



Standard Test Methods for Iodide and Bromide Ions in Brackish Water, Seawater, and Brines¹

This standard is issued under the fixed designation D 3869; 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 methods² 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 to 2000 mg/L iodide and from 5 to 6500 mg/L bromide (Sections 7-15).

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

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

1.1.4 *Test Method D for Bromide Ion*—Colorimetric, for concentrations from 40 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 to 2000 mg/L of iodide or 5 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 and health practices and determine the applicability of regulatory limitations prior to use. For specific precautionary statements, see 20.2 and 39.2.

2. Referenced Documents

2.1 *ASTM Standards*:³

D 1129 Terminology Relating to Water

D 1193 Specification for Reagent Water

D 2777 Practice for Determination of Precision and Bias of Applicable Test Methods of Committee D19 on Water

D 3370 Practices for Sampling Water from Closed Conduits

D 5810 Guide for Spiking into Aqueous Samples

D 5847 Practice for Writing Quality Control Specifications for Standard Test Methods for Water Analysis

E 60 Practice for Analysis of Metals, Ores, and Related Materials by Molecular Absorption Spectrometry

E 200 Practice for Preparation, Standardization, and Storage of Standard and Reagent Solutions for Chemical Analysis

E 275 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 D 1129.

4. Significance and Use

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

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.

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.

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

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 **D 1193**, 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 **D 3370**.

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.

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.

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 $\pm 1^\circ\text{C}$.

10.5 *Erlenmeyer Flasks*, 250-mL.

11. Reagents

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 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* ($\text{KF}\cdot 2\text{H}_2\text{O}$)—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 ($\text{NaC}_2\text{H}_3\text{O}_2\cdot 3\text{H}_2\text{O}$) 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 **E 200**.

11.17 *Sodium Thiosulfate Solution (0.01 N)*—With a calibrated pipet transfer 25 mL of the 0.1 N $\text{Na}_2\text{S}_2\text{O}_3$ solution (**11.16**) into a 250-mL volumetric flask. Dilute to the mark with water that has been freshly boiled and cooled then mix well. This solution shall be prepared not more than 2 days before it is to be used.

11.18 *Starch Indicator Solution*—Make a paste of 6 g of arrowroot or soluble iodometric starch with cold water. Pour the paste into 1 L of boiling water. Add 20 g of KOH, mix thoroughly, and allow to stand for 2 h. Add 6 mL of glacial acetic acid. Mix again and add sufficient HCl (sp gr 1.19) to adjust the pH to 4.0. Store in a glass-stoppered bottle. Starch solution prepared in this manner will remain chemically stable for at least 1 year.

11.18.1 If a proprietary starch indicator powder is used, it shall be so indicated in reporting the results of the analysis.

12. Procedure

12.1 To remove iron, manganese, and organic matter from the sample, add exactly 100 mL of sample to a bottle. Add 1 g of calcium oxide (11.5), stopper, and place the mixture in a shaker for 1 h. Allow the mixture to stand overnight and filter on a dry folded filter, discarding the first 20 mL that come through. Brines with specific gravities less than 1.009 may be filtered without standing overnight. Prepare a blank in the same manner.

12.2 Transfer an aliquot of the filtrate containing 1 to 2 mg of iodide to a 250-mL Erlenmeyer flask. Add sufficient water to provide a total volume of 75 mL.

12.3 Add 3 drops of methyl red indicator (11.9). Add HCl (1 + 199) (11.8) dropwise until the mixture is just slightly acid.

12.4 Add 10 mL of sodium acetate solution (11.12), 1 mL of glacial acetic acid (11.1), 4 mL of bromine water (11.3), and allow to stand for 5 min.

12.5 Add 2 mL of sodium formate solution (11.14), blow out any bromine vapor from the neck of the flask, and wash down the sides with water.

12.6 When the solution is completely colorless, add 0.2 g of KF (11.10) and 0.5 g of KI (11.11). Mix until dissolved and add 15 mL of HCl (1 + 1) (11.6).

12.7 For final treatment and titration of the sample, proceed as directed in (12.13).

12.8 To determine the combined iodide and bromide, transfer an aliquot of the filtrate (12.1) containing 1 to 2 mg of bromide to a 250-mL Erlenmeyer flask. Add sufficient water to make the total volume 75 mL.

12.9 If necessary add sufficient NaCl (11.13) to produce a 3-g chloride content. Add, in order, 10 mL of sodium hypochlorite solution (11.15) and approximately 0.4 g of CaCO₃ (11.4) (or enough so that approximately 0.1 g will remain after the next step).

12.10 Adjust the pH of the solution with HCl (1 + 3) (11.7) to a pH between 5.5 and 6.0. Heat at 90°C for 10 min. (A small amount of undissolved CaCO₃ should remain at this point.)

12.11 Remove the flask and cautiously add 10 mL of sodium formate solution (11.14), return the flask to the water bath, and keep the contents hot for 5 min more. Observe the timing closely. Rinse down the inside of the flask with a few millilitres of water and allow the solution to cool to room temperature. Do not use a water bath.

12.12 Add 3 drops of ammonium molybdate solution (11.2), 0.5 g of KF (11.10) (if iron is present), 0.5 g of KI (11.11), mix until dissolved, and acidify with 15 mL of HCl (1 + 1) (11.6).

12.13 Titrate the sample (12.7) for iodide or the sample (12.12) for combined iodide and bromide with 0.01 N sodium thiosulfate solution (11.17) using starch indicator (11.18). Disregard any return of blue color after the endpoint.

13. Calculation

13.1 Calculate the concentration of iodide and bromide ions in milligrams per litre as follows:

13.2 *Iodide*:

TABLE 1 Determination of Precision and Bias of Iodide Ions, Volumetric Methods

Amount Added, mg/L	Amount Found, mg/L	S _O	S _T	±Bias	Statistically Significant (95 % Confidence Level)
12.1	11.4	1	1	-5.78	yes
116.3	112.5	2	3	-3.27	yes
771	743	12	15	+2.63	no
1375	1282	40	73	-6.76	yes

$$C = E - D$$

where:

C = corrected millilitres of Na₂S₂O₃ solution,
 E = millilitres of Na₂S₂O₃, sample solution, and
 D = millilitres of Na₂S₂O₃ blank solution.

$$I^-, \text{ mg/L} = \frac{CN}{S} \times 21150$$

where:

N = normality of Na₂S₂O₃ solution, and
 S = millilitres of sample.

13.3 *Bromide*:

$$C = E - D$$

$$Br^-, \text{ mg/L} = \frac{CN}{S} \times 13320 - X$$

where:

X = concentration of I⁻ as determined above.

14. Precision and Bias⁵

14.1 The overall precision (S_T) and single-operator precision (S_O) of this test method within their designated ranges vary with the quantity being tested in accordance with Table 1 and Table 2.

14.2 The bias of the test method determined from recoveries of known amounts of iodide and bromide in a series of prepared standards are given in Table 1 and Table 2.

NOTE 2—The precision and bias estimates are based on the interlaboratory study on four artificial brine samples containing various amounts of iodide, bromide, and interfering ions as shown in Table 3. Two analysts in each of three laboratories performed duplicate determinations on each of 2 days. Practice D 2777 was used in developing these precision and bias estimates.

14.3 Precision and bias for this test method conforms to Practice D 2777 – 77, which was in place at the time of collaborative testing. Under the allowances made in 1.4 of D 2777 – 08, these precision and bias data do meet existing requirements for interlaboratory studies of Committee D19 test methods.

⁵ Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR: D19-1061.