



Standard Test Method for Barium in Water, Atomic Absorption Spectrophotometry, Graphite Furnace¹

This standard is issued under the fixed designation D 4382; 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 most waters and wastewaters.

1.2 This test method was evaluated in the range from 33.5 to 132 µg/L of barium. The range can be increased or decreased by varying the volume of sample injected or the instrumental settings. High concentrations may be diluted but preferably should be analyzed by direct aspiration atomic absorption spectrophotometry.

1.3 This test method has been used successfully with waste treatment plant effluent water, lake water, filtered tap water, and well water. It is the responsibility of the analyst to determine the suitability of the test method for other matrices.

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.*

2. Referenced Documents

2.1 ASTM Standards:

- D 858 Test Methods for Manganese in Water²
- D 1068 Test Methods for Iron in Water²
- D 1129 Terminology Relating to Water²
- D 1193 Specification for Reagent Water²
- D 1687 Test Methods for Chromium in Water²
- D 1688 Test Methods for Copper in Water²
- D 1886 Test Methods for Nickel in Water²
- D 2972 Test Methods for Arsenic in Water²
- D 3373 Test Method for Vanadium in Water²
- D 3557 Test Methods for Cadmium in Water²
- D 3558 Test Methods for Cobalt in Water²
- D 3559 Test Methods for Lead in Water²
- D 3859 Test Methods for Selenium in Water²
- D 3866 Test Methods for Silver in Water²
- D 3919 Practice for Measuring Trace Elements in Water by Graphite Furnace Atomic Absorption Spectrophotometry²
- D 4691 Practice for Measuring Elements in Water by Flame

¹ This test method is under the jurisdiction of ASTM Committee D-19 on Water and is the direct responsibility of Subcommittee D19.05 on Inorganic Constituents in Water.

Current edition approved Sept. 10, 1995. Published November 1995. Originally published as D 4382 – 84. Last previous edition D 4382 – 91.

² Annual Book of ASTM Standards, Vol 11.01.

Atomic Absorption Spectrophotometry²

D 4841 Practice for Estimation of Holding Time for Water Samples Containing Organic and Inorganic Constituents²

3. Terminology

3.1 Definitions:

3.1.1 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*—an arbitrary analytical term relating to the recoverable forms of barium that are determinable by the digestion method which is included in this test method.

4. Summary of Test Method

4.1 Barium is determined by an atomic absorption spectrophotometer used in conjunction with a graphite furnace. A sample is placed in a graphite tube, evaporated to dryness, charred (pyrolyzed or ashed), and atomized. The absorption signal produced during atomization may be recorded and compared with values obtained from standards that have been carried through the same process. This facilitates interpolation of the level of barium in the solution being analyzed. Since the graphite furnace uses the sample much more efficiently than flame atomization, the detection of low concentrations in small sample volumes is possible.

NOTE 1—The same graphite furnace procedure may be applicable to determination of arsenic (see Test Methods D 2972), cadmium (see Test Methods D 3557), chromium (see Test Methods D 1687), cobalt (see Test Methods D 3558), copper (see Test Methods D 1688), iron (see Test Methods D 1068), lead (see Test Methods D 3559), manganese (see Test Methods D 858), nickel (see Test Methods D 1886), selenium (see Test Methods D 3859), and silver (see Test Methods D 3866).

4.2 Dissolved barium is determined on a sample filtered through a 0.45-µm membrane filter. The definition of dissolved barium is arbitrary since very fine crystals of barium sulfate may pass through the membrane filter.

4.3 Total recoverable barium is determined following acid digestion and filtration. Because chlorides interfere with furnace procedures for some metals, the use of hydrochloric acid in any digestion or solubilization step is to be avoided. If suspended material is not present, this digestion and filtration may be omitted. The holding time for the samples may be calculated in accordance with Practice D 4841.

5. Significance and Use

5.1 Barium ranks about sixth in order of abundance in nature; however, it is normally found in only trace quantities in drinking water. Consumption, inhalation, or absorption of 500 to 600 mg is considered fatal to human beings.³ 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 barium/1 L.

6. Interferences

6.1 For a complete discussion on general interferences with furnace procedures, refer to Practice D 3919.

7. Apparatus

7.1 *Atomic Absorption Spectrophotometer*, for use at 553.6 nm with background correction. A general guide for flame atomic absorption applications is given in Practice D 4691.

NOTE 2—A wavelength other than 553.6 nm may be used if it has been determined to be suitable. At high concentration, greater linearity may be obtained by using a less sensitive wavelength.

NOTE 3—The manufacturer's instructions should be followed for all instrumental parameters.

7.2 *Barium Light Source*—Barium hollow-cathode lamp. A single-element lamp is preferred. Multielement lamps containing calcium are not recommended.

7.3 *Graphite Furnace*, capable of reaching temperatures sufficient to atomize the element of interest.

7.4 *Graphite Tubes*, compatible with furnace device. To eliminate the formation of carbides, pyrolytically coated graphite tubes are recommended.

7.5 *Pipets*, microlitre with disposable tips. Sizes may range from 1 L to 100 µL, as required.

