Designation: D4458 – 15

Standard Test Method for
Chloride Ions in Brackish Water, Seawater, and Brines[1]

This standard is issued under the fixed designation D4458; 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.

1. Scope*

1.1 This test method[2] is applicable to the measurement of chloride in highly mineralized waters such as oil field brines, seawater, and brackish water. The test method is based upon the titration of chloride with silver nitrate, using a visual indicator.

1.2 Samples containing from 10 to 150 mg of chloride can be analyzed by this test method. These levels are achieved by dilution as described in the test method.

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 It is the user's responsibility to assure the validity of the method for untested types of water.

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.*

2. Referenced Documents

2.1 *ASTM Standards:*[3]

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
D5810 Guide for Spiking into Aqueous Samples
D5847 Practice for Writing Quality Control Specifications for Standard Test Methods for Water Analysis

3. Terminology

3.1 *Definitions*—For definitions of terms used in this test method, refer to Terminology D1129.

4. Summary of Test Method

4.1 This test method is based upon the Mohr procedure for determining chloride ion with silver nitrate. The chloride reacts with the silver ion before any silver chromate forms, due to the lower solubility of silver chloride. The potassium chromate indicator reacts with excess silver ion to form a red silver chromate precipitate. The end point is the appearance of the first permanent orange color.

4.2 This test method is suitable for analyzing solutions with a pH between 6.0 and 8.5.

5. Significance and Use

5.1 Chloride is present in virtually all oil field brines, seawaters, and many waste waters. Identification of the origin of the water and selection of its disposal method may be based upon the chloride content. The chloride content is also used to estimate the resistivity of formation waters and to differentiate between subsurface formations.

6. Interferences

6.1 Sulfide, bromide, iodide, thiocyanate, cyanide, phosphate, sulfite, carbonate, hydroxide, and iron interfere in this test method. Sulfide, sulfite, and thiosulfate can be removed with a peroxide treatment, but usually no attempt is made to remove bromide and iodide because they are usually present in insignificant quantities compared to chloride. If necessary, the pH can be raised and the hydroxides of several metals, including iron, can be filtered off. Iron, barium, lead, and bismuth precipitate with the chromate indicator.

7. Apparatus

7.1 *Laboratory Glassware.*

7.2 *Buret,* 25-mL capacity.

7.3 *Hotplate.*

7.4 *Magnetic Stirrer and TFE-fluorocarbon-Coated Stirring Bars.*

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[1] This test method is under the jurisdiction of ASTM Committee D19 on Water and is the direct responsibility of D19.05 on Inorganic Constituents in Water.

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[2] Hillebrand, W. F., Lundell, G. E. F., Bright, H. A., and Hoffman, J. I., *Applied Inorganic Analysis*, 2nd Ed., 732, John Wiley & Sons, Inc., New York, NY, 1953.

[3] 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.

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

8. Reagents and Materials

8.1 *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 specification of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.[4] 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.

8.2 *Purity of Water*—Unless otherwise indicated, reference to water shall be understood to mean reagent water conforming to Specification D1193, Type I. 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 affecting the precision and bias of the test method. Type III water was specified at the time of round robin testing of this test method.

8.3 *Silver Nitrate Solution, Standard* (equivalent to 5 mg Cl^-/mL)—Dissolve 23.9582 g of $AgNO_3$ in approximately 700 mL of water. Add 1 drop concentrated nitric acid (HNO_3) and dilute to 1 L in a volumetric flask. The HNO_3 will eliminate any precipitation of silver hydroxide which would change the concentration. Standardize against sodium chloride (NaCl) by the procedure described in 8.4. Store in an amber-brown bottle to protect the solution from light.

8.4 *Silver Nitrate Solution, Standard* (equivalent to 2 mg Cl/mL)—For lower chloride concentrations, this more dilute standard will give a more accurate titration. Dissolve 9.5834 g of $AgNO_3$ in approximately 700 mL of water. Add 1 drop concentrated nitric acid (HNO_3) and dilute to 1 L in a volumetric flask. Standardize against sodium chloride (NaCl) by the procedure described below. Store in an amber-brown bottle to protect the solution from the light.

