Designation: D3986 − 17

Standard Test Method for Barium in Brines, Seawater, and Brackish Water by Direct-Current Argon Plasma Atomic Emission Spectroscopy[1]

This standard is issued under the fixed designation D3986; 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 dissolved and total recoverable barium in brines, seawater, and brackish waters by direct-current argon plasma atomic emission spectroscopy (DCP–AES).

1.2 This test method has been tested in the range from 10 mg/L to 20 mg/L. Samples shall be diluted to contain concentrations within the calibration range (see 11.1 and 12.5). Higher concentrations can also be determined by changing to a less sensitive emission line.

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

1.4 *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.*

1.5 *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:*[2]

D1129 Terminology Relating to Water
D1193 Specification for Reagent Water
D3352 Test Method for Strontium Ion in Brackish Water, Seawater, and Brines
D3370 Practices for Sampling Water from Closed Conduits
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
E1097 Guide for Determination of Various Elements by Direct Current Plasma Atomic Emission Spectrometry

3. Terminology

3.1 *Definitions:*

3.1.1 For definitions of terms used in this standard, refer to Terminology D1129.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *continuing calibration blank, n*—a solution containing no analytes (of interest) which is used to verify blank response and freedom from carryover.

3.2.2 *continuing calibration verification, n*—a solution (or set of solutions) of known concentration used to verify freedom from excessive instrumental drift; the concentration is to cover the range of calibration curve.

3.2.3 *laboratory control sample, n*—a solution with a certified concentration of barium.

3.2.4 *total recoverable barium, n*—a descriptive term relating to the forms of barium recovered in the acid-digestion procedure specified in this test method.

4. Summary of Test Method

4.1 This test method is dependent upon excitation of the barium atom by a direct-current plasma source. When the excited barium atom decays to a lower energy state it emits energy of a wavelength characteristic to the barium atom. The intensity of this emitted radiation will increase in direct proportion to the concentration of barium in the sample, when working in the linear response range.

4.2 Since the variable and often high concentration of matrix materials in brines, seawater, and brackish water affect emission differently, it is a difficult task to prepare standards sufficiently similar to the samples. To overcome this problem, the standards are buffered with lithium ion and the samples are diluted and buffered in the same manner. The standards are used to construct a calibration curve and the concentration of

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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**

the samples are calculated from this curve. Alternatively, the instrument may be calibrated using a blank and a standard or bracketing standards. The sample concentration can then be read out directly from the instrument.

4.3 The 455.4-nm line has been found to be the most satisfactory for analysis.

NOTE 1—The barium lines at 230.4 nm, 233.5 nm, and 553.6 nm have been checked and found to be unsatisfactory for this analysis.

4.4 Dissolved barium is determined by filtering the sample through a 0.45-µm pore size membrane filter (Note 2) at the time of sampling. This definition of "dissolved" barium is arbitrary since very fine crystals of barium sulfate may pass through the membrane filter.

NOTE 2—These filters have been found to be contaminated to various degrees with heavy metals depending on the manufacturer. Care should be exercised in selecting a source for these filters. It has been found to be a good practice to wash the filters with nitric acid and then reagent water before filtering a sample.

4.5 If there are no visible suspended solids in the sample, total recoverable barium may be determined on an acidified unfiltered sample in the same manner as dissolved barium.

4.6 When the sample contains suspended solids total recoverable barium is determined by an acid digestion step to destroy organic and inorganic particulates.

5. Significance and Use

5.1 All waters containing acid soluble barium compounds are known to be toxic. This test method is useful for the determination of barium in brines, seawater, and brackish waters.

5.2 Consumption, inhalation, or absorption of 500 to 600 mg of barium is considered fatal to human beings. Lower levels may result in disorders of the heart, blood vessels, and nerves. The drinking water standards set the maximum contaminant level for barium as 2 mg/L barium.

6. Interferences

6.1 Calcium interferes in concentrations greater than 300 mg/L, however, this can be overcome by dilution of the sample. The method of standard additions as described in Test Method D3352 will also overcome this interference.

6.2 High concentrations of sulfate anion are also known to interfere in this test method by causing precipitation of barium in the form of barium sulfate.

7. Apparatus

7.1 See the manufacturer's instruction manual on installation and operation of direct-current argon plasma spectrometers. Refer to Guide E1097 for information on DCP spectrometers.

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 reagents shall conform to the specifications of the committee on analytical reagents of the American Chemical Society,[3] 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 *Purity of Water*—Unless otherwise indicated, reference to water shall be understood to mean reagent water conforming to Type II of Specification D1193. 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 II water was specified at the time of round robin testing of this test method.

