



Designation: 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

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.

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

*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 ($\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$) 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 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.

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.