



Designation: D512 – 12

Standard Test Methods for Chloride Ion In Water¹

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This standard has been approved for use by agencies of the U.S. 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 D2777 – 86. Refer to Sections 14, 21, and 29 for further information.

1.3 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.4 *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.

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

2. Referenced Documents

2.1 *ASTM Standards:*²

- D1066 Practice for Sampling Steam
- D1129 Terminology Relating to Water
- D1193 Specification for Reagent Water
- D2777 Practice for Determination of Precision and Bias of Applicable Test Methods of Committee D19 on Water
- D3370 Practices for Sampling Water from Closed Conduits

¹ These test methods are under the jurisdiction of ASTM Committee D19 on Water and are the direct responsibility of Subcommittee D19.05 on Inorganic Constituents in Water.

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² For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

- D4127 Terminology Used with Ion-Selective Electrodes
- D5810 Guide for Spiking into Aqueous Samples
- D5847 Practice for Writing Quality Control Specifications for Standard Test Methods for Water Analysis
- E200 Practice for Preparation, Standardization, and Storage of Standard and Reagent Solutions for Chemical Analysis

3. Terminology

3.1 *Definitions*—For definitions of terms used in these test methods, refer to Terminologies D1129 and D4127.

4. Significance and Use

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

5.2 *Purity of Water*— Unless otherwise indicated, references to water shall be understood to mean Type I reagent water conforming to Specification D1193. Other reagent water types may be used provided it is first ascertained that the water is of sufficiently high purity to permit its use without adversely

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.

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

affecting the precision and bias of the test method. Type II water was specified at the time of round robin testing of this test method.

6. Sampling

6.1 Collect the sample in accordance with Practice **D1066** and Practices **D3370**, as applicable.

TEST METHOD A—MERCURIMETRIC TITRATION⁴

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 range 8.0 to 250 mg/L 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, iodide, and fluoride will be titrated or 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

NOTE 1—Consult the manufacturer Material Safety Data Sheet for safe work practices before working with reagents.

11.1 *Hydrogen Peroxide* (30 % H₂O₂).

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* (0.0125M; 0.025N)—Dissolve 4.2830 g of mercuric nitrate (Hg(NO₃)₂·H₂O) in 50 mL of water acidified with 0.5 mL of concentrated nitric acid (HNO₃, sp gr 1.42). Dilute the acidified Hg(NO₃)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 2).

NOTE 2—*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*⁵—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 3). Store in a brown bottle and discard after 6 months (Note 4).

NOTE 3—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 4—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 (HNO₃, 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)—Purchase a commercially available standard or prepare as follows: Dry several grams of reagent grade sodium chloride (NaCl) for 2 h at 110°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 HNO₃ (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 HNO₃ (3 + 997) dropwise until the color changes to yellow and further add 1 mL excess of acid (Note 5).

NOTE 5—The prescribed acidification provides a satisfactory pH range

⁴ 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.

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

from 3.0 to 3.5. Acidified samples on which electrometric pH measurements have been made can be used for chloride determinations only if the pH electrode fill solution contains no chloride, for example, use a pH half cell and a double junction reference electrode with a sodium nitrate outer fill solution. Alternately, 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 Hg(NO₃)₂ solution until a blue-violet color, as viewed by transmitted light, persists throughout the solution (Note 6). Record the millilitres of Hg(NO₃)₂ solution added in each case.

NOTE 6—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 alphasurine 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 2) 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 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 H₂O₂ 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:

$$\text{Chloride, mg/L} = [(V_s - V_b) \times N \times 35.453] / S$$

where:

V_s = standard Hg(NO₃)₂ solution required for titration of the sample, mL,

V_b = standard Hg(NO₃)₂ solution required for titration of the blank, mL,

N = normality of the Hg(NO₃)₂ solution (see Note 7),

S = sample used in 12.1, mL, and

35.453 = 35.453 g/mole chloride * 1000 mg/g.

NOTE 7—The normality of the mercuric nitrate solution standard is based on a 2:1 (Cl:Hg) reaction.

14. Precision and Bias⁶

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_T = overall precision, mg/L,

S_O = 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 D2777, 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_O and 0.9993 for S_T .

