



Designation: D3645 – 15

## Standard Test Methods for Beryllium in Water<sup>1</sup>

This standard is issued under the fixed designation D3645; 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 ( $\epsilon$ ) 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 17
Test Method B—Atomic Absorption, Graphite Furnace	10 to 50 $\mu\text{g/L}$	18 to 26

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 The values stated in SI units are to be regarded as standard. The values given in parentheses are mathematical conversions to inch-pound units that are provided for information only and are not considered 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.* For specific hazard statements, see Section 12 and 24.4.

### 2. Referenced Documents

#### 2.1 ASTM Standards:<sup>2</sup>

D858 Test Methods for Manganese in Water

D1068 Test Methods for Iron in Water

D1129 Terminology Relating to Water

<sup>1</sup> 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.

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<sup>2</sup> 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.

D1193 Specification for Reagent Water  
D1687 Test Methods for Chromium in Water  
D1688 Test Methods for Copper in Water  
D1691 Test Methods for Zinc in Water  
D1886 Test Methods for Nickel in 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  
D3557 Test Methods for Cadmium in Water  
D3558 Test Methods for Cobalt in Water  
D3559 Test Methods for Lead in Water  
D3919 Practice for Measuring Trace Elements in Water by Graphite Furnace Atomic Absorption Spectrophotometry  
D4841 Practice for Estimation of Holding Time for Water Samples Containing Organic and Inorganic Constituents  
D5673 Test Method for Elements in Water by Inductively Coupled Plasma—Mass Spectrometry  
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 Definitions:

3.1.1 For definitions of terms used in these test methods, refer to Terminology D1129.

#### 3.2 Definitions of Terms Specific to This Standard:

3.2.1 *total recoverable beryllium, n*—a descriptive term relating to the beryllium forms recovered in the acid-digestion procedure specified in 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

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

specifications are available.<sup>3</sup> 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 **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 bias and precision of the test method. Type II water was specified at the time of round robin testing of this test method.

## 6. Sampling

6.1 Collect the samples in accordance with Practices **D3370**. The holding time for samples may be calculated in accordance with Practice **D4841**.

6.2 Preserve samples with  $\text{HNO}_3$  (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- $\mu\text{m}$  membrane filter.

NOTE 1—Alternatively, the pH may be adjusted in the laboratory if the sample is returned within 14 days. However, acid must be added at least 24 hours before analysis to dissolve any metals that adsorb to the container walls. This could reduce hazards of working with acids in the field when appropriate.

## 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 **D3557**), chromium (Test Methods **D1687**), cobalt (Test Methods **D3558**), copper (Test Methods **D1688**), iron (Test Methods **D1068**), lead (Test Methods **D3559**), manganese (Test Methods **D858**), nickel (Test Methods **D1886**), and zinc (Test Methods **D1691**).

<sup>3</sup> *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.

## 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 2—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. (Beryllium is toxic and the solution should be prepared in a well-ventilated hood.) A purchased metal stock solution of appropriate known purity is also acceptable.

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 ( $\text{HNO}_3$ , 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 ( $\text{HNO}_3$ , 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 *Filter Paper*—Purchase suitable filter paper. Typically the filter papers have a pore size of 0.45- $\mu\text{m}$  membrane. Material such as fine-textured, acid-washed, ashless paper, or glass fiber paper are acceptable. The user must first ascertain that the filter paper is of sufficient purity to use without adversely affecting the bias and precision of the test method.

11.6 *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. (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.)

11.7 *Hydrochloric Acid* (1 + 1)—Mix 1 volume of HCl (sp gr 1.19) with 1 volume of water. Always add acid to water.

11.8 *Nitric Acid* (sp gr 1.42)—Concentrated nitric acid ( $\text{HNO}_3$ ).

NOTE 4—If a high reagent blank is obtained, distill the HNO<sub>3</sub> or use spectrograde acid.

11.9 *Nitric Acid* (1 + 499)—Add 1 volume of HNO<sub>3</sub> (sp gr 1.42) to 499 volumes of water.

11.10 *Oxidant*:

11.10.1 *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.

11.10.2 *Nitrous Oxide* is the required oxidant.

11.11 *Fuel*:

11.11.1 *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 517 kPa (75 psi). (“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<sub>3</sub> (1 + 499) (11.9). Analyze at least three working standards containing concentrations of beryllium that bracket the expected sample concentration prior to analysis of samples to calibrate the instrument. Prepare the standards (100 mL) each time the test is to be performed or as determined by Practice D4841.

