



Standard Test Method for Barium in Brackish Water, Seawater, and Brines¹

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1. Scope*

1.1 This test method covers the determination of soluble barium ion in brackish water, sea-water, and brines by atomic absorption spectrophotometry.

1.2 The actual working range of this test method is 1 to 5 mg/L barium.

1.3 This test method was used successfully on artificial brine samples. It is the user's responsibility to ensure the validity of this test method for waters of untested matrices.

1.4 The values stated in either SI or inch-pound units are to be regarded as the standard. The values given in parentheses are for information only.

1.5 *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*:²

[D1129 Terminology Relating to Water](#)

[D1193 Specification for Reagent Water](#)

[D2777 Practice for Determination of Precision and Bias of Applicable Test Methods of Committee D19 on Water](#)

[D3370 Practices for Sampling Water from Closed Conduits](#)

[D4691 Practice for Measuring Elements in Water by Flame Atomic Absorption Spectrophotometry](#)

[D4841 Practice for Estimation of Holding Time for Water Samples Containing Organic and Inorganic Constituents](#)

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.

[D5810 Guide for Spiking into Aqueous Samples](#)

[D5847 Practice for Writing Quality Control Specifications for Standard Test Methods for Water Analysis](#)

3. Terminology

3.1 For definitions of terms used in this test method, refer to Terminology [D1129](#).

4. Summary of Test Method

4.1 This test method³ is dependent upon the fact that metallic atoms, in the ground state, will absorb light of the same wavelength they emit when excited. When radiation from a given excited element is passed through a flame containing ground state atoms of that element, the intensity of the transmitted radiation will decrease in proportion to the amount of the ground state element in the flame. A hollow-cathode lamp whose cathode is made of the element to be determined provides the radiation.

4.2 The metal atoms⁴ to be measured are placed in the beam of radiation by aspirating the specimen into an oxidant-fuel flame. A monochromator isolates the characteristic radiation from the hollow-cathode lamp and a photosensitive device measures the attenuated transmitted radiation.

4.3 Since the variable and sometimes high concentrations of matrix materials in the waters and brines affect absorption differently, it becomes imperative to prepare standard samples with matrices similar to the unknown samples. This is accomplished by preparing synthetic standard samples with similar compositions as the unknowns. The standard samples and

³ Fletcher, G. F. and Collins, A. G., *Atomic Absorption Methods of Analysis of Oil Field Brines: Barium, Calcium, Copper, Iron, Lead, Lithium, Magnesium, Manganese, Potassium, Sodium, Strontium, and Zinc*, U. S. Bureau of Mines, Report of Investigations 7861, 1974, 14 pp. Collins, A. G., *Geochemistry of Oil Field Waters*, Elsevier Publishing Co., Amsterdam, The Netherlands, 1974.

⁴ Angino, E. E. and Billings, G. K., *Atomic Absorption Spectrophotometry in Geology*, Elsevier Publishing Co., New York, NY 1967. Dean, J. A. and Rains, T.C., Editors, *Flame Emission and Atomic Absorption Spectrophotometry*, Vol. 1, Theory, 1969, Vol 2, Components, 1971, and Vol 3, Elements and Matrices, 1975, Marcel Dekker, New York, NY.

*A Summary of Changes section appears at the end of this standard.

unknown samples are aspirated, the absorption readings recorded, a calibration curve for the standard samples constructed, and the original sample concentration calculated.

5. Significance and Use

5.1 Since water containing acid-soluble barium compounds is known to be toxic, this test method serves the useful purpose of determining the barium in brackish water, seawater, and brines.

6. Interferences

6.1 Ionization interference is controlled by adding potassium.

6.2 Matrix interferences, caused by high concentrations of varied ions, and spectral interference, caused by high calcium concentrations, are controlled by matching the matrices.

6.3 This test method is subject to calcium interference, but the procedure provided eliminates the interference effect of up to 750 mg/L calcium. Calcium interference can also be minimized by using a secondary wavelength of 455.4 nm.

