



Designation: D 3645 – 02

Standard Test Methods for Beryllium in Water¹

This standard is issued under the fixed designation D 3645; 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 These test methods cover the determination of dissolved and total recoverable beryllium in most waters and wastewaters:

| | Concentration Range | Sections |
|---|---------------------------|----------|
| Test Method A—Atomic Absorption, Direct | 10 to 500 $\mu\text{g/L}$ | 7 to 16 |
| Test Method B—Atomic Absorption, Graphite Furnace | 10 to 50 $\mu\text{g/L}$ | 17 to 25 |

1.2 The analyst should direct attention to the precision and bias statements for each test method. It is the user's responsibility to ensure the validity of these test methods for waters of untested matrices.

1.3 *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.* For specific hazard statements, see Section 12 and 23.4.

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 1691 Test Methods for Zinc in Water²
- D 1886 Test Methods for Nickel in Water²
- D 2777 Practice for Determination of Precision and Bias of Applicable Test Methods of Committee D19 on Water²
- D 3370 Practices for Sampling Water from Closed Conduits²
- D 3557 Test Methods for Cadmium in Water²
- D 3558 Test Methods for Cobalt in Water²
- D 3559 Test Methods for Lead in Water²

¹ These test methods are under the jurisdiction of ASTM Committee D19 on Water and are the direct responsibility of Subcommittee D19.05 on Inorganic Constituents in Water.

Current edition approved July 10, 2002. Published August 2002. Originally published as D 3645 – 78. Last previous edition D 3645 – 97.

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

- D 3919 Practice for Measuring Trace Elements in Water by Graphite Furnace Atomic Absorption Spectrophotometry²
- D 4841 Practice for Estimation of Holding Time for Water Samples Containing Organic and Inorganic Constituents²
- D 5810 Guide for Spiking into Aqueous Samples²
- D 5847 Practice for Writing Quality Control Specifications for Standard Test Methods for Water Analysis³

3. Terminology

3.1 *Definitions*—For definitions of terms used in these test methods, refer to Terminology D 1129.

3.2 Definitions of Terms Specific to This Standard:

3.2.1 *total recoverable beryllium*—total recoverable beryllium relates only to the recoverable forms of beryllium by these test methods.

4. Significance and Use

4.1 These test methods are significant because the concentration of beryllium in water must be measured accurately in order to evaluate potential health and environmental effects.

5. Purity of Reagents

5.1 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 sufficiently high in purity to permit its use without lessening the accuracy of the determination.

5.2 Unless otherwise indicated, reference 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.

³ *Annual Book of 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 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.

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

6. Sampling

6.1 Collect the samples in accordance with Practices D 3370. The holding time for samples may be calculated in accordance with Practice D 4841.

6.2 Preserve samples with HNO_3 (sp gr 1.42), adding about 2 mL/L, to a pH of 2 or less immediately at the time of collection. If only dissolved beryllium is to be determined, filter the sample, before acidification, through a 0.45- μm membrane filter.

TEST METHOD A—ATOMIC ABSORPTION, DIRECT

7. Scope

7.1 This test method is applicable in the range from 10 to 500 $\mu\text{g/L}$ of beryllium. The range may be extended upward by dilution of the sample.

7.2 The precision and bias data were obtained on reagent water, tap water, salt water, river water, lake water, spring water, and untreated wastewater. The information on precision and bias may not apply to other waters. It is the user's responsibility to ensure the validity of this test method for waters of untested matrices.

8. Summary of Test Method

8.1 Beryllium is determined by atomic absorption spectrophotometry. Dissolved beryllium is determined by aspirating a filtered sample directly with no pretreatment. Total recoverable beryllium in the sample is determined in a portion of the filtrate obtained after a hydrochloric-nitric acid digestion of the sample. The same digestion procedure is used to determine total recoverable cadmium (Test Methods D 3557), chromium (Test Methods D 1687), cobalt (Test Methods D 3558), copper (Test Methods D 1688), iron (Test Methods D 1068), lead (Test Methods D 3559), manganese (Test Methods D 858), nickel (Test Methods D 1886), and zinc (Test Methods D 1691).

9. Interferences

9.1 Aluminum at concentrations greater than 500 $\mu\text{g/L}$ has been reported to depress the beryllium absorbance.

9.2 Sodium and silicon at concentrations in excess of 1000 mg/L have been reported to severely depress the beryllium absorbance.

