



Designation: D4458 – 09

## Standard Test Method for Chloride Ions in Brackish Water, Seawater, and Brines<sup>1</sup>

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 ( $\epsilon$ ) indicates an editorial change since the last revision or reapproval.

### 1. Scope\*

1.1 This test method<sup>2</sup> 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*:<sup>3</sup>
- 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

<sup>1</sup> This test method is under the jurisdiction of ASTM Committee D19 on Water and is the direct responsibility of D19.05 Inorganic Constituents in Water.05 on Inorganic Constituents in Water.

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<sup>2</sup> 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.

<sup>3</sup> 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. 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.*

### 8. Reagents

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

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.<sup>4</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.

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<sup>-</sup>/mL)—Dissolve 23.9582 g of AgNO<sub>3</sub> in approximately 700 mL of water. Add 1 drop concentrated nitric acid (HNO<sub>3</sub>) and dilute to 1 L in a volumetric flask. The HNO<sub>3</sub> 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<sup>-</sup>/mL)—For lower chloride concentrations, this more dilute standard will give a more accurate titration. Dissolve 9.5834 g of AgNO<sub>3</sub> in approximately 700 mL of water. Add 1 drop concentrated nitric acid (HNO<sub>3</sub>) 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<sup>-</sup>.

8.4.3 Pipet 50 mL aliquots of the NaCl solution to standardize the weaker AgNO<sub>3</sub> solution (2 mg Cl<sup>-</sup>/mL) and dilute to 100 mL with water. Use 100 mL of the NaCl solution to standardize the more concentrated AgNO<sub>3</sub> solution (5 mg of Cl<sup>-</sup>/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.

<sup>4</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 *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 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<sup>-</sup> per mL AgNO<sub>3</sub>, 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<sub>3</sub> (1 + 19) or NaHCO<sub>3</sub> powder described in 8.6 and 8.7.

8.6 *Sodium Bicarbonate* (NaHCO<sub>3</sub>)—Powder to adjust the sample pH to 8.3.

8.7 *Nitric Acid Solution* (1 + 19) —Add 1 volume of HNO<sub>3</sub> (sp. gr. 1.42) to 19 volumes water.

## 9. Sampling

9.1 Collect the sample in accordance with Practices D3370.

## 10. Procedure

10.1 Filter 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.

10.7 Record the volume of AgNO<sub>3</sub> required to the end point and calculate the chloride content.