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An American National Standard

Standard Test Method for Bromide Ion in Water[1]

This standard is issued under the fixed designation D 1246; 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.

This standard has been approved for use by agencies of the Department of Defense.

1. Scope

1.1 This test method is applicable to the measurement of bromide ion in water, ground water, and drinking water.

1.2 Samples containing 0.5 mg/L to 1000 mg/L of bromide may be analyzed by this test method. The concentration range may be extended by the dilution of an appropriate aliquot.

1.3 The precision and bias statements were determined on natural and ground waters. It is the responsibility of the analyst to assure the validity of this test method for untested matrices.

1.4 A titrimetric and two colorimetric test methods for iodide and bromide were discontinued. Refer to Appendix X1 for historical information.

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:*

D 1066 Practice for Sampling Steam [2]

D 1129 Terminology Relating to Water [2]

D 1193 Specification for Reagent Water [2]

D 2777 Practice for Determination of Precision and Bias of Applicable Methods of Committee D-19 on Water [2]

D 3370 Practices for Sampling Water from Closed Conduits [2]

D 4127 Terminology Used with Ion-Selective Electrodes [2]

3. Terminology

3.1 *Definitions*—For definitions of terms used in this test method, refer to Terminologies D 1129 and D 4127.

4. Summary of Test Method

4.1 Bromide ion is measured potentiometrically using a bromide ion-selective electrode in conjunction with a single-junction, sleeve-type reference electrode. Potentials are read on a pH meter having an expanded millivolt scale capable of being read to the nearest 0.1 mV, or a selective ion meter having a direct concentration scale for bromide. For less precise work, a pH meter having a millivolt scale capable of being read to the nearest 1.0 mV is adequate, however, no supporting data are available.

4.2 The electrodes are calibrated in known bromide solutions and the concentrations of unknowns are determined in solutions with the same background. In most cases, addition of an ionic strength adjustor to both standards and samples is sufficient to maintain constant background ionic strength. For samples above 0.1 M in ionic strength, prepare standard solutions similar to the sample composition.

5. Significance and Use

5.1 By analysis for bromide in water, wastewater, and brackish waters, it is possible to evaluate the origin of the water, its potential as a source of bromide, and its condition with regard to pollution.

6. Interferences

6.1 Strongly reducing solutions and solutions containing ions which form insoluble silver salts may coat the electrode membrane. These may be removed by polishing the membrane surface. Sulfide ion and cyanide ion both poison the electrode, and should be removed (see Section 11).

6.2 Halide ions form complexes with some metals. Since the electrode responds only to free bromide ions, the presence of any complexing agents lowers the measured concentrations. Concentrations of free metal ions causing a 10 % error of a bromide concentration of 8.1 mg/L are bismuth $^{+3}$, 80 mg/L; cadmium $^{+2}$, 100 mg/L; lead $^{+2}$, 1600 mg/L; tin $^{+2}$, 2400 mg/L; and thallium $^{+3}$, 4 mg/L.

6.3 Chloride ion and hydroxide ion do not interfere when present in the concentrations of up to 400 and 30 000 times the bromide concentration, respectively. There will be no interference from ammonia when present in concentrations twice that of bromide, nor from thiosulfate 20 times as concentrated as bromide. Iodide is an interference at a concentration ratio as low as 2×10^{-4}. Mercury should be absent from samples.

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[1] This test method is under the jurisdiction of ASTM Committee D-19 on Water and is the direct responsibility of Subcommittee D19.05 on Inorganic Constituents in Water.

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[2] *Annual Book of ASTM Standards*, Vol 11.01.

7. Apparatus

7.1 *pH Meter*, capable of reading to 0.1 mV, or a selective-ion meter.

7.2 *Bromide Ion-Selective Electrode*.

7.3 *Sleeve-Type Single-Junction Reference Electrode*, filled with manufacturer's filling solution.

7.4 *Mixer*, magnetic, with a TFE fluorocarbon-coated stirring bar.

