**Designation: D 4382 – ~~95~~02**

# Standard Test Method for Barium in Water, Atomic Absorption Spectrophotometry, Graphite Furnace[1]

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:*

[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.~~ March 10, ~~1995.~~ 2002. Published ~~November 1995.~~ May 2002. Originally published as D 4382 – 84. Last previous edition D 4382 – 9~~1~~5.

D 858 Test Methods for Manganese in Water[2]
D 1068 Test Methods for Iron in Water[2]
D 1129 Terminology Relating to Water[2]
D 1193 Specification for Reagent Water[2]
D 1687 Test Methods for Chromium in Water[2]
D 1688 Test Methods for Copper in Water[2]
D 1886 Test Methods for Nickel in Water[2]
D 2777 Practice for Determination of Precision and Bias of Applicable Methods of Committee D19 on Water[2]
D 2972 Test Methods for Arsenic in Water[2]
D 3373 Test Method for Vanadium in Water[2]
D 3557 Test Methods for Cadmium in Water[2]
D 3558 Test Methods for Cobalt in Water[2]
D 3559 Test Methods for Lead in Water[2]
D 3859 Test Methods for Selenium in Water[2]
D 3866 Test Methods for Silver in Water[2]
D 3919 Practice for Measuring Trace Elements in Water by Graphite Furnace Atomic Absorption Spectrophotometry[2]
D 4691 Practice for Measuring Elements in Water by Flame Atomic Absorption Spectrophotometry[2]
D 4841 Practice for Estimation of Holding Time for Water Samples Containing Organic and Inorganic Constituents[2]
D 5810 Guide for Spiking into Aqueous Samples[2]
D 5847 Practice for Writing Quality Control Specifications for Standard Test Methods for Water Analysis[3]

## 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), and vanadium (see Test Method D 3373).

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.[4] 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/1L.

## 6. Interferences

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

---

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

[3] *Standards Method for the Examination Annual Book of Water and Wastewater,* 15th Edition, American Public Health Assn., 1015 15th St., NW, Washington, DC 20005. ASTM Standards, Vol 11.02.

[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 Standards Method for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia Examination of Water and National Formulary*, U.S. Pharmaceutical Convention, Inc. (USPC), Rockville, MD. Wastewater, 15th Edition, American Public Health Assn., 1015 15th St., NW, Washington, DC 20005.

## 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~~ etc.).

7.6 *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. [5] 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, 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 ($BaCl_2 \cdot 2H_2O$) in 50 mL of concentrated hydrochloric acid (HCl) (sp gr 1.19) and about 700 mL of water. Dilute to 1 L with water. A purchased stock solution of appropriate purity is also acceptable.

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.

---

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

[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.

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 [6]

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.

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

| Amount Added, µg/L | Amount Found, µg/L | $S_T$, µg/L | Bias, µg/L | Bias, % | Statistically Significant |
|---|---|---|---|---|---|
| | | *Reagent Water Type II* | | | |
| 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 |
| | | *Water of Choice* | | | |
| 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 |

12.2 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.

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.

12.5 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 meet existing requirements for interlaboratory studies of Committee D19 test methods.

## 13. Quality Control

13.1 In order to be certain that analytical values obtained using this test method are valid and accurate within the confidence limits of the test, the following QC procedures must be followed when analyzing Barium by graphite furnace AA.

13.2 *Calibration and Calibration Verification*:

13.2.1 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.

13.2.2 Verify instrument calibration after standardization by analyzing a standard at the concentration of one of the calibration standards. The absorbance shall fall within 4 % of the absorbance from the calibration. Alternately, the concentration of a mid-range standard should fall within ±10 % of the known concentration.

13.2.3 If calibration cannot be verified, recalibrate the instrument.

13.3 *Initial Demonstration of Laboratory Capability*:

13.3.1 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, etc., a precision and bias study must be performed to demonstrate laboratory capability.

[6] Supporting data are available from ASTM International Headquarters. Request RR: D19-1104.

13.3.2 Analyze seven replicates of a standard solution prepared from an Independent Reference Material containing 100 µg/L 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. The replicates may be interspersed with samples.

13.3.3 Calculate the mean and standard deviation of the seven values and compare to the acceptable ranges of bias in Table 1 above. 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 Test Method D 5847 for information on applying the F test and t test in evaluating the acceptability of the mean and standard deviation.

13.4 *Laboratory Control Sample (LCS)* :

13.4.1 To ensure that the test method is in control, analyze a LCS containing a mid-range concentration of barium with each batch or 10 samples. If large numbers of samples are analyzed in the batch, analyze the LCS after every 10 samples. The LCS must be taken through all of the steps of the analytical method including sample preservation and pretreatment. The result obtained for the LCS shall fall within ±15 % of the known concentration.

13.4.2 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.

13.5 *Method Blank*:

13.5.1 Analyze a reagent water test blank with each 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.

13.6 *Matrix Spike (MS)*:

13.6.1 To check for interferences in the specific matrix being tested, perform a MS on at least one sample from each batch by spiking an aliquot of the sample with a known concentration of barium and taking it through the analytical method.

13.6.2 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.

13.6.3 Calculate the percent recovery of the spike (P) using the following formula:

$$P = \frac{100\,[A(V_s + V) - B\,V_s]}{C\,V} \quad (1)$$

where

A =Analyte Concentration (µg/L) in Spiked Sample

B =Analyte Concentration (µg/L) in Unspiked Sample

C =Concentration (µg/L) of Analyte in Spiking Solution

$V_s$=Volume (mL ) of Sample Used

V =Volume (mL) added with Spike

13.6.4 The percent recovery of the spike shall fall within the limits, based on analyte concentration, listed in Guide D 5810, 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: acceptable spike recoveries are dependent on the concentration of the component of interest. See Guide 5810 for additional information.

13.7 *Duplicate*:

13.7.1 To check the precision of sample analyses, analyze a sample in duplicate with each batch. If the concentration of the analyte is less than five times the detection limit for the analyte, an MSD should be used.

13.7.2 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 Test Method D 5847 for information on applying the F test.

13.7.3 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.

13.8 *Independent Reference Material (IRM)*:

13.8.1 In order to verify the quantitative value produced by the test method, analyze an IRM submitted as a regular sample (if practical) to the laboratory at least once per quarter. The concentration of the reference material should be in the range of 50-75 µg/L barium. The value obtained must fall within the control limits established by the laboratory.

## 14. Keywords

134.1 atomic absorption; barium; furnace; total recoverable metals