



Designation: D7202 – 14

# Standard Test Method for Determination of Beryllium in the Workplace by Extraction and Optical Fluorescence Detection<sup>1</sup>

This standard is issued under the fixed designation D7202; 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 This test method is intended for use in the determination of beryllium by sampling workplace air and surface dust.

1.2 This test method assumes that air and surface samples are collected using appropriate and applicable ASTM International standard practices for sampling of workplace air and surface dust. These samples are typically collected using air filter sampling, vacuum sampling or wiping techniques. See Guide [E1370](#) for guidance on air sampling strategies, and Guide [D7659](#) for guidance on selection of surface sampling techniques.

1.3 Determination of beryllium in soil is not within the scope of this test method. See Test Method [D7458](#) for determination of beryllium in soil samples.

1.4 This test method includes a procedure for extraction (dissolution) of beryllium in weakly acidic medium (pH of 1 % aqueous ammonium bifluoride is 4.8), followed by field analysis of aliquots of the extract solution using a beryllium-specific-optically fluorescent dye.

1.5 The procedure is suitable for on-site use in the field for occupational and environmental hygiene monitoring purposes. The method is also applicable for use in fixed-site laboratories.

1.6 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.

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

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

<sup>1</sup> This test method is under the jurisdiction of ASTM Committee [D22](#) on Air Quality and is the direct responsibility of Subcommittee [D22.04](#) on Workplace Air Quality.

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1.9 *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:*<sup>2</sup>

- [D1193](#) Specification for Reagent Water
- [D1356](#) Terminology Relating to Sampling and Analysis of Atmospheres
- [D4840](#) Guide for Sample Chain-of-Custody Procedures
- [D5337](#) Practice for Flow Rate Adjustment of Personal Sampling Pumps
- [D6966](#) Practice for Collection of Settled Dust Samples Using Wipe Sampling Methods for Subsequent Determination of Metals
- [D7035](#) Test Method for Determination of Metals and Metalloids in Airborne Particulate Matter by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES)
- [D7144](#) Practice for Collection of Surface Dust by Microvacuum Sampling for Subsequent Metals Determination
- [D7296](#) Practice for Collection of Settled Dust Samples Using Dry Wipe Sampling Methods for Subsequent Determination of Beryllium and Compounds
- [D7458](#) Test Method for Determination of Beryllium in Soil, Rock, Sediment, and Fly Ash Using Ammonium Bifluoride Extraction and Fluorescence Detection
- [D7659](#) Guide for Strategies for Surface Sampling of Metals and Metalloids for Worker Protection
- [D7707](#) Specification for Wipe Sampling Materials for Beryllium in Surface Dust
- [E177](#) Practice for Use of the Terms Precision and Bias in ASTM Test Methods
- [E691](#) Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method

<sup>2</sup> For referenced ASTM standards, visit the ASTM website, [www.astm.org](http://www.astm.org), or contact ASTM Customer Service at [service@astm.org](mailto:service@astm.org). For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

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

**E1370** Guide for Air Sampling Strategies for Worker and Workplace Protection

**E1792** Specification for Wipe Sampling Materials for Lead in Surface Dust

### 3. Terminology

3.1 *Definitions*—For definitions of terms not appearing here, see Terminology **D1356**.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *wipe, n*—a disposable towelette that is moistened with a wetting agent such as water. **E1792; D6966**

3.2.1.1 *Discussion*—These towelettes are used for collecting samples of dust, potentially containing beryllium, from surfaces.

3.2.2 *wipe sample, n*—sample collected by wiping a representative surface of known area, as determined by Practice **D6966**, or equivalent method, with an acceptable wipe material as defined in Specification **D7707**.

### 4. Summary of Test Method

4.1 Particles potentially containing beryllium from workplace air or surfaces, or both, are collected in the field using procedures described in ASTM International standards. To extract (or dissolve) beryllium in the collected samples, the media in or on which the samples are collected (that is, air sample, vacuum sample or wipe) are treated using an acidic extraction solution containing dilute ammonium bifluoride,  $\text{NH}_4\text{HF}_2$  (**1**).<sup>3</sup> The presence of active fluoride ions (HF by dissociation of ammonium bifluoride in acidic medium) enables dissolution of refractory materials such as “high-fired” beryllium oxide. 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 optical fluorescence reagent (**1**, **2**). The fluorescence exhibited by this final solution is then measured on a calibrated fluorometer to quantify the amount of beryllium in the sample (**3**).

### 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 (**4**, **5**). 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 on-site and fixed-site laboratory measurement of trace beryllium. Beryllium analysis results can then be used as a basis for exposure assessment and protection of human health.

<sup>3</sup> The boldface numbers in parentheses refer to a list of references at the end of this standard.