13.2 For total recoverable beryllium, add 0.5 mL of HNO<sub>3</sub> (sp gr 1.42) (11.8) 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 (11.4) 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 HNO<sub>3</sub> (1 + 499) between each standard. (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) (11.6) 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. (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.

NOTE 7—Many laboratories have found block digestion systems a useful way to digest samples for trace metals analysis. Systems typically consist of either a metal or graphite block with wells to hold digestion tubes. The block temperature controller must be able to maintain uniformity of temperature across all positions of the block. For trace metals analysis, the digestion tubes should be constructed of polypropylene and have a volume accuracy of at least 0.5 %. All lots of tubes should come with a certificate of analysis to demonstrate suitability for their intended purpose.

14.4 Cool and filter the samples through a suitable filter (11.5) (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 (11.4) to a 10.0-mL aliquot of each sample and mix thoroughly.

14.6 Aspirate each sample and determine its absorbance or concentration. Aspirate HNO<sub>3</sub> (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.

TABLE 1 Overall S(+) and Single-Operator (S<sub>O</sub>) Interlaboratory Precision for Beryllium by Flame AAS, Test Method A

	Reagent Water		
Concentration (X), µg/L	15.4	211.0	444.8
S <sub>T</sub>	2.7	10.8	21.3
S <sub>O</sub>	1.2	4.4	11.9
	Natural Water		
Concentration (X), µg/L	16.9	214.7	444.4
S <sub>T</sub>	2.9	7.7	19.2
S <sub>O</sub>	2.2	5.4	10.3

TABLE 2 Precision and Bias, Atomic Absorption, Direct

Amount Added, µg/L	Amount Found, µg/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

## 16. Precision and Bias<sup>4</sup>

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

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 [D2777 – 77](#), which was in place at the time of collaborative testing. Under the allowances made in 1.4 of Practice [D2777 – 13](#), these precision and bias data do meet existing requirements for interlaboratory studies of Committee D19 test methods.

## 17. Quality Control

17.1 In order to be certain that analytical values obtained using these test methods are valid and accurate within the confidence limits of the test, the following QC procedures must be followed when analyzing beryllium.

17.2 *Calibration and Calibration Verification:*

17.2.1 Analyze at least three working standards containing concentrations of beryllium that bracket the expected sample concentration prior to analysis of samples to calibrate the instrument ([13.1](#)). The calibration correlation coefficient shall be equal to or greater than 0.990.

17.2.2 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  $\pm 15$  % of the known concentration. Analyze a calibration blank to verify system cleanliness.

17.2.3 If calibration cannot be verified, recalibrate the instrument.

17.2.4 It is recommended to analyze a continuing calibration blank (CCB) and continuing calibration verification (CCV) at a 10 % frequency. The results should fall within the expected precision of the method or  $\pm 15$  % of the known concentration.

17.3 *Initial Demonstration of Laboratory Capability:*

17.3.1 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.

17.3.2 Analyze seven replicates of a standard solution prepared from an Independent Reference Material containing mid-range concentration of beryllium. 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.

17.3.3 Calculate the mean and standard deviation of the seven values and compare to the acceptable range of bias in [16.1](#). This study should be repeated until the recoveries are within the limits given in [16.1](#). If a concentration other than the recommended concentration is used, refer to Practice [D5847](#) for information on applying the *F* test and *t* test in evaluating the acceptability of the mean and standard deviation.

17.4 *Laboratory Control Sample (LCS):*

17.4.1 To ensure that the test method is in control, prepare and analyze a LCS containing a mid-range concentration of beryllium with each batch (laboratory-defined or twenty samples). The laboratory control samples for a large batch should cover the analytical range when possible. 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  $\pm 15$  % of the known concentration.

17.4.2 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.

17.5 *Method Blank:*

17.5.1 Analyze a reagent water test blank with each laboratory-defined batch. The concentration of beryllium found in the blank should be less than 0.5 times the lowest calibration standard. If the concentration of beryllium 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.

17.6 *Matrix Spike (MS):*

17.6.1 To check for interferences in the specific matrix being tested, perform a matrix spike (MS) on at least one sample from each laboratory-defined batch by spiking an aliquot of the sample with a known concentration of beryllium and taking it through the analytical method.

17.6.2 The spike concentration plus the background concentration of beryllium 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.

17.6.3 Calculate the percent recovery of the spike (*P*) using the following calculation:

$$P = \frac{100[A(V_s + V) - BV_s]}{CV} \quad (1)$$

<sup>4</sup> Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D19-1043. Contact ASTM Customer Service at [service@astm.org](mailto:service@astm.org).