



Designation: D7458 – 08

Standard Test Method for Determination of Beryllium in Soil, Rock, Sediment, and Fly Ash Using Ammonium Bifluoride Extraction and Fluorescence Detection¹

This standard is issued under the fixed designation D7458; 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 is intended for use in the determination of beryllium in samples of soil, rock, sediment, and fly ash. This test method can be used for purposes such as environmental remediation projects where beryllium is a contaminant of concern. It is also useful for characterization of levels of beryllium in soil at sites where beryllium is in mining or manufacturing applications, and for determination of background levels of beryllium in soil.

1.2 This test method assumes that samples of soil, rock, sediment, or fly ash are collected using appropriate and applicable ASTM International standard practices.

1.3 This test method includes a procedure for on-site extraction (dissolution) of beryllium in dilute ammonium bifluoride, followed by analysis of aliquots of the extract solution using a beryllium-specific fluorescent dye.

1.4 No detailed operating instructions are provided because of differences among various makes and models of suitable fluorometric instruments. Instead, the analyst shall follow the instructions provided by the manufacturer of the particular instrument. This test method does not address comparative accuracy of different devices or the precision between instruments of the same make and model.

1.5 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.6 All observed and calculated values shall conform to the guidelines for significant digits and rounding established in Practice D6026.

1.6.1 The procedures used to specify how data are collected/recorded, or calculated, in this standard are regarded as the industry standard. In addition, they are representative of the significant digits that generally should be retained. The procedures

used do not consider material variation, purpose for obtaining the data, special purpose studies, or any considerations for the user's objectives; and it is common practice to increase or reduce significant digits of reported data to be commensurate with these considerations. It is beyond the scope of this standard to consider significant digits used in analytical methods for engineering design.

1.7 This test method contains notes that are explanatory and not part of mandatory requirements of the standard.

1.8 *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.* Specific hazards associated with performance of this test method are described in Section 9.

2. Referenced Documents

2.1 ASTM Standards:²

- D653 Terminology Relating to Soil, Rock, and Contained Fluids
- D1193 Specification for Reagent Water
- D3740 Practice for Minimum Requirements for Agencies Engaged in Testing and/or Inspection of Soil and Rock as Used in Engineering Design and Construction
- D4840 Guide for Sample Chain-of-Custody Procedures
- D5730 Guide for Site Characterization for Environmental Purposes With Emphasis on Soil, Rock, the Vadose Zone and Ground Water
- D6026 Practice for Using Significant Digits in Geotechnical Data
- D7202 Test Method for Determination of Beryllium in the Workplace Using Field-Based Extraction and Optical Fluorescence Detection
- E177 Practice for Use of the Terms Precision and Bias in ASTM Test Methods

¹ This test method is under the jurisdiction of ASTM Committee D18 on Soil and Rock and is the direct responsibility of Subcommittee D18.01 on Surface and Subsurface Characterization.

Current edition approved Oct. 1, 2008. Published October 2008. DOI: 10.1520/D7458-08.

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.

E691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method

E882 Guide for Accountability and Quality Control in the Chemical Analysis Laboratory

2.2 Other Standard:

EN ISO 8655-2 Piston-Operated Volumetric Pipettes—Part 2: Piston Pipettes³

3. Terminology

3.1 Definitions—For definitions of terms not appearing here, see Terminology **D653**.

4. Summary of Test Method

4.1 This standard test method is used to determine the beryllium content of soil, rock, sediment, and fly ash. Samples are collected in the field using procedures described in ASTM International standards (see Guide **D5730** for listings of appropriate sample collection standards). A 0.5-gram aliquot is extracted using 3 % ammonium bifluoride solution heated at 90°C for 40 hours. The presence of active fluoride ions (HF by dissociation of ammonium bifluoride in acidic medium) enables dissolution of refractory forms of beryllium, including silicates, borosilicates, and oxides. The extraction solution produced from each sample is then filtered and an aliquot of this extract is added to a pH-adjusted detection solution which contains a beryllium-specific fluorescence reagent. The fluorescence of this final solution is then measured on a calibrated fluorometer to quantify the amount of beryllium in the sample. This standard test method is adapted from Test Method **D7202**.

4.2 The limit of quantification of this test method is 0.013 milligrams beryllium per kilogram of sample, based on a 0.5-gram sample **(1)**.⁴

5. Significance and Use

5.1 Exposure to beryllium can cause a potentially fatal disease, and occupational exposure limits for beryllium in air and on surfaces have been established to reduce exposure risks to potentially affected workers **(2, 3)**. Measurement of beryllium in matrices such as soil, rock, sediment, and fly ash is important in environmental remediation projects involving beryllium contamination **(4)** and for establishment of background levels of beryllium at sites where anthropogenic beryllium may have been used **(2)**. Sampling and analytical methods for beryllium are needed in order to meet the challenges relating to exposure assessment and risk reduction. Sampling and analysis methods, such as the procedure described in this test method, are desired in order to facilitate measurements of beryllium that can be used as a basis for management of remediation projects and protection of human health.