### 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 (**1**). In case the sample is suspected of having fluorescent organic contaminants that are suspected to be present, then their presence can be checked and removed (**6**).

NOTE 1—If the samples are suspected of having a contaminant that fluoresces and has excitation and emission spectra that overlap with that of the signal produced by the fluorescent dye bound to beryllium, then this contaminant needs to be removed. The presence of such a contaminant can be verified by subjecting the filtered sample to fluorescence excitation after the extraction step (without adding the fluorescent dye). If a fluorescence signal is detected, then that signal is ascribed to the presence of a fluorescent contaminant. To remove the contaminant, high-purity activated charcoal is added to the beryllium extraction solution and the extraction procedure is carried out at elevated temperature (80 to 90°C for at least 45 minutes). If the beryllium extraction procedure has already been performed, then after the addition of activated charcoal, the extraction process is repeated at the elevated temperature. The solution is filtered to remove the activated charcoal before making the measurement solution. The measurement solution is made by the addition of the fluorescent dye solution to an aliquot of the extraction solution. Details of this process have been published (**6**).

6.2 If iron is present in high excess in the sample (typically more than 20  $\mu\text{M}$ ), the resulting measurement solution may appear golden-yellow. In this case the solution should be left for an hour or more for the iron to precipitate. The solution should then be 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:*

7.1.1 *Air Sampling*—Use air samplers and filters for collecting personal air samples as described in Test Method **D7035**.

7.1.2 *Wipe Sampling*—Use wipe sampling apparatus for collecting surface dust samples as described in Practice **D6966** (or Practice **D7296** in special cases), using wipes meeting the specifications described in Specification **D7707**.

7.1.3 *Vacuum Sampling*—If wipe sampling is not advisable for surface sample collection, use vacuum sampling apparatus for collecting surface dust samples as described in Practice **D7144**.

7.2 *Instrumentation:*

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

7.2.2 *Mechanical Agitator or Heating Source*, shaker, rotator or ultrasonic bath; or heat block, oven or heating bath.

NOTE 2—For routine samples, a shaker, rotator, or ultrasonic bath is adequate. To achieve higher recoveries from beryllium oxide (especially “high-fired” BeO), a heat block, oven or heating bath is required.

7.3 *Laboratory Supplies:*

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

7.3.2 *Syringe filters*, 0.2 to 0.45- $\mu\text{m}$  nylon, polyethersulfone or hydrophilic polypropylene, 13- or 25-mm diameter, in plastic housings.

7.3.3 *Syringes*, plastic, 5-mL or 10-mL.

7.3.4 *Pipettors*, mechanical, of assorted sizes as needed.

7.3.5 *Pipet tips*, plastic, disposable, of assorted sizes as needed.

7.3.6 *Fluorescence cuvettes*, disposable, low fluorescence, 10-mm path length, transparent to UV/Vis radiation.

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

7.3.8 *Forceps*, plastic or plastic-coated.

7.3.9 *Personal protective wear*, for example, respirators, masks, gloves, lab coats, safety eyewear, etc., as needed.

7.3.10 *Thermometer*, to at least 100°C.

7.3.11 Other general laboratory apparatus, as needed.

#### 7.4 *Reagents*:

7.4.1 *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 MΩ-cm or equivalent)

7.4.2 *Calibration Stock Solution*—1000 ppm beryllium in dilute nitric acid or equivalent.

7.4.3 Ethylenediaminetetraacetic acid (EDTA) disodium salt dihydrate.

7.4.4 L-lysine monohydrochloride.

7.4.5 10-hydroxybenzo[h]quinoline-7-sulfonate (10-HBQS).

7.4.6 Sodium hydroxide.

7.4.7 *Extraction (or Dissolution) Solution*—1 % ammonium bifluoride (NH<sub>4</sub>HF<sub>2</sub>) solution (aqueous) for dissolution of beryllium in collected particulate matter. (**Warning**—Ammonium bifluoride will etch glass, so it is essential that all NH<sub>4</sub>HF<sub>2</sub> solutions be contained in plastic labware.)

7.4.8 *Detection Solution*—63.4 μM 10-hydroxybenzo[h]quinoline-7-sulfonate (10-HBQS) / 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 10.7 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 (**1-3**).

NOTE 3—For on-site analysis, it is recommended that the extraction and detection solutions be prepared in a fixed-site laboratory or other such controlled environment prior to transport to the field.

## 8. Procedure

### 8.1 *Sampling*:

8.1.1 *Air Samples*—Collect workplace air samples for beryllium in accordance with Test Method **D7035**, using personal sampling pumps calibrated in accordance with Practice **D5337**.

8.1.2 *Wipe Samples*—Collect surface wipe samples for beryllium in accordance with Practices **D6966** and **D7296** using wipe materials that comply with Specification **D7707**.

