Standard Test Methods for Chloride Ion In Water[1]

This standard is issued under the fixed designation D512; 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 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
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

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[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.

[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 TITRATION [4]

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 % H_2O_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 (*0.0125M; 0.025*N)*—Dissolve 4.2830 g of mercuric nitrate ($Hg(NO_3)_2 \cdot H_2O$) in 50 mL of water acidified with 0.5 mL of concentrated nitric acid (HNO_3, sp gr 1.42). Dilute the acidified $Hg(NO_3)_2$ 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 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 (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* (0.025*N*)—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 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 HNO_3 (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

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[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* $Hg(NO_3)_2$ solution until a blue-violet color, as viewed by transmitted light, persists throughout the solution (Note 6). Record the millilitres of $Hg(NO_3)_2$ 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 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 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 H_2O_2 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:

$$\text{Chloride, mg/L} = \left[\left(V_S - V_b \right) \times N \times 35\,453 \right] / S$$

where:

V_S = standard $Hg(NO_3)_2$ solution required for titration of the sample, mL,
V_b = standard $Hg(NO_3)_2$ solution required for titration of the blank, mL,
N = normality of the $Hg(NO_3)_2$ 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 Bias[6]

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 method[7] 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.

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[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 %) (H_2O_2).

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 (K_2CrO_4) in 100 mL of water, and add silver nitrate ($AgNO_3$) until a slight red precipitate is produced. Allow the solution to stand, protected from light, for at least 24 h after the addition of $AgNO_3$. 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 ($AgNO_3$) 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_2SO_4, 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 (H_2O_2) 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 H_2SO_4, (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 K_2CrO_4 indicator solution and mix. Add standard $AgNO_3$ 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 $AgNO_3$ added in titrating the original sample, S, as prepared in 19.1, mL,
V_2 = standard solution, $AgNO_3$ added in titrating one-half the volume of the original sample, as prepared in 19.3, mL,
N = normality of standard $AgNO_3$ 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 Bias[6]

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.

21.5 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 C—ION-SELECTIVE ELECTRODE

22. Scope

22.1 This test method is applicable to the measurement of chloride ion in natural waters, drinking water, and waste waters.

22.2 Samples containing 2 to 1000 mg/L of chloride may be analyzed by this test method. The concentration range may be extended by dilution of an appropriate aliquot before the addition of the ionic strength adjustor.

22.3 The precision and bias statements were obtained using reagent water and a water matrix of choice that included natural and waste waters. It is the responsibility of the analyst to determine the acceptability of this test method for the matrix being analyzed.

23. Summary of Test Method

23.1 Chloride ion is measured potentiometrically using a chloride ion-selective electrode (ISE) in conjunction with a double junction, sleeve-type reference electrode or a combination chloride electrode. Potentials are read using a pH meter having an expanded millivolt scale, or a selective-ion meter having a direct concentration readout capability.

23.2 The electrodes are calibrated in known chloride solutions, and the concentrations of unknowns are determined in solutions with the same background. Samples and standards should be at the same temperature.

23.3 Standards and samples are diluted with an ionic strength adjustor that also minimizes possible interferences such as ammonia, bromide, iodide, cyanide, or sulfide.

24. Interferences

24.1 There is no interference from up to 500 mg/L of sulfide, 100 mg/L of bromide or iodide, 100 mg/L of ammonia, or a hundredfold excess of cyanide over chloride, when using chloride ionic strength adjustor (CISA).

25. Apparatus

25.1 *pH Meter,* with expanded millivolt scale. This test method can be adapted for use with a *selective-ion meter.*

25.2 *Chloride Ion-Selective Electrode,* combination electrode or half cell, having a light-desensitized silver chloride (AgCl) membrane. Not all chloride ion-selective electrodes are suitable for this test method, since the ionic strength adjustor is incompatible with some membranes. In particular, silver chloride/silver sulfide membranes are inappropriate, since the sulfide can be oxidized by the ionic strength adjustor.