5.2 This test method can be used for purposes such as environmental remediation projects where beryllium is a contaminant of concern. It is also useful for characterization of

levels of beryllium in soil at sites where beryllium is in mining or manufacturing applications, and for determination of background levels of beryllium in soil.

NOTE 1—The quality of the result produced by this standard is dependent on the competence of the personnel performing it, and the suitability of the equipment and facilities used. Agencies that meet the criteria of Practice **D3740** are generally considered capable of competent and objective testing, sampling, inspection, etc. Users of this standard are cautioned that compliance with Practice **D3740** does not in itself assure reliable results. Reliable results depend on many factors; Practice **D3740** provides a means of evaluating some of those factors.

6. Interferences

6.1 This test method is highly specific for beryllium. Other solvated metal ions are either bound by ethylenediaminetetraacetic acid (EDTA) in the detection solution, or they precipitate out due to the high alkalinity of the detection solution. The fluorophore used for detection is highly specific for the beryllium divalent cation (Be^{+2}).

6.2 If iron or titanium are present in high excess in the sample (typically above 7 %), the resulting measurement solution may appear golden-yellow. In this case the solution is left for two hours or more for the iron or titanium (or both) to precipitate. The solution is then re-filtered using the same procedure as for filtering the dissolution solution (after the dissolution step), prior to fluorescence measurement.

7. Apparatus

7.1 Sampling Equipment—Use sampling apparatus appropriate for the type of media being collected (for example, soil, rock, sediment, fly ash) and its location (for example, surface, subsurface, vadose zone). Guidance on selection of appropriate sampling apparatus is found in the ASTM International standards referenced in Guide **D5730**.

7.2 Instrumentation:

7.2.1 Ultraviolet/Visible (UV/Vis) Fluorometer, with irradiance excitation lamp or light-emitting diode (excitation $\lambda = 380$ nm) and time-integrating visible detector (400–700 nm, $\lambda_{\text{max}} \approx 475$ nm).

7.2.2 Laboratory Balance, capable of measuring to the nearest 0.1 mg.

7.2.3 Laboratory Oven, capable of maintaining a temperature of $90 \pm 2^\circ\text{C}$.

7.3 Laboratory Supplies:

7.3.1 Centrifuge Tubes, plastic, 15-mL (plus 50-mL, if necessary).

7.3.2 Polypropylene Bottles, 60 to 100 mL, with screw caps.

7.3.3 Syringe Filters, 0.45- μm or smaller pore size filters, for example, 13 or 25-mm diameter nylon filters, in plastic housings.

7.3.4 Syringes, plastic, 5-mL or 10-mL.

7.3.5 Pipetters, mechanical, of assorted sizes as needed, with tolerances in accordance with EN ISO 8655-2.

7.3.6 Pipet Tips, plastic, disposable, of assorted sizes as needed, with tolerances in accordance with EN ISO 8655-2.

7.3.7 Fluorescence Cuvettes, disposable, low fluorescence, 10-mm path length, transparent to UV/Visible radiation.

7.3.8 Labware, plastic (for example, beakers, flasks, graduated cylinders, etc.), of assorted sizes as needed.

³ Available from American National Standards Institute (ANSI), 25 W. 43rd St., 4th Floor, New York, NY 10036, <http://www.ansi.org>.

⁴ The boldface numbers in parentheses refer to the list of references at the end of this standard.

7.3.9 *Forceps*, plastic or plastic-coated.

7.3.10 *Personal Protective Wear*, for example, respirators, masks, gloves, lab coats, safety eyewear, etc. as needed.

7.3.11 *Thermometer*, to at least 100°C (accuracy $\pm 1^\circ\text{C}$).

7.3.12 Other general laboratory supplies as needed.

8. Reagents

8.1 *Purity of Reagents*—Reagent grade chemicals shall be used. Unless otherwise indicated, it is intended that all reagents conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society 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 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent as defined by Type I of Specification **D1193** (ASTM Type I Water: minimum resistance of 18 M Ω -cm or equivalent).

8.3 *Calibration Stock Solution*—1000 ppm beryllium in dilute nitric acid.

8.4 Ethylenediaminetetraacetic acid (EDTA) disodium salt dihydrate.

8.5 L-lysine monohydrochloride.

8.6 10-hydroxybenzo[h]quinoline-7-sulfonate (10-HBQS).