NOTE 4—Practice **D7296** should only be used when wetted wipe sampling is not physically feasible (for example, if the surface to be wiped would be compromised by use of wetted wipes). Otherwise, Practice **D6966** should be used.

8.1.3 *Vacuum Samples*—If wipe sampling is inadvisable for surface dust sampling, collect surface vacuum samples for beryllium in accordance with Practice **D7144**.

8.1.4 *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**.

8.2 *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.

#### 8.2.1 *Extraction of Air Filter or Vacuum Samples*:

8.2.1.1 Don clean gloves and open the samplers. Use either technique (1) or (2) to perform sample extraction on each collected sample:

(1) Using forceps, remove the filter from the cassette and place it into 15-mL centrifuge tube. The interior of the cassette shall be rinsed with extraction solution or wiped with another clean filter, and included in the centrifuge tube. For each vacuum sample, quantitatively transfer all loose dust into the centrifuge tube before removing the filter and then rinsing or wiping the inside walls of the sampler.

(2) Alternatively, the extraction shall be carried out directly within the sampling cassette (see Test Method **D7035**).

8.2.1.2 Pipet 5 mL of 1 % ammonium bifluoride extraction solution (see **7.4.7**) into the centrifuge tubes or cassettes containing the air filter or vacuum samples.

8.2.1.3 Cap the centrifuge tubes or cassettes, and agitate or heat the samples:

(1) Activate the shaker, rotator, or ultrasonic bath, and agitate for a minimum of 30 minutes; or

(2) Preheat the heat block, oven or heating bath to 85°C (±5°C), and heat the samples for a minimum of 30 minutes.

NOTE 5—Extraction is an example of a dissolution and solvating process. Method evaluation might indicate that for complete dissolution of beryllium, it may be necessary for the dissolution process to be assisted by ultrasonic energy, heat or longer treatment periods to obtain acceptable recoveries. This will be dependent upon the sample media, particle physical characteristics (such as shape and size) and the inertness of beryllium-containing compounds. Heating to between 80 and 90°C is required for the dissolution of refractory compounds such as “high-fired” beryllium oxide.

8.2.1.4 If the samples are heated during the extraction step, they shall be cooled to ambient temperature before aliquots are removed prior to addition of the detection solution.

#### 8.2.2 *Extraction of Wipe Samples*:

8.2.2.1 Don clean gloves and, using forceps, place the wipes into 15- or 50-mL centrifuge tubes.

NOTE 6—The size of the wipes used for sampling (8.1.2) will determine the size of the centrifuge tubes to use for extraction. Smaller wipes can be placed into 15-mL centrifuge tubes. Larger wipes, however, will require the use of larger tubes such as 50-mL volume. Use of 15-mL centrifuge tubes will facilitate achievement of the lower detection limit.

8.2.2.2 Pipet 5 mL or 10 mL of 1 % ammonium bifluoride extraction solution (see **7.4.7**) into the centrifuge tubes containing the wipe samples.



NOTE 7—The size of the wipes used for sampling (8.1.2) and the size of the centrifuge tubes used for extraction will determine the volume of extraction solution to add. Smaller wipes in 15-mL tubes will require only 5 mL of extraction solution, but larger wipes in 50-mL tubes will require a minimum of 10 mL of extraction solution to ensure complete wetting and effective extraction. Use of a 15-mL centrifuge tube and 5 mL of extraction solution will result in a lower detection limit than with use of the larger centrifuge tube and a larger extraction solution volume.

8.2.2.3 Cap the centrifuge tubes, and agitate or heat the samples:

(1) Activate the mechanical shaker, agitator, or ultrasonic bath, and agitate the samples for a minimum of 30 minutes; or

(2) Preheat the heat block, oven, or heating bath to 85°C ( $\pm 5^\circ\text{C}$ ), and heat the samples for a minimum of 60 minutes.

NOTE 8—Extraction is an example of a dissolution and solvating process. Method evaluation might indicate that for complete dissolution of beryllium, it may be necessary for the dissolution process to be assisted by ultrasonic energy, heat or longer treatment periods to obtain acceptable recoveries. This will be dependent upon the sample media, particle physical characteristics (such as shape and size) and the inertness of beryllium-containing compounds. Heating to between 80 and 90°C is required for the dissolution of refractory compounds such as “high-fired” beryllium oxide.

8.2.2.4 If the samples are heated during the extraction step, they shall be cooled to ambient temperature before aliquots are removed prior to addition of the detection solution.

8.2.3 *Filtration*—Filter aliquots (for example, 5 mL) of extract solution through inert microfilters.

NOTE 9—Filters with 0.2 to 0.45-micrometre pore size have been found to be acceptable. Preferred filters are made out of nylon, polyethersulfone or hydrophilic polypropylene.

NOTE 10—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.

