



Designation: ~~D3986~~—~~11~~ D3986 – 17

Standard Test Method for Barium in Brines, Seawater, and Brackish Water by Direct-Current Argon Plasma Atomic Emission Spectroscopy¹

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 ~~Defenitions—Definitions:~~ For definitions of terms used in this test method refer to Terminology D1129.

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 ~~total recoverable barium~~, continuing calibration blank, n—recoverable barium forms that are determinable by the digestion method that is included in the procedure; 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.*

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. Current edition approved Sept. 1, 2011; June 1, 2017. Published September 2011; June 2017. Originally approved in 1981. Last previous edition approved in 2007, 2011 as ~~D3986—07~~ D3986 – 11. DOI: 10.1520/D3986-11; 10.1520/D3986-17.

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

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 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- μ m 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

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.

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 ($\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$) 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 adequate-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. 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 Practice 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~~ 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.

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.