8.3 *Barium Solution, Stock* (1g/L Ba)—Dissolve 1.7787 g of barium chloride dihydrate ($BaCl_2 \cdot 2H_2O$) in 100 mL of water, add 2 mL of nitric acid (sp gr 1.42) and dilute to 1 L. A purchased stock solution of appropriate known purity is also acceptable.

8.4 *Barium Solution, Standard* (50 mg/L)—To 5.0 mL of barium stock solution add 5.0 mL of lithium solution (8.8) and dilute to 100 mL with HCl (1 + 499) (8.10). Working standards (11.1) are prepared from this solution.

8.5 *Hydrochloric Acid* (sp gr 1.19)—Concentrated hydrochloric acid (HCl).

NOTE 3—If a high reagent blank is obtained for either acid, distill the acid or use spectrograde acid.

8.5.1 **Caution**—When HCl is distilled, an azeotropic mixture is obtained (approximately 6 *N* HCl).

8.6 *Hydrochloric Acid* (1 + 499)—Add 1 volume of hydrochloric acid (sp gr 1.19) to 499 volumes of water.

8.7 *Lithium Carbonate*—High-purity lithium carbonate (Li_2CO_3).[4]

8.8 *Lithium Solution* (40 g/L Li)—Dissolve 213.0 g of Li_2CO_3 in a minimum amount of hydrochloric acid (sp gr 1.19) and dilute to 1 L with water. Approximately 250 mL of HCl (sp gr 1.19) is needed to completely dissolve the lithium carbonate. If distilled HCl is used double the amount (see 8.5, Note 3). Store in a cleaned polyethylene or TFE-fluorocarbon bottle.

8.9 *Nitric Acid* (sp gr 1.42)—Concentrated nitric acid (HNO_3).

8.10 *Nitric Acid* (1 + 499)—Add 1 volume of nitric acid (sp gr 1.42) to 499 volumes of water.

8.11 *Filter Paper*—Purchase suitable filter paper. Typically the filter papers have a pore size of 0.45-µm membrane.

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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 *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.

[4] The sole source of supply of the apparatus known to the committee at this time is LI 30 or its equivalent from Spex Industries, Inc., Box 798, Metuchen, NJ 08840. If you are aware of alternative suppliers, please provide this information to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee,[1] which you may attend.

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. Hazards

9.1 As with any method where pumping or aspiration of samples is employed, the viscosity of blank, standards, and samples must be controlled within reasonable limits (that is, do not use reagent water standards to analyze oil field brines).

9.2 To analyze waters containing a high percentage of dissolved solids it is necessary to prepare standards and blanks with matrices similar to the unknown samples. In many cases this is almost impossible and the problem can be solved by high dilution and introduction of lithium ion as an emission enhancement buffer.

10. Sampling

10.1 Collect the sample in accordance with Practices D3370.

10.2 Preserve the samples with high-purity hydrochloric acid to a pH of two or less immediately at the time of collection (about 2 mL/L). If only dissolved barium is to be determined, filter the samples through a 0.45-µm membrane (Note 2) filter before acidification.

NOTE 4—Alternatively, the pH may be adjusted in the laboratory within 14 days of collection. However, acid must be added at least 24 hours before analysis to dissolve any metals that adsorb to the container walls. This could reduce hazards of working with acids in the field when appropriate.

11. Standardization and Calculation

11.1 Prepare 100 mL each of a blank and 0.01, 0.02, 0.05, and 0.10 mg/L standards by diluting 5 mL of lithium solution (8.8) and 20, 40, 100, and 200 µL of barium standard solution (8.4) with HCl (1 + 499). Prepare standards and blank each time the test is performed, or as determined by Practice D4841.

11.2 Aspirate the blank and standards. Aspirate HNO_3 (1 + 499) between each standard and sample.

11.3 Using the instrument software, verify that the instrument calibration is within user acceptable QC limits and report the barium concentrations accordingly.

12. Procedure

12.1 When determining dissolved barium the sample should be previously filtered through a 0.45-µm membrane filter (8.11) and acidified (10.2) then proceed with 12.5.

12.2 When determining total recoverable barium and precipitation has occurred or large amounts of suspended solids are present, add 5 mL each of nitric acid (sp gr 1.42) and HCl (sp gr 1.19) to 100 mL of the sample and proceed with 12.3 and 12.4.

12.3 Heat the samples (between 65°C and 95°C) on a steam bath or hot plate below boiling until the volume is reduced to 15 to 20 mL, making certain that the samples do not boil.

NOTE 5—When analyzing samples of brines or samples containing large amounts (>5 %) of dissolved solids. The amount of reduction in volume is left to the discretion of the analyst.