7.6 *Data Storage and Reduction Devices*—Computer and microprocessor controlled devices, or a strip chart recorder, shall be utilized for data collection, storage, reduction, and problem recognition (drift, incomplete atomization, changes in sensitivity, etc.). Strip chart recorders shall have a full-scale deflection time of 0.2 s or less to ensure accuracy.

7.7 *Automatic Sampling* accessory should be used, if available.

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, where such specifications are available.⁴ 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.

³ *Standards Method for the Examination of Water and Wastewater*, 15th Edition, American Public Health Assn., 1015 15th St., NW, Washington, DC 20005.

⁴ *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.

8.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water conforming to Specification D 1193, 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 bias and precision 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* (1.0 mL = 1000 µg barium)—Dissolve 1.779 g of barium chloride ($\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$) in 50 mL of concentrated hydrochloric acid (HCl) (sp gr 1.19) and about 700 mL of water. Dilute to 1 L with water.

8.4 *Barium Solution, Intermediate* (1.0 mL = 10 µg barium)—Dilute 10.0 mL of barium solution, stock (8.3) and 1 mL of HNO_3 (sp gr 1.42) to 1 L with water.

8.5 *Barium Solution, Standard* (1.0 mL = 0.10 µg barium)—Dilute 10.0 mL of barium intermediate solution (8.4) and 1 mL of HNO_3 (sp gr 1.42) to 1 L with water. This standard is used to prepare working standards at the time of the analysis.

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

NOTE 4—If the reagent blank concentration is greater than the method detection limit, distill the HNO_3 or use a spectrograde acid.

8.7 *Argon*, standard, welders grade, commercially available. Nitrogen and hydrogen may also be used, if recommended by the instrument manufacturer.

9. Standardization

9.1 Initially, set the instrument in accordance with the manufacturer's specifications. Follow the general instructions as provided in Practice D 3919.

10. Procedure

10.1 Clean all glassware to be used for preparation of standard solutions or in the digestion step, or both, by rinsing first with HNO_3 (1 + 1) and then with water. Alternatively, soaking the glassware overnight in (1 + 1) HNO_3 is useful for low levels.

10.2 Measure 100 mL of each standard and well-mixed sample into a 125-mL beaker or flask.

10.3 For total recoverable barium, add 5 mL HNO_3 (sp gr 1.42) to each standard and sample and proceed as directed in 10.4–10.6. If only dissolved barium is to be determined, take an aliquot of sample that has been filtered through a 0.45-µm membrane filter and proceed to 10.6.

10.4 Heat the samples at approximately 95°C on a steam bath or hotplate in a well-ventilated fume hood until the volume has been reduced to 15 to 20 mL, making certain that the samples do not boil.

NOTE 5—When analyzing samples of brines or samples containing appreciable amounts of suspended matter or dissolved solids, the amount of reduction in volume is left to the discretion of the analyst.

10.5 Cool and filter the sample through a suitable filter such as fine-textured, acid washed, ashless paper, into a 100-mL volumetric flask. Wash the filter paper two or three times with water and bring to volume.

NOTE 6—If suspended material is not present, this filtration may be omitted; however, sample must still be diluted to 100 mL.

10.6 Inject a measured aliquot of sample into the furnace device following the directions as provided by the particular instrument manufacturer. Refer to Practice D 3919. Matrix modification using ammonium nitrate (NH_4NO_3) should be employed if levels of chloride and sulfate are sufficiently high to cause interference.

11. Calculation

11.1 Determine the concentration of barium in each sample by referring to the Sample Analysis Procedure section of Practice D 3919.

12. Precision and Bias ⁵

12.1 Based on data from six participating laboratories, the overall precision of the test method and recoveries from a series of standards containing known amounts of barium, are as given in Table 1.

12.2 Because of the large number of metals analyzed in this study, the requirements for replicate tests have been waived; therefore, single-operator precision is not available.

TABLE 1 Determination of Precision and Bias, Barium Graphite Furnace Atomic Absorption

Amount Added, $\mu\text{g/L}$	Amount Found, $\mu\text{g/L}$	S_T , $\mu\text{g/L}$	Bias, $\mu\text{g/L}$	Bias, %	Statistically Significant
<i>Reagent Water Type II</i>					
33.5	35.0	4	+ 1.5	4.5	no
74.6	81.2	19.5	+ 6.6	8.8	no
132.0	131.2	16.9	-0.8	0.6	no
<i>Water of Choice</i>					
33.5	35.8	4.1	+ 2.3	6.9	no
74.6	83.6	8.4	+ 9.0	12.3	no
132	139.6	22.6	+ 7.6	5.8	no

12.3 Each participating laboratory evaluated this test method in reagent water. Individual laboratories selected one water of choice as an additional matrix of interest in which to test recovery. Listed among those choices were: waste treatment plant effluent, lake water, tap water, and well water.

12.4 These data may not apply to waters of other matrices.

13. Keywords

13.1 atomic absorption; barium; furnace; total recoverable metals

⁵ Supporting data are available from ASTM Headquarters. Request RR: D19-1104.

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