25.3 *Sleeve-Type Double Junction Reference Electrode (for use with chloride half cell),* using solution prepared in 26.4 as the outer sleeve filling solution.

NOTE 10—Other types of double junction reference electrodes may be suitable, but supporting data included in this test method reflect only the recommended type.

25.4 *Mixer,* magnetic, with a TFE-fluorocarbon-coated stirring bar.

26. Reagents

26.1 *Chloride Ionic Strength Adjustor (CISA)*—Dissolve 15.1 g of sodium bromate in 800 mL of water. Add 75 mL of concentrated nitric acid (HNO_3, sp. gr 1.42) (Note 11). Stir well. Dilute with water to 1 L. Store CISA in a polyethylene or glass container.

NOTE 11—For low-level chloride measurement (less than 5 mg/L) the nitric acid used must not contain more than 0.005 % chloride and the sodium bromate must not contain more than 0.003 % chloride. A test for reagent purity is included in this test method.

26.1.1 **Caution**—Sodium bromate is a strong oxidant and should be handled appropriately. Also note that preparation and dilutions of CISA should be made in a well-ventilated area, preferably a hood.

26.2 *Chloride Solution, Stock* (1000 mg/L)—Dissolve 1.648 g of sodium chloride (dried for 2 h at 110°C), in water in a volumetric flask and dilute to 1 L.

26.3 *Chloride Solutions, Standard* (100, 10, and 1 mg/L)—Using volumetric pipets, transfer 100, 10, and 1.0 mL of the chloride stock solution into separate 1-L volumetric flasks and dilute each to 1 L with water.

26.4 *Double-Junction Reference Electrode Outer Filling Solution*—Dilute 1 volume of CISA (26.1) with 1 volume of water.

27. Calibration

27.1 Mix equal volumes of the 1000 mg/L of chloride standard solution, and CISA reagent. Do the same for each of the other three standards.

27.2 Mix equal volumes of water and CISA reagent.

27.3 Place the electrodes in the solution from 27.2, stir well, wait 3 to 5 min, and record the millivolt reading. This solution contains no added chloride, and the potential reading will not be very stable.

27.4 Rinse the electrodes thoroughly, place them in the 1 mg Cl^-/L-CISA mixture and stir well. Wait 1 to 2 min and record the result.

27.4.1 If the difference in readings between 27.3 and 27.4 is less than 15 mV, there is chloride contamination of the reagent that will affect low-level readings, and purer reagents must be obtained.

27.5 Rinse the electrodes, place them in the 10 mg Cl^-/L-CISA mixture and stir well. Wait 1 min, or until stable, and record the results.

27.6 Repeat 27.5 with 100 and 1000 mg Cl^-/L-CISA mixtures.

27.7 Prepare a calibration curve by plotting, in a spreadsheet, the potential observed (on the x-axis) versus the log concentration of each of the standards used (on the y-axis).

Note that volume corrections are incorporated into the calibration, so that samples analyzed in accordance with Section 28 can be read directly. Alternately, calibrate the meter at 1, 10, and 100 mg/L chloride according to manufacturer's instructions.

28. Procedure

28.1 Mix the sample with an equal volume of CISA reagent, and stir thoroughly for 1 to 2 min.

28.2 Insert the electrodes, wait 1 to 2 min, and record the reading.

28.3 Read chloride concentration of the sample in milligrams per litre directly from the calibration curve.

29. Precision and Bias[6]

29.1 *Precision*—The overall and single-operator precision of this test method, within its designated range, varies with the quantity tested, as shown in Fig. 1, for reagent water, and in Fig. 2, for selected water matrices. These matrices included natural and waste waters.

29.2 *Bias*—Recoveries of known amounts of chloride from reagent water and selected water matrices are as shown in Table 1.