#### 8.2.4 *Measurement Solution Preparation:*

8.2.4.1 For routine samples, pipet 100  $\mu\text{L}$  of filtered solution extracts into fluorescence cuvettes. To this add 1.9 mL of detection (dye) solution and ensure these are mixed well. This is a 20 $\times$  dilution.

8.2.4.2 For samples where ultra-trace beryllium measurements are required, pipet 400  $\mu\text{L}$  of filtered solution extracts into fluorescence cuvettes. To this add 1.6 mL of detection (dye) solution and ensure these are mixed well. This is a 5 $\times$  dilution (7).

NOTE 11—If excess iron is present (typically more than 20  $\mu\text{M}$ ) in the sample, the resulting measurement solution may be golden-yellow. In this case the solution should be left for an hour for iron to precipitate and the solution to clarify to colorless/near colorless. The solution should be re-filtered using the same procedure as was conducted for filtering the dissolution solution and then used for the fluorescence measurement. The waiting time is reduced when 0.2-micrometre pore size filters made out of polyethersulfone or hydrophilic polypropylene are used.

NOTE 12—A 20 $\times$  dilution is typically used for samples between about 0.2 and 4  $\mu\text{g}$  of beryllium (the method detection limit for beryllium is about 0.005  $\mu\text{g}$  or lower depending on the fluorescence instrument). Preparation for ultra-trace analysis uses a 5 $\times$  dilution for samples between about 0.02 and 0.4  $\mu\text{g}$  of beryllium (the method detection limit for beryllium is about 0.0008  $\mu\text{g}$  or lower depending on the fluorescence instrument) (7).

8.3 *Fluorometer Set-Up*—Set up the fluorometer for excitation radiation from 360 to 390 nm and measurement of

emission in a spectral window selected from a range of (at least) 440 to 490 nm. Allow appropriate warm-up of the system prior to analysis (follow manufacturer’s instructions).

NOTE 13—For fluorescence measurement, an emission band pass filter with peak transmission wavelength at  $\sim 475$  nm and with a full width at half maximum (FWHM) of less than  $\pm 10$  nm have been shown to be effective (1).

8.4 *Preparation of Calibration Standards*—Using calibration stock solution and 1 % aqueous ammonium bifluoride solution, prepare at least four standards covering the concentration range of interest.

NOTE 14—For example: To measure from about 0.02 to 4  $\mu\text{g}$  of beryllium in samples, calibration standards from 0 to 800 parts per billion (ppb) are recommended (see Table 1).

#### 8.5 *Calibration and Specifications:*

8.5.1 *Calibration Blank and Calibration Stock Standard Solutions Preparation*—The calibration blank is prepared by adding in a proportion of 1:19 (by volume) the 0 ppb standard and the detection solution in a cuvette suitable for fluorescent measurements. Ensure that these are mixed properly. Calibration standard solutions are made in a similar fashion, where the calibration standard and the detector solution are mixed in a volumetric ratio of 1:19 (a 20 $\times$  dilution). At least four standard measurement solutions, plus a blank, shall be made for calibration.

NOTE 15—For routine beryllium analyses, calibration stock standard solution concentrations of 0, 10, 40, 200 and 800 ppb beryllium in 1 % ammonium bifluoride are preferred; see Table 1. For ultra-trace beryllium determinations, calibration stock standard solution concentrations of 0, 1, 4, 20 and 80 ppb beryllium in 1 % ammonium bifluoride are preferred; see Table 1. The calibration stock solution standards for ultra-trace determinations may be prepared by a 10 $\times$  dilution of the routine calibration stock solution standards preferably using 1 % ammonium bifluoride as the dilutant (a volumetric ratio of 1:9 of routine calibration stock solution standard to 1 % ammonium bifluoride solution).

8.5.2 *Instrument Calibration*—Using the calibration standard solutions prepared above, calibrate the instrument for fluorescence intensity versus the concentration of beryllium. A calibration curve using linear regression shall be obtained between the fluorescent intensity and the concentration of beryllium. The correlation coefficient should be equal or greater than 0.999. Verify calibration by measuring the highest concentration standard, which should yield a value of within 10 % of the known value. The calibration must be verified at a minimum of once every hour (for example, after completing the measurement of the unknowns) to ensure that calibration still holds.

NOTE 16—Changes in temperature can cause a drift in the readings, thus it is important to verify calibration periodically. In addition the samples must not be left in the instrument for longer than necessary for measurement, as this can also cause drift in temperature and consequent change in signal intensity. If the calibration solutions have been properly capped and protected from light, they may be reused for calibration repeatedly over a period of seven days.

8.5.3 The calibration of fluorescence intensity due to the amount of beryllium present can be accomplished in either of two ways: by examining instrument response due to (a) the concentration of beryllium in calibration solutions, or (b) in terms of the amount of beryllium in the media (wipe or filter); see Table 1.