Designation: D 3986 – 02

An American National Standard

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

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 *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 1129 Terminology Relating to Water[2]

D 1192 Specification for Equipment for Sampling Water and Steam in Closed Conduits[2]

D 1193 Specification for Reagent Water[2]

D 3352 Test Method for Strontium Ion in Brackish Water, Seawater, and Brines[3]

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

D 5847 Practice for Writing Quality Control Specifications for Standard Test Methods for Water Analysis [3]

E 1097 Guide for Direct Current Plasma Emission Spectrometry Analysis[4]

3. Terminology

3.1 *Definitions*—For definitions of terms used in this test method refer to Terminology D 1129.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *total recoverable barium*—recoverable forms of barium that are determinable by the digestion method which is included in the procedure.

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

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 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.

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

[3] *Annual Book of ASTM Standards,* Vol 11.02.

[4] *Annual Book of ASTM Standards,* Vol 03.05.

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 D 3352 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 E 1097 for information on DCP spectrometers.

8. Reagents

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[5], 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 D 1193. 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.

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). [6]

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.

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 the applicable method, Specification D 1192, or Practices D 3370.

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.

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

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[5] *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.

[6] A lithium carbonate that has been found satisfactory for preparing this solution is LI 30 or its equivalent from Spex Industries, Inc., Box 798, Metuchen, NJ 08840.

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

(8.4) with HCl (1 + 499). Prepare standards and blank each time the test is performed.

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 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 on a steam bath or hot plate until the volume is reduced to 15 to 20 mL, making certain that the samples do not boil.

NOTE 4—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.

12.4 Cool and filter the samples through fine ashless filter paper 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 [7]

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.

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.

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 D 2777-77, which was in place at the time of collaborative testing. Under the allowances made in 1.4 of D 2777-98, these precision and bias data do meet existing requirements for interlaboratory studies of Committee D19 test methods.

14. Quality Control (QC)

14.1 The following quality control information is recommended for the determination of Barium in Brines, Seawater, and Brackish Water.

14.2 The instrument shall be calibrated using a minimum of four calibration standards and a calibration blank. The calibration correlation coefficient shall be equal to or greater than 0.990. In addition to the initial calibration blank, a calibration blank should be analyzed at the end of the batch run to ensure contamination was not a problem during the batch analysis.

14.3 An instrument check standard shall be analyzed at a minimum frequency of 10 % throughout the batch analysis. The value of the instrument check standard shall fall between 80 % and 120 % of the true value.

14.4 Two method blanks shall be prepared ensuring that an adequate method blank volume is present for a minimum of seven repetitive analysis. The standard deviation of the method blank is used to determine the minimum detectable concentration of each sample and control in the batch.

14.5 A Laboratory Control Sample shall be analyzed with each batch of sample at a minimum frequency of 10 %.

14.6 If the QC for the sample batch is not within the established control limits, reanalyze the samples or qualify the results with the appropriate flags, or both (Practice D 5847).

14.7 Blind control samples should be submitted by an outside agency in order to determine the laboratory performance capabilities.

15. Keywords

15.1 barium; brackish water; brines; direct-current argon plasma atomic emission; seawater; spectroscopy

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[7] Supporting data are available from ASTM International Headquarters. Request RR: D19-1071.

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