7.5 *Laboratory Glassware*.

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 specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. [3] 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 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 bias and precision of the test method. Type II water was specified at the time of round robin testing of this test method.

8.3 *Ionic Strength Adjustor* (42.5 g/100 mL $NaNO_3$)—In a 100-mL volumetric flask, dissolve 42.5 g of sodium nitrate ($NaNO_3$) in water and dilute to volume.

8.4 *Nickel Sulfate Solution, 1 M*—In a 100 mL volumetric flask dissolve 26.3 g of nickel sulfate hexahydrate ($NiSO_4 \cdot 6H_2O$) in water and dilute to volume.

8.5 *Sodium Bromide Standard Solution, 1000 mg/L*—In a 1 L volumetric flask dissolve 1.288 g dried sodium bromide in water and dilute to volume.

8.6 *Sodium Bromide Standard Solutions*, (100, 10, and 1 mg/L)—Dilute 1 volume of the 1000 mg/L bromide standard with 9 volumes of water to prepare the 100 mg/L standard. By further 1+9 serial dilutions, prepare the 10 and 1 mg/L standards.

9. Sampling

9.1 Collect the samples in accordance with Practice D 1066 and Practices D 3370, as applicable.

10. Calibration and Standardization

10.1 To 100 mL of the 1, 10, 100, and 1000 mg/L standards add 2 mL of the ionic strength adjustor (ISA). If any samples require treatment for interferences, prepare standards with the same background.

10.2 Connect and fill electrodes in accordance with manufacturer's instructions.

10.3 Transfer the 1 mg/L standard-ISA mixture to a 150 mL beaker and stir gently using the magnetic mixer. Immerse the electrodes in the solution and wait 2 min for the potential to stabilize. Record the value.

10.4 Rinse electrodes thoroughly and repeat for the 10, 100, and 1000 mg/L standard-ISA mixtures. Wait 2 min and record the potential.

10.5 The calibration curve is generated by plotting on semilogarithmic graph paper, the potential observed versus the concentration of the standard used. Note that volume corrections are incorporated into the calibration, so that samples analyzed according to Section 11 of this test method can be read directly.

11. Procedure

11.1 To any sample containing sulfide or cyanide ion, add 0.1 mL nickel sulfate solution to 100 mL sample.

NOTE 1—This concentration of nickel sulfate will react with 58 mg/L sulfide and 117 mg/L cyanide.

11.2 Transfer 100 mL sample to a 150 mL beaker and add 2 mL ionic strength adjustor. Stir thoroughly for 1 min using the magnetic mixer.

11.3 Immerse the electrodes in the sample-ISA mixture and wait 2 min for the potential to stabilize. Record the value.

11.4 Read bromide concentration of the sample, in mg/L, directly from the calibration curve. Note that volume corrections are incorporated into the calibration.

12. Precision and Bias [4]

12.1 *Precision*—The overall and single-operator precision of this test method may be expressed as follows:

12.1.1 *For Reagent Water:*

$$S_T = 0.077X + 1.10, \text{ coefficient of correlation} = 1.0$$

$$S_O = 0.067X + 0.79, \text{ coefficient of correlation} = 1.0$$

12.1.2 *For Water Matrices:*

$$S_T = 0.064X + 0.84, \text{ coefficient of correlation} = 1.0$$

$$S_O = 0.049X + 0.09, \text{ coefficient of correlation} = 1.0$$

where:

S_T = overall precision, mg/L,
S_O = single-operator precision, mg/L, and
X = concentration of bromide determined.

12.2 The selected water matrices included natural waters, ground waters, and tap water. These data on precision and bias may not apply to waters of other matrices.

12.3 *Bias*—Recoveries of known amounts of bromide from reagent water and selected water matrices were as shown in Table 1.

12.4 This information is derived from round-robin testing, in which five laboratories, including eight operators, participated. Of the eight sets of data ranked, as described in Practice D 2777, none was rejected. One operator submitted reagent

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[3] *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.