29.3 The information in Table 1 is derived from round-robin testing in which five laboratories, including seven operators, participated. Of seven data sets ranked as described in Practice D2777, none was rejected in the case of reagent water and one was rejected in the case of selected water matrices. Eight "outlier" data points within the sets were also rejected. Four sample levels were run on three days, and blanks were obtained for the water used.

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

29.5 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.

30. Quality Control

30.1 In order to be certain that analytical values obtained using these test methods are valid and accurate within the confidence limits of the test, the following QC procedures must be followed when analyzing for chloride.

30.2 *Calibration and Calibration Verification:*

30.2.1 For titration, standardize the titrant as directed above. For ISE, analyze at least three working standards containing concentrations of chloride that bracket the expected sample concentration prior to analysis of samples to calibrate the titration or instrument.

30.2.2 Verify titrant concentration after standardization or verify ISE instrument calibration by analyzing a standard at a mid-range concentration. The measured concentration of a mid-range standard should fall within ±15 % of the known concentration.

30.2.3 If calibration cannot be verified, recalibrate the instrument.

30.3 *Initial Demonstration of Laboratory Capability:*

30.3.1 If a laboratory has not performed the test before, or if there has been a major change in the measurement system, for example, new analyst, new instrument, and so forth, a precision and bias study must be performed to demonstrate laboratory capability.

30.3.2 Analyze seven replicates of a standard solution prepared from an Independent Reference Material containing a mid-range concentration of chloride. The matrix and chemistry

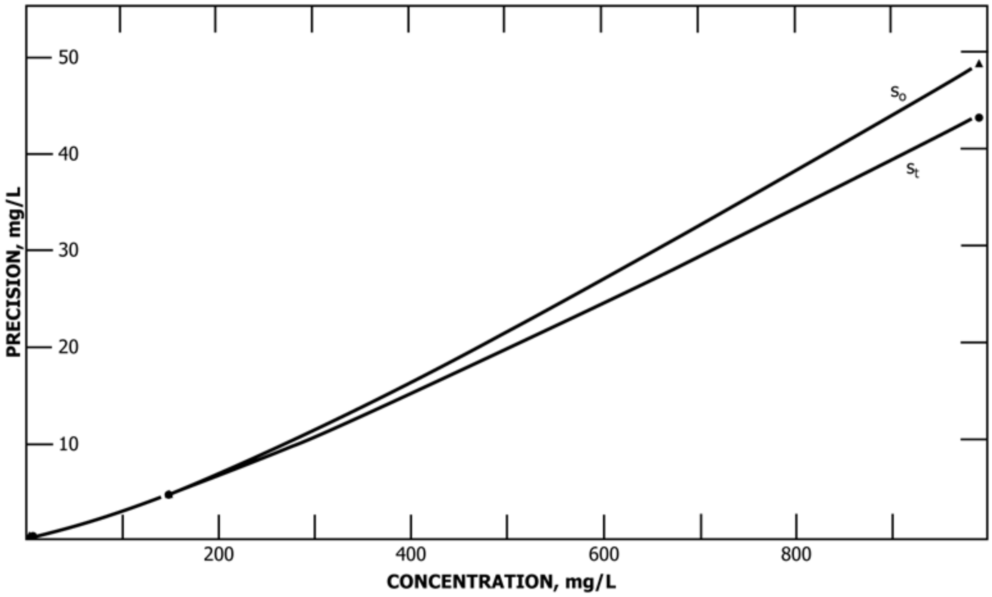

FIG. 1 Interlaboratory Precision for Chloride Found in Reagent Water (Ion Selective Electrode)