8.4.1 Dry 2 to 6 g of high purity (minimum 99.5 %) sodium chloride crystals at 110°C for 2 h and cool in a desiccator to room temperature.

8.4.2 Weigh 1.6484 g of the NaCl crystals. Transfer the crystals into a 1-L volumetric flask, dissolve, dilute, and mix well. A quantity of 1 mL of this solution provides 1 mg of Cl^-.

8.4.3 Pipet 50 mL aliquots of the NaCl solution to standardize the weaker $AgNO_3$ solution (2 mg Cl^-/mL) and dilute to 100 mL with water. Use 100 mL of the NaCl solution to standardize the more concentrated $AgNO_3$ solution (5 mg of Cl^-/mL).

8.4.4 Add 1 mL of 5 % indicator solution (see 8.5), 1 g of sodium bicarbonate powder, and titrate to the appearance of a permanent orange color preceding a red precipitate. The analyst must practice this titration to become familiar with this color.

8.4.5 Determine the indicator blank by substituting 100 mL of reagent grade water for the sample in 10.3 to 10.6.

TABLE 1 Aliquot Size for Chloride Determination

Specific Gravity	Sample Dilution	Equivalent Aliquot, mL
1.000 to 1.010	None—Take 50 mL for analysis	50
1.010 to 1.025	None—Take 25 mL for analysis	25
1.025 to 1.050	Dilute 25 mL to 100 mL, take 50 mL	12.5
1.025 to 1.090	Dilute 25 mL to 100 mL, take 25 mL	6.25
1.090 to 1.120	Dilute 25 mL to 500 mL, take 25 mL	1.25
1.120 to 1.150	Dilute 25 mL to 1000 mL, take 25 mL	0.625

8.4.6 The titre (*T*) of the silver nitrate solution is given in the following equation:

$$T = \frac{\text{mg Cl}^- \text{ used}}{\text{mL AgNO}_3 \text{ required} - \text{blank}}$$

8.4.7 If the titre (*T*) of the solutions are not exactly 2.0 or 5.0 mg of Cl^- per mL $AgNO_3$, it may be desirable to dilute the solutions if they are too concentrated or add more silver nitrate if too weak. In either case, restandardize the resulting solution.

8.5 *Potassium or Sodium Chromate, Indicator Solution*—Prepare a 5 % solution (5 g/100 mL) and adjust the pH to 7.0 with HNO_3 (1 + 19) or $NaHCO_3$ powder described in 8.6 and 8.7.

8.6 *Sodium Bicarbonate* ($NaHCO_3$)—Powder to adjust the sample pH to 8.3.

8.7 *Nitric Acid Solution* (1 + 19)—Add 1 volume of HNO_3 (sp. gr. 1.42) to 19 volumes water.

8.8 *Filter Paper*—Purchase suitable filter paper. The user must first ascertain that the filter paper is of sufficient purity to use without adversely affecting the bias and precision of the test method.

9. Sampling

9.1 Collect the sample in accordance with Practices D3370.

10. Procedure

10.1 Filter (8.8) the sample to remove any insoluble or suspended materials.

10.2 Pipet an aliquot of sample into a 150-mL Erlenmeyer flask. Dilute to 100 mL with water. Refer to Table 1 for approximate volume.

10.3 Measure the pH and adjust to near neutral.

10.4 Add 1 g of sodium bicarbonate and stir to dissolve. The pH should be between 6.5 and 8.0.

10.5 Add 1 mL of 5 % chromate indicator.

10.6 Titrate with one of the silver nitrate solutions to a permanent orange color preceding the brick red colored precipitate.

NOTE 1—Endpoint detection may be improved by selecting background and lighting conditions that enhance color contrast between the solution and precipitate.