[4] Supporting data for this test method have been filed at ASTM Headquarters. Request Research Report RR:D19-1078.

TABLE 1 Recoveries of Known Amounts of Bromide from Reagent Water and Selected Water Matrices

	Amount added, mg/L	Amount found, mg/L	±Bias, %	Statistically Significant (95 % Confidence Level)
Reagent Water	0.65	0.77	+ 18.5	yes
	1.00	1.19	+ 19.0	no
	92.7	96.4	+ 3.99	no
	864	854	− 1.16	no
Water	0.65	0.80	+ 23.1	yes
	1.00	1.21	+ 21.5	yes
	92.7	95.6	+ 3.2	no
	864	836	− 3.3	yes

water data only. One outlier data point within each set was also rejected. Four sample levels were run on three days and blanks were obtained for the water used.

12.5 This section on precision and bias conforms to Practice D 2777 – 77, which was in place at the time of collaborative testing. Under the allowances made in 1.5 of Practice D 2777 – 86, these precision and bias data do meet existing requirements for interlaboratory studies of Committee D–19 test methods.

13. Keywords

13.1 bromide; ISE; ion-selective electrode

APPENDIX

(Nonmandatory Information)

X1. RATIONALE FOR DISCONTINUATION OF TEST METHODS

X1.1 *Colorimetric and Titrimetric Test Methods for Iodide and Bromide*

X1.1.1 These test methods were discontinued in 1988, and the title of the standard was changed because no iodide test methods remained in the standard. These test methods may be found in their entirety in the *1988 Annual Book of ASTM Standards*, Vol 11.01. Additional relevant data may be found in Research Report RR:D-19-57, which is filed at ASTM Headquarters.

X1.1.2 *Former Test Method A*—Colorimetric for Iodide

X1.1.2.1 This test method covers the colorimetric determination of iodide in water when concentrations up to 100 µg/L are present.

X1.1.2.2 This test method is based on the catalytic effect of traces of iodide on the rate of oxidation of arsenious ion by ceric ion in acid solution. In the presence of a small amount of iodide, the reaction follows first-order reaction rate kinetics, and, at any given temperature and reaction time, the extent of reduction of ceric ion is directly proportional to iodide concentration. Since solutions of ceric ions are yellow and those of cerous ions colorless, the extent of the reaction may be determined photometrically.

X1.1.3 *Former Test Method B*—Colorimetric for Bromide

X1.1.3.1 This test method covers colorimetric determination of bromide in water when concentrations equivalent to no more than 100 µg/L are present.

X1.1.3.2 This test method is based on the catalytic effect of traces of bromide ion on the rate of oxidation of iodine to iodate by potassium permanganate in sulfuric acid solution. Under controlled conditions of pH, temperature, and concentration of reactants, and for a given reaction time, the concentration of unreacted iodine is inversely proportional to the concentration of bromide. To determine bromide, the reaction is stopped after a given time by extraction of the unreacted iodine with carbon tetrachloride and measuring the color intensity of the exact solution at 515 nm.

X1.1.4 *Former Test Method C*—Titrimetric, for Iodide and Bromide

X1.1.4.1 This test method is recommended for samples containing appreciable amounts of iodide or bromide, or both, at concentrations greater than 5 mg/L.

X1.1.4.2 Any iodide in the sample is oxidized with bromine to the iodate in a buffered solution, the excess bromine being destroyed subsequently. Iodine equivalent to the iodate is liberated from potassium iodide and titrated with sodium thiosulfate.

X1.1.4.3 Iodide and bromide occurring together are oxidized to iodate and bromate, respectively, with hypochlorite. Iodine equivalent to the combined reaction products is liberated and measured after destroying the excess hypochlorite.

X1.1.4.4 The bromide content of the sample is calculated by difference between the iodide and combined iodide and bromide determinations.

X1.1.5 These test methods were discontinued because there were insufficient laboratories interested in participating in a collaborative study to obtain the necessary precision and bias data as required by Practice D 2777.

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