8.7 Sodium hydroxide (NaOH).

8.8 *Extraction (or Dissolution) Solution*—3 % ammonium bifluoride (NH_4HF_2) solution (aqueous) for dissolution of beryllium in collected particulate matter. The solution may be prepared by dissolving 30 ± 0.3 g of solid NH_4HF_2 in water to a total volume of 1000 mL. (**Warning**—Ammonium bifluoride will etch glass, so it is essential that all NH_4HF_2 solutions be contained in plastic labware.)

8.9 *Detection Solution*—63.4 μM 10-hydroxybenzo[h]quinoline-7-sulfonate (10-HBQS) (**5**) / 2.5 mM ethylenediaminetetraacetic acid (EDTA)/50.8 mM lysine monohydrochloride (pH adjusted to 12.8 with NaOH): The aqueous detection reagent is prepared by the addition of 12.5 mL of 2.5 mM ethylenediaminetetraacetic acid (EDTA) disodium salt dihydrate and 25 mL of 107 mM L-lysine monohydrochloride to 3 mL of 1.1 mM 10-hydroxybenzo[h]quinoline-7-sulfonate (10-HBQS). The pH is adjusted to 12.85 with addition of sodium hydroxide and water added to a total of 50 mL.

9. Hazards

9.1 Ammonium bifluoride is highly corrosive, and is very toxic when in contact with the skin. Effects to the skin, including irritation and burns, may not be felt for several hours. Avoid exposure by contact with the skin. Use suitable personal protective equipment (including impermeable gloves and eye protection) when working with NH_4HF_2 . See **Appendix X1** for further pertinent safety information.

10. Procedure

10.1 Sampling:

10.1.1 *Sample Collection*—Collect samples in accordance with applicable ASTM International standards for the type of media (for example, soil, rock, sediment, fly ash) and the location being sampled (for example, surface, vadose zone). Refer to Guide **D5730** in selecting applicable ASTM International standards for sample collection.

10.1.2 *Sample Transport*—If applicable (that is, if samples are transported to a different location prior to sample preparation and analysis), follow sampling chain-of-custody procedures to document sample traceability. Ensure that the documentation that accompanies the samples is suitable for a chain of custody to be established in accordance with Guide **D4840**.

10.2 *Sample Preparation*—Wear appropriate personal protection during sample preparation and analysis activities. Perform sample preparation and analysis in a clean area that is well removed from any possible beryllium contamination.

10.2.1 Digestion of Samples:

10.2.1.1 Accurately weigh (to the nearest 0.1 mg) a 0.5-gram aliquot of sample into a polypropylene bottle. Close the lid and gently tap the lid to ensure that all of the sample falls to the bottom of the bottle. The bottle size is typically 10 to 50 mL larger than the liquid to be added.

NOTE 2—Care should be taken to ensure that the aliquot(s) used are representative of the soil, rock, sediment, or fly ash from which the samples were taken. Guidance may be found in references (**6-9**).

10.2.1.2 Remove the lid and, using a graduated cylinder, add 50 ± 0.5 mL of 3 % ammonium bifluoride (NH_4HF_2) extraction solution (see **8.8**). Replace the lid, making sure the lid is tight.

10.2.1.3 Swirl the bottle to ensure complete wetting of the sample.

10.2.1.4 Repeat steps **10.2.1.1** through **10.2.1.3** for all samples.

10.2.1.5 Place sample bottles in a laboratory oven, preheated to $90 \pm 2^\circ\text{C}$, for 40 hours.

NOTE 3—The 40-hour heating step may be reduced by using a more concentrated solution (up to 10 %) of NH_4HF_2 . After extraction using concentrations at or above 5 % NH_4HF_2 , dilution with water is required to maintain a pH of 12 or higher when mixed with the dye solution; this pH is required to achieve quantitative recovery (**10**). Method evaluation should consider the sample media, particle physical characteristics (such as shape and size) and the inertness of beryllium-containing compounds in the samples being analyzed.

NOTE 4—The sample size of 0.5 grams is typically required to sufficiently account for the heterogeneous nature of soil, rock, sediment, and fly ash samples (**11**). In cases where the matrix is sufficiently homogenous to allow a smaller sample size (for example, 50 mg), the amount of extraction solution may be reduced (for example, to 5 mL instead of 50 mL).

10.2.1.6 Remove samples from the oven and allow them to cool to ambient temperature.

10.2.2 *Filtration*—Filter aliquots (for example, 5 mL) of extract solution through inert microfilters into 15-mL centrifuge tubes.

NOTE 5—The filtration process can be carried out by attaching a 25-mm diameter syringe filter to a 5 or 10-mL Luer lock syringe and pouring the liquid contents into the syringe. The liquid is forced out through the filter into a separate 15-mL centrifuge tube.

10.2.3 Preparation of Measurement