Designation: D7202 – 06

Standard Test Method for Determination of Beryllium in the Workplace Using Field-Based Extraction and Fluorescence Detection[1]

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 (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 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.

1.3 This test method includes a procedure for on-site 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 fluorescent dye.

1.4 The procedure is targeted for on-site use in the field for occupational and environmental hygiene monitoring purposes.

1.5 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.

1.6 The values stated in SI units are to be regarded as standard.

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.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

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 Calibration 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 Micro-vacuum 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

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

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 *Definition of Term Specific to This Test Method:*

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.

[1] 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 Atmospheres.

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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.

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 on-site using an acidic extraction solution. 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 fluorescence reagent. The fluorescence of this final solution is then measured on a calibrated field-portable fluorometer to quantify the amount of beryllium in the sample.

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 (**1**, **2**). Sampling and analytical methods for beryllium are needed in order to meet the challenges relating to exposure assessment and risk reduction. Field-portable sampling and analysis methods, such as the procedure described in this test method, are desired in order to facilitate on-site measurement of beryllium. On-site beryllium analysis results can then be used as a basis for management of protection of human health.

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.

6.2 If iron is present in high excess in the sample (typically more than 20 µM), 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 Practices D6966 and D7296.

7.1.3 *Vacuum Sampling*—If wipe sampling is not advisable, use vacuum sampling apparatus 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, $\lambda max \approx 475$ nm)

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

NOTE 1—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 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*, 0.45-µm nylon, 13- or 25-mm diameter, in plastic housings

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

7.3.4 *Pipetters*, 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 supplies 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_4HF_2) solution (aqueous) for dissolution of beryllium in collected particulate matter. (**Warning—**Ammonium bifluoride will etch glass, so it is essential that all NH_4HF_2 solutions be contained in plastic labware.)

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

NOTE 2—It is recommended to prepare the extraction and detection solutions in a fixed-site laboratory 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.

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 Samples*

8.2.1.1 Don clean gloves and open the samplers. Using forceps, remove the filters from the cassette and place them into 15-mL centrifuge tubes.

NOTE 3—If the entire contents of the sampler are regarded as part of the sample, the interior of the cassette should be rinsed with extraction solution, or wiped with another clean filter, and included in the centrifuge tube. Alternatively, the extraction can be carried out 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 containing the air filter samples.

8.2.1.3 Cap the centrifuge tubes, 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 or heating bath to 85°C (±5°C). and heat for a minimum of 30 minutes.

NOTE 4—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 5—The size of the wipes used for sampling (8.1.2) will determine the size of the centrifuge tubes to use for extraction. Small wipe materials, such as 47-mm diameter filters, 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 6—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. Small 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 or heating bath to 85°C (±5°C), and heat the samples for a minimum of 30 minutes.

NOTE 7—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 8—0.45-micrometre filters are acceptable. Preferred filters are made out of nylon.

NOTE 9—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 µL 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× dilution.

8.2.4.2 For samples where ultra-trace beryllium measurements are required, pipet 400 µL 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× dilution.

NOTE 10—If iron is present in high excess (typically more than 20 µM) 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 then be re-filtered using the same procedure as for filtering the dissolution solution and then used for fluorescence measurement.

NOTE 11—A20× dilution is typically used for samples between about 0.2 and 4 µg of beryllium (method detection limit about 0.02 µg of beryllium). Preparation for ultra-trace analysis uses a 5× dilution for samples between about 0.02 and 0.4 µg of beryllium (method detection limit about 0.002 µg of beryllium).

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 12—For fluorescence measurement, a band pass filter with peak