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 D2777 – 77, which was in place at the time of collaborative testing. Under the allowances made in 1.5 of Practice D2777 – 08, these precision and bias data do meet existing requirements for interlaboratory studies of Committee D19 test methods.

TEST METHOD B—SILVER NITRATE TITRATION

15. Scope

15.1 This test method⁷ 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.

⁶ Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D19-1076. Contact ASTM Customer Service at service@astm.org.

⁷ Mohr, F., *ANN.*, 97, 335 (1856).

15.3 This test method was validated for the concentration range 8.0 to 250 mg/L Cl⁻.

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 %) (H₂O₂).

18.2 *Phenolphthalein Indicator Solution* (10 g/L)—Prepare as directed in Practice E200.

18.3 *Potassium Chromate Indicator Solution*—Dissolve 50 g of potassium chromate (K₂CrO₄) in 100 mL of water, and add silver nitrate (AgNO₃) until a slight red precipitate is produced. Allow the solution to stand, protected from light, for at least 24 h after the addition of AgNO₃. Then filter the solution to remove the precipitate, and dilute to 1 L with water.

18.4 *Standard Solution, Silver Nitrate* (0.025M; 0.025 N)—Crush approximately 5 g of silver nitrate (AgNO₃) 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* (0.025N)—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 (H₂SO₄, sp gr 1.84) to 19 volumes of water, while mixing.

19. Procedure

19.1 Pour 50 mL, or less, of the sample, containing not more than 20 nor less than 0.25 mg of chloride ion, into a white porcelain container (see Note 8). If sulfite ions are present, add 0.5 mL of hydrogen peroxide (H₂O₂) to the sample, mix, and let stand for 1 min. Dilute to approximately 50 mL with water, if necessary. Adjust the pH to the phenolphthalein end point (pH 8.3), using H₂SO₄, (1 + 19) or NaOH solution (10 g/L).

NOTE 8—An 80 mL white porcelain dish, a 1-in stirrer bar, and a magnetic stirrer have been found useful for this purpose.

19.2 Add approximately 1.0 mL of K₂CrO₄ indicator solution and mix. Add standard AgNO₃ solution dropwise from a 25-mL buret until the brick-red (or pink) color persists throughout the sample when illuminated with a yellow light or viewed with yellow goggles.

19.3 Repeat the procedure described in 19.1 and 19.2, using exactly one half as much original sample, diluted to 50 mL with water.

19.4 If the volume of titrant used in 19.3 is one-half of that used in titrating the aliquot in 19.1, proceed to the calculation section. If not, significant interferences are present and compensation must be made; alternatively, another method must be used.

20. Calculation

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

$$\text{Chloride, mg/L} = [(V_1 - V_2) \times N \times 70906] / S$$

where:

V_1 = standard solution AgNO₃ added in titrating the original sample, S, as prepared in 19.1, mL,

V_2 = standard solution, AgNO₃ added in titrating one-half the volume of the original sample, as prepared in 19.3, mL,

N = normality of standard AgNO₃ solution (see Note 9),

S = original sample in the 50-mL test specimen prepared in 19.1, mL, and

70906 = 35.453 g/mole chloride * 2 * 1000 mg/g, where the factor of 2 accounts for one-half the sample volume (19.3).

NOTE 9—The normality calculation is based on a 1:1 (Cl:Ag) reaction.

21. Precision and Bias⁶

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

$$S_T = 0.013X + 0.70$$

$$S_O = 0.007X + 0.53$$

where:

S_T = overall precision, mg/L,

S_O = single-operator precision, mg/L, and

X = concentration of chloride ion determined.

21.2 *Bias*—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	yes
80.00	79.1	-1.13	yes
8.00	7.77	-2.88	yes

21.3 The information in 21.2 is derived from round-robin testing in which six laboratories, including ten operators, participated. Though not clearly specified in the test report, the matrix is presumed to be Type II reagent water. Of ten data sets ranked as described in Practice D2777, none was rejected, but one data point was determined to be an “outlier.” 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 0.9959 for S_O and 0.9940 for S_T .

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