



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

This standard is issued under the fixed designation D 4458; 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 approval. 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 It is the user's responsibility to assure the validity of the method for untested types of water.

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.*

## 2. Referenced Documents

### 2.1 ASTM Standards:

D 1129 Terminology Relating to Water<sup>3</sup>

D 1193 Specification for Reagent Water<sup>3</sup>

D 2777 Practice for Determination of Precision and Bias of Applicable Methods of Committee D-19 on Water<sup>3</sup>

D 3370 Practices for Sampling Water from Closed Conduits<sup>3</sup>

## 3. Terminology

3.1 *Definitions*—For definitions of terms used in this test method, refer to Terminology D 1129.

## 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

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

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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> *Annual Book of ASTM Standards*, Vol 11.01.

<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 *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.

sufficiently high purity to permit its use without lessening the accuracy of the determination.

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

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 1 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.

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 D 3370.

**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                  |

## 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.

## 11. Calculation

11.1 Calculate the chloride content as follows:

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

where:

*T* = titre, mg Cl<sup>-</sup>/mL of AgNO<sub>3</sub>, and

*B* = indicator blank, as determined in 8.4.5.

## 12. Precision and Bias<sup>5</sup>

12.1 *Precision*—The overall and single operator precision of this test method varies with the quantity being tested in accordance with Table 1.

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 D 2777, 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.

<sup>5</sup> Supporting data are available from ASTM Headquarters. Request RR: D-19-1115.

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

| Amount Added, mg/L | Amount Found, mg/L | S <sub>o</sub> mg/L | S <sub>T</sub> 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  |

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

12.5 Precision and bias of this test method conforms to Practice D 2777 – 77, which was in place at the time of collaborative testing. Under allowances made in the scope of Practice D 2777 – 86, these precision and bias do meet existing requirements for interlaboratory studies of Committee D-19 test methods.

### 13. Keywords

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

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