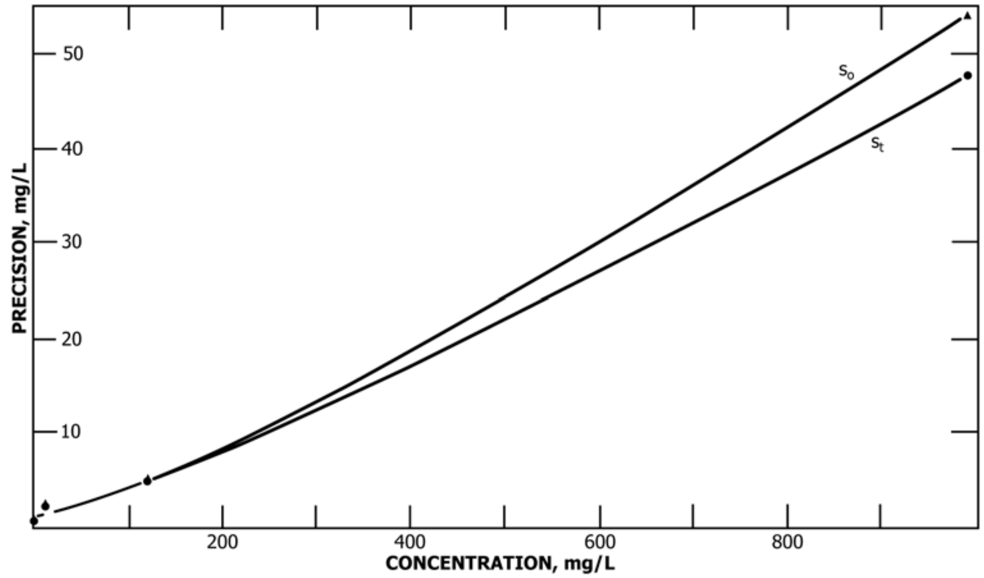

FIG. 2 Interlaboratory Precision for Chloride Found in Selected Water Matrices (Ion Selective Electrode)

TABLE 1 Determination of Bias (Ion Selective Electrode)

	Amount Added, mg/L	Amount Found, mg/L	Bias, ± %	Statistically Significant (95 % Confidence Level)
Reagent water	1.1	1.03	–6.4	no
	10.0	9.94	–0.6	no
	150	148.8	–0.8	no
	1000	992	–0.8	no
Water matrices	1.1	1.04	–5.5	no
	10.0	10.24	+2.4	no
	150	146.0	–2.7	no
	1000	991	–0.9	no

of the solution should be equivalent to the solution used in the collaborative study. Each replicate must be taken through the complete analytical test method including any sample preservation and pretreatment steps.

30.3.3 Calculate the mean and standard deviation of the seven values and compare to the acceptable ranges of bias in sections 14.2, 21.2 and 29.2. This study should be repeated until the recoveries are within the limits given in sections 14.2, 21,.2 and 29.2. If a concentration other than the recommended concentration is used, refer to Practice D5847 for information on applying the F test and t test in evaluating the acceptability of the mean and standard deviation.

30.4 *Laboratory Control Sample (LCS):*

30.4.1 To ensure that the test method is in control, analyze a LCS containing a mid-range concentration of chloride with each batch or 10 samples. If large numbers of samples are analyzed in the batch, analyze the LCS after every 10 samples. The LCS must be taken through all of the steps of the analytical method including sample preservation and pretreatment. The result obtained for the LCS shall fall within ± 15 % of the known concentration.

30.4.2 If the result is not within these limits, analysis of samples is halted until the problem is corrected, and either all the samples in the batch must be reanalyzed, or the results must be qualified with an indication that they do not fall within the performance criteria of the test method.

30.5 *Method Blank:*

30.5.1 Analyze a reagent water test blank with each batch. The concentration of chloride found in the blank should be less than 0.5 times the lowest calibration standard. If the concentration of chloride is found above this level, analysis of samples is halted until the contamination is eliminated, and a blank shows no contamination at or above this level, or the results must be qualified with an indication that they do not fall within the performance criteria of the test method.

30.6 *Matrix Spike (MS):*

30.6.1 To check for interferences in the specific matrix being tested, perform a MS on at least one sample from each batch by spiking an aliquot of the sample with a known concentration of chloride and taking it through the analytical method.