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[4] *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 *Annual Standards for Laboratory Chemicals,* BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary,* U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

TABLE 2 Determination of Precision and Bias of Chloride Ions in Synthetic Brines

Amount Added, mg/L	Amount Found, mg/L	S_o mg/L	S_T mg/L	% ± Bias	Statistically Significant (95 % Confidence Level)
994	995	0.0	0.0	+ 0.10	no
48 324	47 868	130	340	−0.94	yes
143 524	142 959	740	1 450	0.39	no

10.7 Record the volume of $AgNO_3$ required to the end point and calculate the chloride content.

11. Calculation

11.1 Calculate the chloride content as follows:

$$\text{mg Cl}^-/L = \frac{(\text{mL AgNO}_3 \text{ used} - B) \times T \times 1000}{\text{mL sample}}$$

where:

T = titre, mg Cl^-/mL of $AgNO_3$, and
B = indicator blank, as determined in 8.4.5.

12. Precision and Bias[5]

12.1 *Precision*—The overall and single operator precision of this test method varies with the quantity being tested in accordance with Table 2.

12.2 *Bias*—Recoveries of known amounts of chloride in synthetic brines are given in Table 2.

12.3 The information in Table 2 is derived from round robin testing in which five laboratories, including eight operators, participated. Of eight data sets ranked as described in Practice D2777, none was rejected. One data point out of seventy-two was rejected. Three synthetic brines were analyzed, on each of three days, at chloride levels representative of the range of the test method.

12.4 These data may not apply to waters of other matrices.

12.5 Precision and bias of this test method conforms to Practice D2777 – 77, which was in place at the time of collaborative testing. Under the allowances made in 1.4 of D2777 – 13, these precision and bias data do meet existing requirements for interlaboratory studies of Committee D19 test methods.

13. Quality Control

13.1 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 chloride.

13.2 *Calibration and Calibration Verification:*

13.2.1 Standardize the titrant as directed above.

13.2.2 Verify titrant concentration after standardization by analyzing a standard at a mid-range concentration. The measured concentration of a mid-range sample should fall within ±15 % of the known concentration.

13.2.3 If standardization cannot be verified, restandardize the solution.

13.2.4 It is recommended to analyze a blank and continuing calibration verification (CCV) at a 10 % frequency. The results should fall within the expected precision of the method or ±15 % of the known concentration.

13.3 *Initial Demonstration of Laboratory Capability:*

13.3.1 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.

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

13.3.3 Calculate the mean and standard deviation of the seven values and compare to the acceptable ranges of bias in Table 2. This study should be repeated until the recoveries are within the limits given in section Table 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.

13.4 *Laboratory Control Sample (LCS):*

13.4.1 To ensure that the test method is in control, prepare and analyze a LCS containing a mid-range concentration of chloride with each batch (laboratory defined or twenty samples). The laboratory control samples for a large batch should cover the analytical range when possible. 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.

13.4.2 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.

13.5 *Method Blank:*

13.5.1 Analyze a reagent water test blank with each laboratory-defined 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.

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[5] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D19-1115. Contact ASTM Customer Service at service@astm.org.

13.6 *Matrix Spike (MS):*

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

13.6.2 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.

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

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

where:

A = analyte concentration (mg/L) in spiked sample,
B = analyte 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.

13.6.4 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 2—Acceptable spike recoveries are dependent on the concentration of the component of interest. See Guide D5810 for additional information.

13.7 *Duplicate:*

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

13.7.2 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.

13.7.3 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.

13.8 *Independent Reference Material (IRM):*

13.8.1 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.

14. Keywords

14.1 brackish water; brines; chloride ion; seawater; silver nitrate

SUMMARY OF CHANGES

Committee D19 has identified the location of selected changes to this standard since the last issue (D4458 – 09) that may impact the use of this standard. (Approved Feb. 1, 2015.)

(1) Added 8.8.
(2) Revised the equation in 11.1.
(3) Revised Section 13.