Designation: D3651 – 16

Standard Test Method for Barium in Brackish Water, Seawater, and Brines[1]

This standard is issued under the fixed designation D3651; 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 This test method covers the determination of soluble barium ion in brackish water, sea-water, and brines by atomic absorption spectrophotometry.

1.2 The actual working range of this test method is 1 to 5 mg/L barium.

1.3 This test method was used successfully on artificial brine samples. It is the user's responsibility to ensure the validity of this test method for waters of untested matrices.

1.4 The values stated in SI units are to be regarded as standard. The values given in parentheses are mathematical conversion to inch-pound units that are provided for information only and are not considered 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.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

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
D4691 Practice for Measuring Elements in Water by Flame Atomic Absorption Spectrophotometry
D4841 Practice for Estimation of Holding Time for Water Samples Containing Organic and Inorganic Constituents
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 Terminology D1129.

4. Summary of Test Method

4.1 This test method[3,4] is dependent upon the fact that metallic atoms, in the ground state, will absorb light of the same wavelength they emit when excited. When radiation from a given excited element is passed through a flame containing ground state atoms of that element, the intensity of the transmitted radiation will decrease in proportion to the amount of the ground state element in the flame. A hollow-cathode lamp whose cathode is made of the element to be determined provides the radiation.

4.2 The metal atoms[5,6] to be measured are placed in the beam of radiation by aspirating the specimen into an oxidant-fuel flame. A monochromator isolates the characteristic radiation from the hollow-cathode lamp and a photosensitive device measures the attenuated transmitted radiation.

4.3 Since the variable and sometimes high concentrations of matrix materials in the waters and brines affect absorption differently, it becomes imperative to prepare standard samples with matrices similar to the unknown samples. This is accomplished by preparing synthetic standard samples with similar compositions as the unknowns. The standard samples and unknown samples are aspirated, the absorption readings recorded, a calibration curve for the standard samples constructed, and the original sample concentration calculated.

[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.

[3] Fletcher, G. F., and Collins, A. G., *Atomic Absorption Methods of Analysis of Oil Field Brines: Barium, Calcium, Copper, Iron, Lead, Lithium, Magnesium, Manganese, Potassium, Sodium, Strontium, and Zinc*, U.S. Bureau of Mines, Report of Investigations 7861, 1974, 14 pp.

[4] Collins, A. G., *Geochemistry of Oil Field Waters*, Elsevier Publishing Co., Amsterdam, The Netherlands, 1974.

[5] Angino, E. E., and Billings, G. K., *Atomic Absorption Spectrophotometry in Geology*, Elsevier Publishing Co., New York, NY, 1967.

[6] Dean, J. A., and Rains, T. C., Editors, *Flame Emission and Atomic Absorption Spectrophotometry,* Volume 1, Theory, 1969, Volume 2, Components, 1971, and Volume 3, Elements and Matrices, 1975, Marcel Dekker, New York, NY.

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

5. Significance and Use

5.1 Since water containing acid-soluble barium compounds is known to be toxic, this test method serves the useful purpose of determining the barium in brackish water, seawater, and brines.

6. Interferences

6.1 Ionization interference is controlled by adding potassium.

6.2 Matrix interferences, caused by high concentrations of varied ions, and spectral interference, caused by high calcium concentrations, are controlled by matching the matrices.

6.3 This test method is subject to calcium interference, but the procedure provided eliminates the interference effect of up to 750 mg/L calcium. Calcium interference can also be minimized by using a secondary wavelength of 455.4 nm.

6.4 In high sulfate waters, such as seawater, barium will be precipitated as barium sulfate and will not be present as soluble barium and will, therefore, be below the detection limit of the test method.

7. Apparatus

7.1 *Atomic Absorption Spectrophotometer*—for use at 553.6 nm. A general guide for the use of flame atomic absorption applications is given in Practice D4691.

NOTE 1—The manufacturer's instructions should be followed for all instrumental parameters. Wavelengths other than 553.6 nm may be used only if they have been determined to be equally suitable.

7.1.1 *Multielement Hollow-Cathode Lamps* are available and have been found satisfactory.

7.2 *Pressure-Reducing Valves*—The supplies of fuel and oxidant shall be maintained at pressures somewhat higher than the controlled operating pressure of the instrument by suitable valves.

8. Reagents and Materials

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,[7] 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.

8.2 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.

8.3 *Barium Solution, Stock* (1 mL = 1 mg Ba)—Dissolve 1.779 g of barium chloride ($BaCl_2 \cdot 2H_2O$) in 50 mL of concentrated hydrochloric acid (HCl) (sp gr 1.19) and about 700 mL of water. Dilute the solution to 1 L with water. One millilitre of this solution contains 1 mg of barium. A purchased stock solution of appropriate known purity is also acceptable.

8.4 *Barium Solution, Standard* (1 mL = 0.1 mg Ba)—Add 100 mL of barium solution stock to 50 mL of concentrated HCl (sp gr, 1.19) and about 600 mL of water. Dilute the solution to 1 L with water. One millilitre of this solution contains 0.1 mg of barium.

