Designation: D1246 – 16

Standard Test Method for Bromide Ion in Water[1]

This standard is issued under the fixed designation D1246; 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 U.S. 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 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.6 *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:*[2]

D1066 Practice for Sampling Steam
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
D4127 Terminology Used with Ion-Selective Electrodes
D5810 Guide for Spiking into Aqueous Samples
D5847 Practice for Writing Quality Control Specifications for Standard Test Methods for Water Analysis

3. Terminology

3.1 *Definitions:*

3.1.1 For definitions of terms used in this standard, refer to Terminologies D1129 and D4127.

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

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

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[2] 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.

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

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.

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 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 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. Alternatively, certified bromide stock solutions of appropriate known purity are commercially available through chemical supply vendors and may be used.

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 D1066 and Practices D3370, as applicable.

10. Calibration and Standardization

10.1 To 100 mL of the 1, 10, 100, and 1000 mg/L NaBr 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 Follow manufacturer instructions for calibrating selective-ion meters with a direct reading of concentration capabilities. For pH meters, generate a calibration curve by creating a calibration curve on semilogrithmic graph paper or by creating a plot of mV potential versus log(10) concentration. 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 meter. 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:

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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 have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D19-1078. Contact ASTM Customer Service at service@astm.org.

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 D2777, none was rejected. One operator submitted reagent 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 D2777 – 77, which was in place at the time of collaborative testing. Under the allowances made in 1.4 of Practice D2777 – 13, these precision and bias data do meet existing requirements for interlaboratory studies of Committee D19 test methods.

13. Quality Control

13.1 In order to be certain that analytical values obtained using these test methods are valid and accurate within the confidence limits of the test, the following QC procedures must be followed when analyzing bromide.

13.2 *Calibration and Calibration Verification:*

13.2.1 Analyze at least three working standards containing concentrations of bromide that bracket the expected sample concentration prior to analysis of samples to calibrate the instrument.

13.2.2 Verify instrument calibration after standardization by analyzing a standard at the concentration of one of the calibration standards. Alternately, the concentration of a mid-range standard should fall within ± 15 % of the known concentration.

13.2.3 If calibration cannot be verified, recalibrate the instrument.

13.3 *Initial Demonstration of Laboratory Capability:*

13.3.1 If a laboratory has not performed the test before, or if there has been a major change in the measurement system, for example, new analyst, new instrument, and so forth, a precision and bias study must be performed to demonstrate laboratory capability.

13.3.2 Analyze seven replicates of a standard solution prepared from an Independent Reference Material containing a mid-range concentration of bromide. The matrix and chemistry of the solution should be equivalent to the solution used in the collaborative study. Each replicate must be taken through the complete analytical test method including any sample preservation and pretreatment steps.

13.3.3 Calculate the mean and standard deviation of the seven values and compare to the acceptable ranges of bias in Table 1. This study should be repeated until the recoveries are within the limits given in Table 1. If a concentration other than the recommended concentration is used, refer to Practice D5847 for information on applying the F test and t test in evaluating the acceptability of the mean and standard deviation.

13.4 *Laboratory Control Sample (LCS):*

13.4.1 To ensure that the test method is in control, prepare and analyze a LCS containing a mid-range concentration of bromide with each batch (laboratory-defined or 20 samples). The laboratory control samples for a large batch should cover the analytical range when possible. It is recommended, but not required to use a second source, if possible and practical for the LCS. The LCS must be taken through all of the steps of the analytical method including sample preservation and pretreatment. The result obtained for the LCS shall fall within ±15 % of the known concentration.

13.4.2 If the result is not within these limits, analysis of samples is halted until the problem is corrected, and either all the samples in the batch must be reanalyzed, or the results must be qualified with an indication that they do not fall within the performance criteria of the test method.

13.5 *Method Blank:*

13.5.1 Analyze a reagent water test blank with each laboratory-defined batch. The concentration of bromide found in the blank should be less than 0.5 times the lowest calibration standard. If the concentration of bromide is found above this level, analysis of samples is halted until the contamination is eliminated, and a blank shows no contamination at or above this level, or the results must be qualified with an indication that they do not fall within the performance criteria of the test method.

13.6 *Matrix Spike (MS):*

13.6.1 To check for interferences in the specific matrix being tested, perform a MS on at least one sample from each

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

laboratory-defined batch by spiking an aliquot of the sample with a known concentration of bromide and taking it through the analytical method.

13.6.2 The spike concentration plus the background concentration of bromide must not exceed the high calibration standard. The spike must produce a concentration in the spiked sample that is 2 to 5 times the bromide concentration in the unspiked sample, or 10 to 50 times the detection limit of the test method, whichever is greater.

13.6.3 Calculate the percent recovery of the spike (P) using the following calculation:

$$P = 100\left[A\left(V_s + V\right) - BV_s\right]/CV$$

where:

A = analyte concentration (mg/L) in spiked sample,
B = analyte concentration (mg/L) in unspiked sample,
C = concentration (mg/L) of analyte in spiking solution,
V_s = volume (mL) of sample used, and
V = volume (mL) of spiking solution added.

13.6.4 The percent recovery of the spike shall fall within the limits, based on the bromide concentration, listed in Guide D5810, Table 1. If the percent recovery is not within these limits, a matrix interference may be present in the sample selected for spiking. Under these circumstances, one of the following remedies must be employed: the matrix interference must be removed, all samples in the batch must be analyzed by a test method not affected by the matrix interference, or the results must be qualified with an indication that they do not fall within the performance criteria of the test method.

NOTE 2—Acceptable spike recoveries are dependent on the concentration of the component of interest. See Guide D5810 for additional information.

13.7 *Duplicate:*

13.7.1 To check the precision of sample analyses, analyze a sample in duplicate with each laboratory-defined batch. If the concentration of the analyte is less than five times the detection limit for the analyte, a matrix spike duplicate (MSD) should be used.

13.7.2 Calculate the standard deviation of the duplicate values and compare to the precision in the collaborative study using an F test. Refer to 6.4.4 of Practice D5847 for information on applying the F test.

13.7.3 If the result exceeds the precision limit, the batch must be reanalyzed or the results must be qualified with an indication that they do not fall within the performance criteria of the test method.

13.8 *Independent Reference Material (IRM):*

13.8.1 In order to verify the quantitative value produced by the test method, analyze an Independent Reference Material (IRM) submitted as a regular sample (if practical) to the laboratory at least once per quarter. The concentration of the IRM should be in the concentration mid-range for the method chosen. The value obtained must fall within the control limits established by the laboratory.

14. Keywords

14.1 bromide; ion-selective electrode ; ISE

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:D19-0057.[5]

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

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[5] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D19-0057. Contact ASTM Customer Service at service@astm.org.

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 D2777.

SUMMARY OF CHANGES

Committee D19 has identified the location of selected changes to this standard since the last issue (D1246 – 10) that may impact the use of this standard. (Approved June 15, 2016.)

(1) Modified 8.5 for the purity of standards.
(2) Modified 10.5 for direct reading meters.
(3) Modified 13.4.1.

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