NOTE 6—Many laboratories have found block digestion systems a useful way to digest samples for trace metals analysis. Systems typically consist of either a metal or graphite block with wells to hold digestion tubes. The block temperature controller must be able to maintain uniformity of temperature across all positions of the block. The digestion block must be capable of maintaining a temperature between 65°C and 95°C. For trace metals analysis, the digestion tubes should be constructed of polypropylene and have a volume accuracy of at least 0.5%. All lots of tubes should come with a certificate of analysis to demonstrate suitability for their intended purpose.

12.4 Cool and filter the samples through fine ashless filter paper (8.11) into 100-mL volumetric flasks. Wash the filter paper at least three times with water and adjust to 100 mL volume.

12.5 *Approximate Barium Concentration*—Aspirate the sample and compare its emission intensity to that of the barium solution standard (50 mg/L, 8.4). It should be stressed that this is not an accurate result and is to be used only to calculate the quantity of sample needed for dilution in 12.6.

12.6 Transfer an aliquot of the sample containing approximately 0.001 to 0.01 mg of barium to a 100-mL volumetric flask. Add 5 mL of lithium solution and dilute to volume with HCl (1 + 499).

12.7 Aspirate the sample and record its emission intensity at 455.4 nm. Concentrations may be read directly if this capability is provided. Aspirate HNO_3 (1 + 499) between samples and standards.

13. Precision and Bias[5]

13.1 *Precision*—The overall and single-operator precision of this method within its designated range for brines, seawater, and brackish water varies with the quantity tested in accordance with Table 1. Eight operators from six laboratories participated in this study by determining three replicates, on different days, at each concentration level as listed in Table 2.

13.2 *Bias*—Recoveries of barium from brines and selected water matrices were as shown in Table 1.

13.3 It is the user's responsibility to ensure the validity of this test method for waters of untested matrices.

13.4 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

TABLE 1 Determination of Precision and Bias for Barium by Direct-Current Argon Plasma Atomic Emission Spectroscopy

Amount Added, mg/L	Amount Found, mg/L	S_t, mg/L	S_O, mg/L	%, Bias	Statistically Significant 95 % Level
10.0	10.88	1.076	0.39	+8.8	yes
15.0	15.50	0.664	0.48	+3.3	yes
20.0	20.32	0.756	0.70	+1.6	yes

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[5] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D19-1071. Contact ASTM Customer Service at service@astm.org.

TABLE 2 Composition of Artificial Brine Samples, g/L

Sample No.	1	2	3
Chemical Compound:			
NaCl [A]	100.0	50.0	150.0
KCl [A]	1.00	2.00	1.00
KBr [A]	1.00	2.00	1.00
KI [A]	0.500	1.00	0.500
$CaCl_2$ [A]	8.00	10.00	8.00
$MgCl_2$ [A]	4.50	5.00	5.00
$SrCl_2$ [A]	1.000	0.500	1.000
Ba^{++} [B]	10.0	15.0	20.0

[A] Concentrations in grams per litre.

[B] Concentrations in milligrams per litre.

D2777 – 13, these precision and bias data do meet existing requirements for interlaboratory studies of Committee D19 test methods.

14. Quality Control (QC)

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:*

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 (see 11.1). The calibration correlation coefficient shall be equal to or greater than 0.990.

14.2.2 Verify instrument calibration after standardization by analyzing a standard at the concentration of one of the calibration standards. The concentration of a mid-range standard should fall within ±15 % of the known concentration. Analyze a calibration blank to verify system cleanliness. The blank result should be less than the method reporting limit.

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 CCB result should be less than the method reporting limit. The CCV 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, and so forth, 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 midrange 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 known concentration of barium 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 a mid-range 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 formula:

$$P = 100[A\,(V_s + V) - BV_s]/CV \qquad (1)$$

where:

A = analyte known concentration (mg/L) in spiked sample,

B = analyte known concentration (mg/L) in unspiked sample,

C = known concentration (mg/L) of analyte in spiking solution,

V_s = volume (mL) of sample used, and

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 7—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 water; brines; direct-current argon plasma atomic emission; seawater; spectroscopy

SUMMARY OF CHANGES

Committee D19 has identified the location of selected changes to this standard since the last issue (D3986 – 11) that may impact the use of this standard. (Approved June 1, 2017.)

(1) Revised Section 2 to include D4841 and D5810.
(2) Revised Section 3 to update and add terms.
(3) Revised Section 8 for the purity of commercial standards and to add information on filter paper.
(4) Revised Note 4 for pH of the samples in the laboratory.
(5) Revised Section 11 for the preparation of standards.
(6) Revised Section 12 with information on the use of block digestion systems.
(7) Rewrote and expanded Section 14.