8.5 *Potassium Solution* (1 mL = 10 mg K)—Dissolve 19.07 g of potassium chloride (KCl) in about 700 mL of water. Dilute the solution to 1 L with water. One millilitre of this solution contains 10 mg of potassium. A purchased stock solution of appropriate known purity is also acceptable.

8.6 *Calcium Solution* (1 mL = 10 mg Ca)—Dissolve 54.66 g of calcium chloride hexahydrate ($CaCl_2 \cdot 6H_2O$) in 500 mL of water. Dilute the solution to 1 L with water. One millilitre of this solution contains 10 mg of calcium. A purchased stock solution of appropriate known purity is also acceptable.

8.7 *Sodium Solution* (1 mL = 10 mg Na)—Dissolve 25.14 g sodium chloride (NaCl) in 500 mL of water. Dilute the solution to 1 L with water. One millilitre of this solution contains 10 mg of sodium. A purchased stock solution of appropriate known purity is also acceptable.

8.8 *Hydrochloric Acid* (sp gr 1.19)—Concentrated hydrochloric acid, ultrapure or equivalent.

8.9 *Oxidant:*

8.9.1 *Nitrous Oxide* is the oxidant required for this test method.

8.10 *Fuel:*

8.10.1 *Acetylene*—Standard, commercially available acetylene is the usual fuel. Acetone, always present in acetylene cylinders, can be prevented from entering and damaging the burner head by replacing a cylinder which has only 690 kPa (100 psig) of acetylene remaining.

8.11 *Filter Paper*—Purchase suitable filter paper. Typically the filter papers have a pore size of 0.45-µm membrane. Material such as fine-textured, acid-washed, ashless paper, or glass fiber paper are acceptable. The user must first ascertain that the filter paper is of sufficient purity to use without adversely affecting the bias and precision of the test method.

9. Sampling

9.1 Collect the sample in accordance with Practices D3370 and D4841.

9.2 Add 2.0 mL of HCl per litre of water to prevent precipitation of soluble barium.

10. Calibration and Standardization

10.1 Prepare standards of 0.0, 1.0, 2.5, 5.0, and 10 mg/L of Ba by adding 0, 1.0, 2.5, 5.0, and 10 mL of barium standard solution to 100-mL volumetric flasks.

[7] *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.

10.2 Add to each standard 5 mL of concentrated HCl (sp gr 1.19), 10 mL of potassium solution (1 mL = 10 mg of K), 7.5 mL of calcium solution (1 mL = 10 mg of Ca), and 15 mL of sodium solution (1 mL = 10 mg of Na). Dilute these solutions to 100 mL with water.

10.3 The method of operation varies with different models of atomic absorption spectrophotometers. Therefore, no attempt is made here to describe in detail the steps for placing an instrument into operation. However, the parameters that follow have been found suitable for some types of equipment.

10.3.1 Turn on the instrument.

10.3.2 Apply the current to the cathode lamp as suggested by the manufacturer: Allow the instrument to warm up until the energy source stabilizes. The time required is from 10 to 20 min.

10.3.3 Ignite an air-acetylene flame. Increase the fuel flow until the flame is luminescent. Let the flame stabilize (about 10–15 s). Switch to the nitrous oxide. Provide concentration of metal in accordance with the instructions outlined by the manufacturer, to give maximum sensitivity.

10.3.4 Let the fuel-oxidant mixture burn for 10 to 15 min before operating the instrument.

10.4 Operate the instrument in the absorption mode and aspirate the 0 mg/L barium standard and set the instrument to zero absorbance.

10.4.1 Aspirate the 10 mg/L barium standard and record the absorbance reading. This value is used for roughly estimating the barium concentration in a sample.

10.4.2 Operate the instrument in the concentration mode and optimize the instrument settings.

10.4.3 Aspirate the 1.0, 2.5, and 5.0 mg/L barium standards and record the absorbance readings.

10.4.4 Construct a calibration curve from the barium concentrations and absorbance readings by plotting the milligrams per litre of barium versus the absorbance readings.

11. Procedure

11.1 Determine barium at the 553.6-nm wavelength with a nitrous oxide-acetylene flame.

11.1.1 Operate instrument in an absorption mode.

11.1.2 *Approximate Barium Concentration*—Aspirate a sample of water or brine (previously filtered through a 0.45-µm filter (8.11) into the flame and record the absorbance reading. The absorbance reading is compared to the 10 mg/L barium standard (10.4.1) absorbance reading.

NOTE 2—All absorbance readings on waters of high mineral content should be made as quickly as possible. Highly saline waters cause clogging of the burner which results in large errors in the determinations. In some instances, the oxidant and fuel have to be turned off and the burner cleaned before completing a series of determinations.

11.1.2.1 Transfer an aliquot of the water or brine, containing approximately 0.1 to 0.5 mg of barium, to a 100-mL volumetric flask.

