n may be averaged in order to develop a relationship between K and chlorine application or between K and pH. If a family of such tests is made at different temperatures, determine the relationship between the logarithm of n and the reciprocal of the absolute temperature as a further aid to interpolation.