6.4 In high sulfate waters, such as seawater, barium will be precipitated as barium sulfate and will not be present as soluble barium and will, therefore, be below the detection limit of the test method.

7. Apparatus

7.1 *Atomic Absorption Spectrophotometer*—for use at 553.6 nm. A general guide for the use of flame atomic absorption applications is given in Practice [D4691](#).

NOTE 1—The manufacturer's instructions should be followed for all instrumental parameters. Wavelengths other than 553.6 nm may be used only if they have been determined to be equally suitable.

7.1.1 *Multielement Hollow-Cathode Lamps* are available and have been found satisfactory.

7.2 *Pressure-Reducing Valves*—The supplies of fuel and oxidant shall be maintained at pressures somewhat higher than the controlled operating pressure of the instrument by suitable valves.

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,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 Unless otherwise indicated, reference to water shall be understood to mean reagent water conforming to Specification [D1193](#), 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 precision and bias of the test method. Type III water was specified at the time of round-robin testing of this test method.

8.3 *Barium Solution, Stock (1 mL = 1 mg Ba)*—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 the solution to 1 L with water. One millilitre of this solution contains 1 mg of barium. A purchased stock solution of adequate purity is also acceptable.

8.4 *Barium Solution, Standard (1 mL = 0.1 mg Ba)*—Add 100 mL of barium solution stock to 50 mL of concentrated HCl (sp gr, 1.19) and about 600 mL of water. Dilute the solution to 1 L with water. One millilitre of this solution contains 0.1 mg of barium.

8.5 *Potassium Solution (1 mL = 10 mg K)*—Dissolve 19.07 g of potassium chloride (KCl) in about 700 mL of water. Dilute the solution to 1 L with water. One millilitre of this solution contains 10 mg of potassium. A purchased stock solution of adequate purity is also acceptable.

8.6 *Calcium Solution (1 mL = 10 mg Ca)*—Dissolve 54.66 g of calcium chloride hexahydrate ($\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$) in 500 mL of water. Dilute the solution to 1 L with water. One millilitre of this solution contains 10 mg of calcium. A purchased stock solution of adequate purity is also acceptable.

8.7 *Sodium Solution (1 mL = 10 mg Na)*—Dissolve 25.14 g sodium chloride (NaCl) in 500 mL of water. Dilute the solution to 1 L with water. One millilitre of this solution contains 10 mg of sodium. A purchased stock solution of adequate purity is also acceptable.

8.8 *Hydrochloric Acid (sp gr 1.19)*—Concentrated hydrochloric acid, ultrapure or equivalent.

8.9 *Oxidant:*

8.9.1 *Nitrous Oxide* is the oxidant required for this test method.

8.10 *Fuel:*

8.10.1 *Acetylene*—Standard, commercially available acetylene is the usual fuel. Acetone, always present in acetylene cylinders, can be prevented from entering and damaging the burner head by replacing a cylinder which has only 690 kPa (100 psig) of acetylene remaining.

9. Sampling

9.1 Collect the sample in accordance with Practices [D3370](#) and [D4841](#).

9.2 Add 2.0 mL of HCl per litre of water to prevent precipitation of soluble barium.

10. Calibration and Standardization

10.1 Prepare standards of 0.0, 1.0, 2.5, 5.0, and 10 mg/L of Ba by adding 0, 1.0, 2.5, 5.0, and 10 mL of barium standard solution to 100-mL volumetric flasks.

10.2 Add to each standard 5 mL of concentrated HCl (sp gr 1.19), 10 mL of potassium solution (1 mL = 10 mg of K), 7.5 mL of calcium solution (1 mL = 10 mg of Ca), and 15 mL of sodium solution (1 mL = 10 mg of Na). Dilute these solutions to 100 mL with water.

10.3 The method of operation varies with different models of atomic absorption spectrophotometers. Therefore, no attempt is made here to describe in detail the steps for placing an

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 *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.