



## Standard Test Methods for Chloride Ion In Water<sup>1</sup>

This standard is issued under the fixed designation D 512; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

*This standard has been approved for use by agencies of the Department of Defense.*

### 1. Scope \*

1.1 These test methods cover the determination of chloride ion in water, wastewater (Test Method C only), and brines. The following three test methods are included:

	Sections
Test Method A (Mercurimetric Titration)	7 to 14
Test Method B (Silver Nitrate Titration)	15 to 21
Test Method C (Ion-Selective Electrode Method)	22 to 29

1.2 Test Methods A, B, and C were validated under Practice D2777 – 77, and only Test Method B conforms also to Practice D 2777 – 86. Refer to Sections 14, 21, and 29 for further information.

1.3 *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 26.1.1.

1.4 A former colorimetric test method was discontinued. Refer to Appendix X1 for historical information.

### 2. Referenced Documents

#### 2.1 ASTM Standards:

- D 1066 Practice for Sampling Steam<sup>2</sup>
- D 1129 Terminology Relating to Water<sup>2</sup>
- D 1193 Specification for Reagent Water<sup>2</sup>
- D 2777 Practice for Determination of Precision and Bias of Applicable Methods of Committee D-19 on Water<sup>2</sup>
- D 3370 Practices for Sampling Water from Closed Conduits<sup>2</sup>
- D 4127 Terminology Used with Ion-Selective Electrodes<sup>2</sup>

### 3. Terminology

3.1 *Definitions*—For definitions of terms used in these test methods, refer to Terminologies D 1129 and D 4127.

### 4. Significance and Use

4.1 Chloride ion is under regulation in water, and must,

<sup>1</sup> These test methods are under the jurisdiction of ASTM Committee D-19 on Water and are the direct responsibility of Subcommittee D19.05 on Inorganic Constituents in Water.

Current edition approved Oct. 2, 1989. Published December 1989. Originally published as D 512 – 38. Last previous edition D 512 – 88.

<sup>2</sup> *Annual Book of ASTM Standards*, Vol 11.01.

therefore, be measured accurately. It is highly detrimental to high-pressure boiler systems and to stainless steel, so monitoring is essential for prevention of damage. Chloride analysis is widely used as a tool for estimating the cycles of concentration, such as in cooling tower applications. Processing waters and pickling solutions used in the food processing industries also require dependable methods of analysis for chloride.

### 5. Purity of Reagents

5.1 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.<sup>3</sup> 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.

5.2 *Purity of Water*— Unless otherwise indicated, all references to water shall be understood to mean Type II reagent water conforming to Specification D 1193.

### 6. Sampling

6.1 Collect the sample in accordance with Practice D 1066 and Practices D 3370, as applicable.

## TEST METHOD A—MERCURIMETRIC TITRATION<sup>4</sup>

### 7. Scope

7.1 This test method can be used to determine chloride ion in water, provided interferences are absent (see Section 9).

7.2 Though not specified in the research report, the precision statement is presumed to have been obtained using Type II reagent water. It is the responsibility of the analyst to assure the validity of this test method for untested matrices.

7.3 This test method was validated for the concentration

<sup>3</sup> *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 Pharmacopoeia and National Formulary*, U.S. Pharmaceutical Convention, Inc. (USPC), Rockville, MD.

<sup>4</sup> For information of interest in connection with this test method, and supporting data, refer to Clark, F. E., "Determination of Chloride in Water," *Analytical Chemistry*, Vol 22, April 1950, pp. 553–555, and Vol 22, November 1950, p. 1458.

\*A Summary of Changes section appears at the end of this standard.

range 8.0 to 250 mg/L  $\text{Cl}^-$ .

## 8. Summary of Test Method

8.1 Dilute mercuric nitrate solution is added to an acidified sample in the presence of mixed diphenylcarbazone-bromophenol blue indicator. The end point of the titration is the formation of the blue-violet mercury diphenylcarbazone complex.

## 9. Interferences

9.1 The anions and cations generally found in water offer no interference. Zinc, lead, nickel, and ferrous and chromous ions affect solution and end-point colors, but do not reduce the accuracy of the titration when present in concentrations up to 100 mg/L. Copper is tolerable up to 50 mg/L. Titration in the presence of chromate ion requires indicator with extra background color (alphazurine) and prior reduction for concentrations above 100 mg/L. Ferric ion above 10 mg/L must be reduced before titration, and sulfite ion must be oxidized. Bromide and fluoride will be partially titrated with the chloride. Quaternary ammonium salts also interfere if present in significant amounts (1 to 2 mg/L). Deep color may also interfere.

## 10. Apparatus

10.1 *Microburet*, 1 or 5-mL, with 0.01-mL graduation intervals.

## 11. Reagents and Materials

11.1 *Hydrogen Peroxide* (30 %  $\text{H}_2\text{O}_2$ ).

11.2 *Hydroquinone Solution* (10 g/L)—Dissolve 1 g of purified hydroquinone in water and dilute to 100 mL.