9.3 Beryllium is slightly ionized in the nitrous oxide-acetylene flame. This ionization is suppressed by adding calcium chloride to give a final concentration of 900 mg/L calcium in all standard and sample solutions.

10. Apparatus

10.1 *Atomic Absorption Spectrophotometer*, for use at 234.9 nm.

NOTE 1—The manufacturer's instructions should be followed for all instrument parameters.

10.2 *Beryllium Hollow Cathode Lamp*.

10.3 *Pressure Regulators*—The supplies of oxidants and fuel shall be maintained at pressures somewhat higher than the controlled operating pressure of the instrument by suitable regulators.

11. Reagents and Materials

11.1 *Beryllium Solution, Stock* (1.00 mL = 1000 $\mu\text{g Be}$)—

Dissolve 1.000 g of beryllium metal in a minimum volume of HCl (1 + 1) and dilute to 1 L. (**Warning**—Beryllium is toxic and the solution should be prepared in a well-ventilated hood.)

NOTE 2—Certified beryllium stock solutions are commercially available through chemical supply vendors.

11.2 *Beryllium Solution, Intermediate* (1.00 mL = 100 $\mu\text{g Be}$)—Dilute 10.0 mL of the beryllium stock solution to 100.0 mL with nitric acid (HNO_3 , 1 + 499).

11.3 *Beryllium Solution, Standard* (1.00 mL = 1.00 $\mu\text{g Be}$)—Dilute 5.00 mL of the beryllium intermediate solution to 500.0 mL with nitric acid (HNO_3 , 1 + 499).

11.4 *Calcium Solution* (10 g/L)—Dissolve 25 g of calcium carbonate in a minimum volume of HCl (1 + 1) and dilute to 1 L with water.

11.5 *Hydrochloric Acid* (sp gr 1.19)—Concentrated hydrochloric acid (HCl).

NOTE 3—If a high reagent blank is obtained, distill the HCl or use spectrograde acid. (**Warning**—When HCl is distilled, an azeotropic mixture is obtained (approximately 6 N HCl). Therefore, whenever concentrated HCl is specified in the preparation of a reagent or in the procedure, use double the amount if distilled acid is used.)

11.6 *Hydrochloric Acid* (1 + 1)—Mix 1 volume of HCl (sp gr 1.19) with 1 volume of water.

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

NOTE 4—If a high reagent blank is obtained, distill the HNO_3 or use spectrograde acid.

11.8 *Nitric Acid* (1 + 499)—Add 1 volume of HNO_3 (sp gr 1.42) to 499 volumes of water.

11.9 *Oxidant*:

11.9.1 *Air*, which has been passed through a suitable filter to remove oil, water, and other foreign substances, is the oxidant used prior to switching to nitrous oxide.

11.9.2 *Nitrous Oxide* is the required oxidant.

11.10 *Fuel*:

11.10.1 *Acetylene*—Standard commercially available acetylene is the required fuel. Acetone, always present in acetylene cylinders, can affect analytical results. The cylinder should be replaced at a gage pressure of 75 psi (517 kPa). (**Warning**—“Prepurified” grade acetylene containing a special proprietary solvent other than acetone should not be used with poly (vinyl chloride) tubing as weakening of the walls can cause a potentially hazardous situation.)

12. Hazards

12.1 Due to the high toxicity of beryllium, all sample preparation and digestion steps should be carried out in a well-ventilated hood. Also, the atomic absorption unit should be vented as recommended by the manufacturer.

13. Standardization

13.1 Prepare a blank and at least four standard solutions to bracket the expected beryllium concentration range of the samples to be analyzed by diluting the beryllium standard solution (11.3) with HNO_3 (1 + 499). Prepare the standards (100 mL) each time the test is to be performed.

13.2 For total recoverable beryllium, add 0.5 mL of HNO_3 (sp gr 1.42) and proceed as directed in 14.2-14.6. For

dissolved beryllium, proceed with 13.3.

13.3 Add 1.0 mL of calcium solution to a 10.0-mL aliquot of each standard and blank solution. Mix thoroughly.

13.4 Aspirate the blank and standards and record the instrument readings. Aspirate HNO₃ (1 + 499) between each standard. (**Warning**—The atomic absorption unit should be vented properly.)

