Designation: D3869 – 15 (Reapproved 2023)

Standard Test Methods for Iodide and Bromide Ions in Brackish Water, Seawater, and Brines[1]

This standard is issued under the fixed designation D3869; 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 These test methods[2] cover the determination of soluble iodide and bromide ions, or both, in brackish water, seawater, and brines. Four test methods are given as follows:

1.1.1 *Test Method A for both Iodide and Bromide Ions*—Volumetric, for concentrations from 0.2 mg/L to 2000 mg/L iodide and from 5 mg/L to 6500 mg/L bromide (Sections 7 – 15).

1.1.2 *Test Method B for Iodide Ion*—Colorimetric, for concentrations from 0.2 mg/L to 2000 mg/L iodide (Sections 16 – 25).

1.1.3 *Test Method C for Iodide Ion*—Selective electrode, for concentrations from 1 mg/L to 2000 mg/L iodide (Sections 26 – 34).

1.1.4 *Test Method D for Bromide Ion*—Colorimetric, for concentrations from 40 mg/L to 6500 mg/L bromide (Sections 35 – 44).

1.2 Test Method A is intended for use on all brackish waters, seawaters, and brines that contain appreciable amounts of iodide or bromide ions or both. Test Methods B, C, and D, because of their rapidity and sensitivity, are recommended for the analysis of brackish waters, seawaters, and brines in the field and in the laboratory.

1.3 Samples containing from 0.2 mg/L to 2000 mg/L of iodide or 5 mg/L to 6500 mg/L of bromide may be analyzed by these methods.

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

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, health, and environmental practices and determine the applicability of regulatory limitations prior to use.* For specific precautionary statements, see 20.2 and 39.2.

1.6 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

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 Flowing Process Streams
D5810 Guide for Spiking into Aqueous Samples
D5847 Practice for Writing Quality Control Specifications for Standard Test Methods for Water Analysis
E60 Practice for Analysis of Metals, Ores, and Related Materials by Spectrophotometry
E200 Practice for Preparation, Standardization, and Storage of Standard and Reagent Solutions for Chemical Analysis
E275 Practice for Describing and Measuring Performance of Ultraviolet and Visible Spectrophotometers

3. Terminology

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

4. Significance and Use

4.1 Identification of a brackish water, seawater, or brine is determined by comparison of the concentrations of their

[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] Additional information is contained in the following references: Collins, A. G., *Geochemistry of Oilfield Waters,* Elsevier, New York, N.Y., 1975, 496 pp.American Petroleum Institute, API *Recommended Practice for Analysis of Oilfield Waters*, Subcommittee on Analysis of Oilfield Waters, API RP, 45 2nd ed, 1968, 49 pp.Hoke, S. H, Fletcher, G. E., and Collins, A. G., "Fluoride and Iodide Selective Electrodes Applied to Oilfield Brine Analysis," US Department of Energy, Report of Investigations, BETC/RI-78/7, 1978.

[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.

dissolved constituents. The results are used to evaluate the origin of the water, determine if it is a possible pollutant or determine if it is a commercial source of a valuable constituent such as iodine or bromine.

5. Reagents

5.1 *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,[4] where such specifications are available. 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, 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.

6. Sampling

6.1 Collect the sample in accordance with Practices D3370.

TEST METHOD A—VOLUMETRIC FOR IODIDE AND BROMIDE

7. Scope

7.1 This test method is applicable to brackish waters, seawaters, and brines, and is recommended for such waters containing appreciable amounts of iodide or bromide, or both. The test method can be used for concentrations as high as 2000 mg/L iodide and 6500 mg/L bromide.

8. Summary of Test Method

8.1 Iodide in the sample is oxidized with bromine to iodate in a buffered solution, the excess bromine is decomposed with sodium formate, and the iodate reacts with added iodide to form iodine which is titrated with sodium thiosulfate.

8.2 Iodide and bromide are oxidized to iodate and bromate, respectively, with hypochlorite. The excess hypochlorite is destroyed with sodium formate, leaving iodate and bromate to react with added iodide to liberate iodine which is titrated with sodium thiosulfate.

8.3 The bromide concentration is calculated by difference between the iodide and combined iodide and bromide determinations.

9. Interferences

9.1 Iron, manganese, and organic matter can interfere (Note 1). They are removed by precipitation and filtration. Remaining traces of iron are masked with fluoride.

NOTE 1—Brines containing surfactants can cause emulsion problems, in which case a suitable emulsion breaker can be used.

10. Apparatus

10.1 *Mechanical Bottle Shaker.*

10.2 *Bottles,* 200-mL, for use on mechanical shaker.

10.3 *Pipets.*

10.4 *Hot-Water Bath,* thermostatically controlled to ±1 °C.

10.5 *Erlenmeyer Flasks,* 250-mL.

11. Reagents and Materials

11.1 *Acetic Acid,* glacial.

11.2 *Ammonium Molybdate Solution*—Dissolve 2 g of ammonium molybdate in water and dilute to 100 mL.

11.3 *Bromine Water (Saturated)*—Add to 250 mL of water slightly more liquid bromine (8 mL to 10 mL) than will dissolve on shaking. Store in a glass-stoppered amber bottle.

11.4 *Calcium Carbonate* ($CaCO_3$), powdered.

11.5 *Calcium Oxide* (CaO), anhydrous powdered.

11.6 *Hydrochloric Acid* (1 + 1)—Add 1 volume of HCl (sp gr 1.19) to 1 volume of water.

11.7 *Hydrochloric Acid* (1 + 3)—Add 1 volume of HCl (sp gr 1.19) to 3 volumes of water.

11.8 *Hydrochloric Acid* (1 + 199)—Add 1 volume of HCl (sp gr 1.19) to 199 volumes of water.

11.9 *Methyl Red Indicator Solution* (0.1 g/L)—Dissolve 0.01 g of water-soluble methyl red in water and dilute to 100 mL.

11.10 *Potassium Fluoride* ($KF{\cdot}2H_2O$), crystalline.

11.11 *Potassium Iodide* (KI), crystals, free of iodates when tested in accordance with American Chemical Society (ACS) specifications.

11.12 *Sodium Acetate Solution* (275 g/L)—Dissolve 275 g of sodium acetate trihydrate ($NaC_2H_3O_2{\cdot}3H_2O$) in water, to dilute to 1 L, and filter.

11.13 *Sodium Chloride* (NaCl), crystals, which, in addition to satisfying ACS specifications, must be free of iodide, iodate, bromide, and bromate.

11.14 *Sodium Formate Solution* (500 g/L)—Dissolve 50 g of sodium formate ($NaCHO_2$) in hot water and dilute to 100 mL. This solution must be freshly prepared.

11.15 *Sodium Hypochlorite Solution*—Use a fresh commercial sodium hypochlorite or bleach solution containing approximately 5 % NaClO.

11.16 *Sodium Thiosulfate Solution* (0.1 *N*)—Prepare and standardize as directed in Practice E200.

[4] *ACS Reagent Chemicals, Specifications and Procedures for Reagents and Standard-Grade Reference Materials*, 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. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.