11.3 *Mercuric Nitrate Solution, Standard* (0.025N)—Dissolve 4.2830 g of mercuric nitrate ( $\text{Hg}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ ) in 50 mL of water acidified with 0.5 mL of concentrated nitric acid ( $\text{HNO}_3$ , sp gr 1.42). Dilute the acidified  $\text{Hg}(\text{NO}_3)_2$  solution with water to 1 L. Filter if necessary, and standardize against the standard sodium chloride (NaCl) solution, using the procedure described in Section 12 (see Note 1).

NOTE 1—*Sharpness of End Point*—The end point, while sharp, can be improved somewhat for certain types of water by adding several drops of a 0.05-g/L solution of xylene cyanole FF or alphazurine blue-green dye (color index 714) to the titration sample.

11.4 *Mixed Indicator Solution*<sup>5</sup>—Dissolve 0.5 g of crystalline diphenylcarbazone and 0.05 g of bromophenol blue powder in 75 mL of ethyl alcohol (95 %), and dilute to 100 mL with the alcohol (Note 2). Store in a brown bottle and discard after 6 months (Note 3).

NOTE 2—Methanol, isopropanol, or ethanol denatured with either methanol or isopropanol (Formula 3A) may be used if pure ethyl alcohol is not available. Other denatured ethanol formulae are not suitable.

NOTE 3—Liquid indicator generally deteriorates to the point that it yields no end-point color after 12 to 18 months of storage. High temperature (above 37.8°C (100°F)) and exposure to bright light may shorten storage life. A dry powder mixture of the two indicator ingredients

is stable for much longer periods. Both the powder mixture (capsule form) and the liquid indicator are available commercially.

11.5 *Nitric Acid* (3 + 997)—Mix 3 volumes of concentrated nitric acid ( $\text{HNO}_3$ , sp gr 1.42) with 997 volumes of water.

11.6 *pH Indicating Paper*, long-range type, covering a pH range 1 to 11.

11.7 *Sodium Chloride Solution, Standard* (0.025N)—Dry several grams of sodium chloride (NaCl) for 1 h at 600°C. Dissolve 1.4613 g of the dry salt in water, and dilute to 1 L at 25°C in a volumetric flask.

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

## 12. Procedure

12.1 Use a volume of sample such that it will contain not more than 20 mg of chloride ion, diluting the sample with water to approximately 50-mL volume if necessary. Determine an indicator blank on 50 mL of chloride-free water, applying the same procedure followed for the sample.

12.2 Add 5 to 10 drops of mixed indicator solution, and shake or swirl the flask. If a blue-violet or red color develops, add  $\text{HNO}_3$  (3 + 997) dropwise until the color changes to yellow. Add 1 mL of excess acid. If a yellow or orange color forms immediately on addition of the mixed indicator, add NaOH solution (10 g/L) dropwise until the color changes to blue-violet; then add  $\text{HNO}_3$  (3 + 997) dropwise until the color changes to yellow and further add 1 mL excess of acid (Note 4).

NOTE 4—The prescribed acidification provides a satisfactory pH range from 3.0 to 3.5. Acidified samples on which electrometric pH measurements have been made shall not be used for chloride determinations, because the use of the calomel reference electrode may introduce error due to chloride contamination. For precise pH adjustment of samples having a low-chloride concentration, instrumental measurements may be made on one sample aliquot to determine treatment needed for another to be used for the chloride test.

12.3 Titrate the solution and a blank with 0.025 N  $\text{Hg}(\text{NO}_3)_2$  solution until a blue-violet color, as viewed by transmitted light, persists throughout the solution (Note 5). Record the millilitres of  $\text{Hg}(\text{NO}_3)_2$  solution added in each case.

NOTE 5—The use of indicator modifications and the presence of heavy metal ions can change solution colors without affecting accuracy of the determination. For example, solutions containing alphazurine may be bright blue when neutral, grayish purple when basic, blue-green when acidic, and blue-violet at the chloride end point. Solutions containing about 100 mg/L nickel ion and normal mixed indicator are purple when neutral, green when acid, and gray at the chloride end point. When applying this test method to samples that contain colored ions or that require modified indicator, it is recommended that the operator be familiar with the specific color changes involved by experimenting with solutions prepared as standards for comparison of color effects.

12.4 If chromate ion is present in the absence of iron and in concentration less than 100 mg/L, use the alphazurine modified mixed indicator (Note 1) and acidify the sample as described in 12.2 but to pH 3 as indicated by pH indicating paper. Titrate the solution as described in 12.3, but to an olive-purple end point.

12.5 If chromate ion is present in the absence of iron and in concentration greater than 100 mg/L, add 2 mL of fresh

<sup>5</sup> This diphenylcarbazone 1-bromophenol blue indicator is covered by U.S. Patent No. 2,784,064.

hydroquinone solution and proceed as described in 12.2 and 12.3.

12.6 If ferric ion is present in the absence or presence of chromate ions, use a sample of such volume as to contain no more than 2.5 mg of ferric ion or of ferric ion plus chromate ion. Add 2 mL of fresh hydroquinone solution, and proceed as described in 12.2 and 12.3.