13.5 Prepare an analytical curve by plotting the absorbance versus the standard concentration for each standard on linear graph paper. Alternatively, use a direct concentration readout if the instrument is so equipped.

14. Procedure

14.1 Measure 100.0 mL of a well-mixed acidified sample into a 150-mL beaker.

NOTE 5—If only dissolved beryllium is to be determined, start with 14.5.

14.2 Add 5 mL of HCl (sp gr 1.19) to each sample.

14.3 Heat the samples on a steam bath or hot plate until the volume has been reduced to 15 or 20 mL, making certain that the samples do not boil. (**Warning**—Perform in a well-ventilated hood.)

NOTE 6—For brines and samples with high levels of suspended matter or total dissolved solids, the amount of reduction is left to the discretion of the analyst.

14.4 Cool and filter the samples through a suitable filter (such as a fine-textured, acid-washed, ashless paper) into 100-mL volumetric flasks. Wash the filter paper two or three times with water and adjust to volume.

14.5 Add 1.0 mL of calcium solution to a 10.0-mL aliquot of each sample and mix thoroughly.

14.6 Aspirate each sample and determine its absorbance or concentration. Aspirate HNO₃ (1 + 499) between each sample.

15. Calculation

15.1 Calculate the concentration of beryllium in each sample, in micrograms per litre, using the analytical curve described in 13.5.

16. Precision and Bias⁵

16.1 Based on the round-robin results from seven laboratories and ten operators, the following precision and bias statements can be made:

⁵ Supporting data are available from ASTM Headquarters. Request RR: D19-1043.

TABLE 1 Overall S_T and Single-Operator (S_O) Interlaboratory Precision for Beryllium by Flame AAS, Test Method A

| | Reagent Water | | |
|--|---------------|-------|-------|
| Concentration (X), $\mu\text{g/L}$ | 15.4 | 211.0 | 444.8 |
| S_T | 2.7 | 10.8 | 21.3 |
| S_O | 1.2 | 4.4 | 11.9 |
| | Natural Water | | |
| Concentration (X), $\mu\text{g/L}$ | 16.9 | 214.7 | 444.4 |
| S_T | 2.9 | 7.7 | 19.2 |
| S_O | 2.2 | 5.4 | 10.3 |

16.1.1 The overall and single-operator precision of this test method, within its designated range for reagent water and selected water matrices, varies with the quantity tested as shown in Table 1.

16.1.2 The bias of this test method is listed in Table 2.

16.2 The precision and bias data were obtained on reagent water, tap water, salt water, river water, lake water, spring water, and untreated wastewater. It is the user's responsibility to ensure the validity of this test method for waters of untested matrices.

16.3 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 Practice D 2777-98, these precision and bias data do meet existing requirements for interlaboratory studies of Committee D19 test methods.

TEST METHOD B—ATOMIC ABSORPTION, GRAPHITE FURNACE

17. Scope

17.1 This test method covers the determination of dissolved and total recoverable beryllium in most waters and wastewaters.

17.2 This test method is applicable in the range from 10 to 50 $\mu\text{g/L}$ of beryllium using a 20- μL injection. 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.

17.3 This test method has been used successfully with reagent water, lake water, river water, well water, filtered tap water, and a condensate from a medium Btu coal gasification process. It is the user's responsibility to ensure validity of this test method to waters of untested matrices.

17.4 The analyst is encouraged to consult Practice D 3919 for a general discussion of interferences and sample analysis procedures for graphite furnace atomic absorption spectrophotometry.

18. Summary of Test Method

18.1 Beryllium 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. Since the graphite

TABLE 2 Precision and Bias, Atomic Absorption, Direct

| Amount Added, $\mu\text{g/L}$ | Amount Found, $\mu\text{g/L}$ | % Bias | Statistically Significant (95 % Confidence Level) |
|-------------------------------|-------------------------------|--------|---|
| Reagent Water, Type II | | | |
| 16 | 15.4 | -3.75 | no |
| 220 | 211.0 | -4.09 | yes |
| 460 | 444.8 | -3.30 | yes |
| Selected Water Matrices | | | |
| 16 | 16.9 | + 5.60 | no |
| 220 | 214.7 | -2.41 | yes |
| 460 | 444.4 | -3.39 | yes |