30.6.2 The spike concentration plus the background concentration of chloride must not exceed the high calibration standard. The spike must produce a concentration in the spiked sample that is 2 to 5 times the analyte concentration in the unspiked sample, or 10 to 50 times the detection limit of the test method, whichever is greater.

30.6.3 Calculate the percent recovery of the spike (P) using the following formula:

$$P = 100\,[A(V_s+V) - BV_s]/CV$$

where:

A = analyte concentration (mg/L) in spiked sample,
B = analyste concentration (mg/L) in unspiked sample,
C = concentration (mg/L) of analyte in spiking solution,
Vs = volume (mL) of sample used, and
V = volume (mL) of spiking solution added.

30.6.4 The percent recovery of the spike shall fall within the limits, based on the analyte concentration, listed in Guide D5810, Table 1. If the percent recovery is not within these limits, a matrix interference may be present in the sample selected for spiking. Under these circumstances, one of the following remedies must be employed: the matrix interference must be removed, all samples in the batch must be analyzed by a test method not affected by the matrix interference, or the results must be qualified with an indication that they do not fall within the performance criteria of the test method.

NOTE 12—Acceptable spike recoveries are dependent on the concentration of the component of interest. See Guide D5810 for additional information.

30.7 *Duplicate:*

30.7.1 To check the precision of sample analyses, analyze a sample in duplicate with each batch. If the concentration of chloride is less than five times the detection limit for the method, a matrix spike duplicate (MSD) should be used.

30.7.2 Calculate the standard deviation of the duplicate values and compare to the precision in the collaborative study using an F test. Refer to 6.4.4 of Practice D5847 for information on applying the F test.

30.7.3 If the result exceeds the precision limit, the batch must be reanalyzed or the results must be qualified with an indication that they do not fall within the performance criteria of the test method.

30.8 *Independent Reference Material (IRM):*

30.8.1 In order to verify the quantitative value produced by the test method, analyze an Independent Reference Material (IRM) submitted as a regular sample (if practical) to the laboratory at least once per quarter. The concentration of the IRM should be in the concentration mid-range for the method chosen. The value obtained must fall within the control limits established by the laboratory.

31. Keywords

31.1 analysis; chloride; electrode; titrametric; water

APPENDIX

(Nonmandatory Information)

X1. RATIONALE FOR DISCONTINUATION OF METHOD

X1.1 Former Test Method C (Colorimetric)

X1.1.1 This test method was discontinued in 1988. The test method may be found in its entirety in the 1988 *Annual Book of ASTM Standards*, Vol 11.01.

X1.1.2 This test method may be applied to waters containing chloride ion in concentrations from 0.10 to 10 mg/L.

X1.1.3 Solutions of ferric ammonium sulfate and mercuric thiocyanate are added to the sample. The chloride ion reacts with the mercuric thiocyanate to produce thiocyanate ion which in turn combines with ferric to form red ferric thiocyanate. The intensity of the color, which is proportional to the concentration of the chloride ions, is measured photometrically at a wavelength of 463 nm, or by visual comparison with standard solutions.

X1.1.4 This test method was discontinued because there were insufficient laboratories interested in participating in another collaborative study to obtain the necessary precision and bias as required by Practice D2777.

SUMMARY OF CHANGES

Committee D19 has identified the location of selected changes to this standard since the last issue (D512 – 04) that may impact the use of this standard. (Approved Sept. 15, 2010.)

(1) The SI statement was added to Section 1.
(2) Slightly modified 4.1, 9.1, 23.1, 24.1, 25.2, 25.3, 26.2, and 27.5.
(3) Clarified type of reagent and drying process in 11.7.
(4) Clarified the acidification process in Note 5.
(5) Added derivation of the factor to 13.1.
(6) In 20.1, corrected the factor from a 1:2 reaction to the correct 1:1 reaction, added note and derivation of the factor.
(7) Revised 27.7.
(8) Added 21.5.
(9) Modified various subsections of Section 30.

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