12.7 If sulfite ion is present, add 0.5 mL of H<sub>2</sub>O<sub>2</sub> to 50 mL of the sample in the Erlenmeyer flask and mix for 1 min. Then proceed as described in 12.2 and 12.3.

**13. Calculation**

13.1 Calculate the chloride ion concentration, in milligrams per litre, in the original sample as follows:

$$\text{Chloride, mg/L} = [(V_1 - V_2) \times N \times 35\,453]/S$$

where:

- V<sub>1</sub> = standard Hg(NO<sub>3</sub>)<sub>2</sub> solution required for titration of the sample, mL,
- V<sub>2</sub> = standard Hg(NO<sub>3</sub>)<sub>2</sub> solution required for titration of the blank, mL,
- N = normality of the Hg(NO<sub>3</sub>)<sub>2</sub> solution, and
- S = sample used in 12.1, mL.

**14. Precision and Bias**<sup>6</sup>

14.1 *Precision Statement*—The precision of this test method may be expressed as follows:

$$S_T = 0.023X + 0.43$$

$$S_O = 0.002X + 0.46$$

where:

- S<sub>T</sub> = overall precision, mg/L,
- S<sub>O</sub> = single-operator precision, mg/L, and
- X = concentration of chloride ion determined.

14.2 *Bias Statement*—Recoveries of known amounts of chloride were as follows:

Amount Added, mg/L	Amount Found, mg/L	± % Bias	Statistically Significant (95 % Confidence Level)
250	248	-0.80	no
80.0	79.3	-0.88	no
8.00	7.51	-6.13	yes

14.3 The information presented in 14.1 and 14.2 is derived from round-robin testing in which five laboratories, including seven operators, participated. Though not clearly specified in the test report, the matrix is presumed to be Type II reagent water. Of seven data sets ranked as described in Practice D 2777, none was rejected, nor were any data points determined to be “outliers.” Three sample levels were run on at least three days. The method of “least squares” was used to determine the precision statement, with correlation of 0.7394 for S<sub>O</sub> and 0.9993 for S<sub>T</sub>.

14.4 It is the responsibility of the analyst to assure the validity of this test method for untested matrices.

14.5 Precision and bias for this test method conforms to Practice D 2777 – 77, which was in place at the time of

collaborative testing. Under the allowances made in 1.5 of Practice D 2777 – 86, these precision and bias data do meet existing requirements for interlaboratory studies of Committee D–19 test methods.

**TEST METHOD B—SILVER NITRATE TITRATION**

**15. Scope**

15.1 This test method<sup>7</sup> is intended primarily for water where the chloride content is 5 mg/L or more, and where interferences such as color or high concentrations of heavy metal ions render Test Method A impracticable.

15.2 Though not specified in the research report, the precision and bias statement is presumed to have been obtained using Type II reagent water. It is the responsibility of the analyst to assure the validity of this test method for untested matrices.

15.3 This test method was validated for the concentration range 8.0 to 250 mg/L Cl<sup>-</sup>.

**16. Summary of Test Method**

16.1 Water adjusted to approximately pH 8.3 is titrated with silver nitrate solution in the presence of potassium chromate indicator. The end point is indicated by persistence of the brick-red silver chromate color.

**17. Interferences**

17.1 Bromide, iodide, and sulfide are titrated along with the chloride. Orthophosphate and polyphosphate interfere if present in concentrations greater than 250 and 25 mg/L, respectively. Sulfite and objectionable color or turbidity must be eliminated. Compounds which precipitate at pH 8.3 (certain hydroxides) may cause error by occlusion.

**18. Reagents**

18.1 *Hydrogen Peroxide* (30 %) (H<sub>2</sub>O<sub>2</sub>).

18.2 *Phenolphthalein Indicator Solution* (10 g/L)—Prepare as directed in Methods E 200.

18.3 *Potassium Chromate Indicator Solution*—Dissolve 50 g of potassium chromate (K<sub>2</sub>CrO<sub>4</sub>) in 100 mL of water, and add silver nitrate (AgNO<sub>3</sub>) until a slight red precipitate is produced. Allow the solution to stand, protected from light, for at least 24 h after the addition of AgNO<sub>3</sub>. Then filter the solution to remove the precipitate, and dilute to 1 L with water.

18.4 *Standard Solution, Silver Nitrate (0.025 N)*—Crush approximately 5 g of silver nitrate (AgNO<sub>3</sub>) crystals and dry to constant weight at 40°C. Dissolve 4.2473 g of the crushed, dried crystals in water and dilute to 1 L. Standardize against the standard NaCl solution, using the procedure given in Section 19.

18.5 *Standard Solution, Sodium Chloride (0.025 N)*— Prepare as described in 11.7.

18.6 *Sodium Hydroxide Solution* (10 g/L)—Prepare as described in 11.8.

18.7 *Sulfuric Acid* (1 + 19)—Carefully add 1 volume of concentrated sulfuric acid (H<sub>2</sub>SO<sub>4</sub>, sp gr 1.84) to 19 volumes of water, while mixing.

<sup>6</sup> Supporting data are available from ASTM Headquarters. Request RR: D19-1076.

<sup>7</sup> Mohr, F., *ANN.*, 97, 335 (1856).