11.1.2.2 Add 5.0 mL of concentrated HCl (sp gr 1.19) and 10 mL of potassium solution (1 mL = 10 mg K) to the flask. Dilute the sample to 100 mL with water.

11.2 Operate the instrument in the concentration mode.

TABLE 1 Determination of Precision and Bias

Amount Added, mg/L	Amount Found, mg/L	S_T	S_O	Bias, ± %	Statistically Significant (95 % confidence level)
53.0	53.3	4.9	4.11	+ 0.43	no
98.0	94.9	9.3	9.21	–3.19	no
603	541	47.8	46.25	–10.4	yes
1009	901	90.7	102.3	–10.7	yes

11.3 Aspirate the sample and record the absorbance reading.

12. Calculation

12.1 Calculate the concentration of barium ion in the original sample in milligrams per litre using the calibration curve prepared in 10.4.2 through 10.4.4 as follows:

$$\text{Barium concentration, mg/L} = A \times D/V$$

where:

A = barium read from the calibration curve,
D = dilution volume (volume the sample was diluted to), and
V = volume of sample.

13. Precision and Bias[8]

13.1 The precision and bias data presented in Table 1 for this test method meet the requirements of Practice D2777. The data shown have been rounded from unrounded data in the research report.

13.2 The precision and bias estimates in Table 1 are based on an interlaboratory study on four artificial brine samples containing various amounts of barium and interfering ions as shown in Table 2. One analyst in one laboratory and two analysts in each of four laboratories performed single determinations on each of three days. Practice D2777 was used in developing these precision and bias estimates. It is the user's responsibility to ensure the validity of this test method for waters of untested matrices.

13.3 Precision and bias for this test method 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.

14. Quality Control

14.1 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 barium.

14.2 *Calibration and Calibration Verification:*

[8] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D19-1046. Contact ASTM Customer Service at service@astm.org.

TABLE 2 Composition of Artificial Brine Samples

Sample No.	g/L			
	1	2	3	4
NaCl	24.0	100.0	50.0	150.0
KCl	0.5	2.0	1.0	3.0
KBr	1.0	2.0	2.0	2.0
KI	0.1	0.5	0.5	1.0
$CaCl_2$	1.5	3.0	2.0	5.0
$MgCl_2$	4.5	5.0	2.0	1.0
$SrCl_2$	0.05	1.0	0.5	0.5
Ba^{++}	0.0530	0.0980	0.6030	1.0090

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

14.2.2 Verify instrument calibration after standardization by analyzing a standard at the concentration of one of the calibration standards. The absorbance shall fall within 4 % of the absorbance from the calibration. Alternately, the concentration of a mid-range standard should fall within ±15 % of the known concentration. Analyze a calibration blank to verify system cleanliness.

14.2.3 If calibration cannot be verified, recalibrate the instrument.

14.2.4 It is recommended to analyze a continuing calibration blank (CCB) and continuing calibration verification (CCV) at a 10 % frequency. The results should fall within the expected precision of the method or ±15 % of the known concentration.

14.3 *Initial Demonstration of Laboratory Capability:*

14.3.1 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, etc., a precision and bias study must be performed to demonstrate laboratory capability.

14.3.2 Analyze seven replicates of a standard solution prepared from an Independent Reference Material containing a mid-range concentration of barium. 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.

14.3.3 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.

14.4 *Laboratory Control Sample (LCS):*

14.4.1 To ensure that the test method is in control, prepare and analyze a LCS containing a mid-range concentration of barium with each batch (laboratory-defined or 10 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.

14.4.2 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.

14.5 *Method Blank:*

14.5.1 Analyze a reagent water test blank with each laboratory-defined batch. The concentration of barium found in the blank should be less than 0.5 times the lowest calibration standard. If the concentration of barium 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.

14.6 *Matrix Spike (MS):*

14.6.1 To check for interferences in the specific matrix being tested, perform a MS on at least one sample from each laboratory-defined batch by spiking an aliquot of the sample with a known concentration of barium and taking it through the analytical method.

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

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

$$P = 100\left[A(Vs+V) - B\ Vs\right]/C\ V$$

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
V = Volume (mL) of spiking solution added

14.6.4 The percent recovery of the spike shall fall within the limits, based on the analyte 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 3—Acceptable spike recoveries are dependent on the concentration of the component of interest. See Guide D5810 for additional information.

14.7 *Duplicate:*

14.7.1 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.

14.7.2 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.

14.7.3 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.

14.8 *Independent Reference Material (IRM):*

14.8.1 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.

15. Keywords

15.1 barium; brackish; brine; seawater

SUMMARY OF CHANGES

Committee D19 has identified the location of selected changes to this standard since the last issue (D3651 – 11) that may impact the use of this standard. (Approved June 1, 2016.)

(1) Modified 1.4 to update the SI statement.
(2) Modified Section 8 to update the purity of commercial standards and add filter paper information.
(3) Modified 14.2.3, 14.2.4, and 14.4.1.