Designation: D7202 − 15

Standard Test Method for Determination of Beryllium in the Workplace by Extraction and Optical Fluorescence Detection[1]

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.

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:*[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 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 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
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

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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.

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, NH_4HF_2 (**1**).[3] 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.

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 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 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, $\lambda max \approx 475$ 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-µm nylon, polyethersulfone or hydrophilic polypropylene, 13- or 25-mm diameter, in plastic housings.

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[3] The boldface numbers in parentheses refer to a list of references at the end of this standard.

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 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_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) / 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**). An alternative preparation of dye solution without lysine may be made by adding 1.104 g of EDTA and 64 µmoles of the 10-HBQS dye in 900 ml of water. After a clear solution is obtained, 114.5 ml of 2.5 N NaOH is added and mixed to obtain the final dye solution. The pH of the dye solution is 13.2. The dye solution without lysine may be used for all analytical purposes and also provides superior detection limits.

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

TABLE 1 Preparation of Calibration Standards (Example)

Concentration of Beryllium Used in Calibration Standards	Final Concentration of Beryllium (ppb) in Calibration Standard Solutions	Corresponding Amount of Beryllium (Be) in Media (Filter or Wipe) (µg)[A]
0.1 mL of 0 ppb standard + 1.9 mL of detection solution (DF = 20)	0.0	Corresponds to 0 µg beryllium per sample when DF = 20
0.1 mL of 10 ppb standard + 1.9 mL of detection solution (DF = 20)	0.50	Corresponds to 0.050 µg beryllium per sample when DF = 20
0.1 mL of 40 ppb standard + 1.9 mL of detection solution (DF = 20)	2.0	Corresponds to 0.20 µg beryllium per sample when DF = 20
0.1 mL of 200 ppb standard + 1.9 mL of detection solution (DF = 20)	10.0	Corresponds to 1.0 µg beryllium per sample when DF = 20
0.1 mL of 800 ppb standard + 1.9 mL of detection solution (DF = 20)	40.0	Corresponds to 4.0 µg beryllium per sample when DF = 20
0.4 mL of 0 ppb standard + 1.6 mL of detection solution (DF = 5)	0.0	Corresponds to 0 µg beryllium per sample when DF = 5
0.4 mL of 1 ppb standard + 1.6 mL of detection solution (DF = 5)	0.20	Corresponds to 0.0050 µg beryllium per sample when DF = 5
0.4 mL of 4 ppb standard + 1.6 mL of detection solution (DF = 5)	0.80	Corresponds to 0.020 µg beryllium per sample when DF = 5
0.4 mL of 20 ppb standard + 1.6 mL of detection solution (DF = 5)	4.0	Corresponds to 0.10 µg beryllium per sample when DF = 5
0.4 mL of 80 ppb standard + 1.6 mL of detection solution (DF = 5)	16.0	Corresponds to 0.40 µg beryllium per sample when DF = 5
0.67 mL of 0 ppb standard + 1.33 mL of detection solution (DF = 3)	0.00	Corresponds to 0 µg beryllium per sample when DF = 3
0.67 mL of 0.1 ppb standard + 1.33 mL of detection solution (DF = 3)	0.033	Corresponds to 0.0005 µg beryllium per sample when DF = 3
0.67 mL of 0.4 ppb standard + 1.33 mL of detection solution (DF = 3)	0.133	Corresponds to 0.002 µg beryllium per sample when DF = 3
0.67 mL of 2 ppb standard + 1.33 mL of detection solution (DF = 3)	0.667	Corresponds to 0.01 µg beryllium per sample when DF = 3
0.67 mL of 8 ppb standard + 1.33 mL of detection solution (DF = 3)	2.67	Corresponds to 0.04 µg beryllium per sample when DF = 3

[A] Incorporating sample dilution factor for 5 mL of dissolution solution; note that volumes other than 5 mL will require a different appropriate dilution factor; DF = 3 can be used with the lysine-dye solution.

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 (±5°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 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. Either of the two dye solutions (with or without lysine) may be used.

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 **(7)**. The lysine-free dye solution may also be used for obtaining even lower detection limits at a dilution ratio of 3×, where 1.33 ml of the dye solution is mixed with 0.67 ml of the filtered solution extracts (Table 1).

NOTE 11—If excess iron is present (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 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× dilution is typically used for samples between about 0.2 and 4 µg of beryllium (the method detection limit for beryllium is about 0.005 µg or lower depending on the fluorescence instrument). Preparation for ultra-trace analysis uses a 5× dilution for samples between about 0.02 and 0.4 µg of beryllium (the method detection limit for beryllium is about 0.0008 µg or lower depending on the fluorescence instrument) (**7**). When 3× dilution ratio is used with lysine-free dye solution, one can determine beryllium down to 0.002 µg (as the method detection limit is about 0.0001 µg).

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 ~475 nm and with a full width at half maximum (FWHM) of less than ±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 µg 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× 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× 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). As an option, when measuring samples suspected of having beryllium lower than 0.005 µg, the calibration stock solutions may be further diluted by a factor of 10× so that they have concentrations of 0, 0.1, 0.4, 2, and 8 ppb beryllium in 1 % ammonium bifluoride. For measuring these low values, if a dilution of 3× is used, then the corresponding amounts of beryllium are also shown in Table 1.

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.

8.5.4 *Fluorescence Measurement*—Place the cuvette in the calibrated fluorometer and read the value of the fluorescence intensity that is measured by the instrument. Follow manufacturer instructions on applicable integration times to be used for fluorescence intensity measurements.

NOTE 17—The intensity calibration on the instrument may have been carried out in terms of absolute intensity or one of the following if the instrument automatically prepared a correlation using linear regression fit: concentration of beryllium in calibration standards, concentration of beryllium in calibration standard solutions, or in terms of amount of beryllium in the medium (for example, a surface wipe sample). Table 1 shows a correlation between various standards, calibration standard solutions, and the amount of beryllium in the sampling medium.

9. Calculation

9.1 *Estimation of Method Detection Limit*—Estimate the method detection limit (MDL) under the working analytical conditions, and repeat this exercise whenever experimental conditions (for example, integration time) are changed.

9.1.1 Prepare at least ten blank test solutions from unused filters or wipes, or both (or vacuum samples, if applicable), of the same type used for sample collection. Follow sample extraction and filtration procedures used to prepare sample test solutions (see 8.2).

9.1.2 For a selected integration time, make fluorescence measurements on the test solutions and calculate the MDL as three times the sample standard deviation of the mean concentration value.

9.2 *Calculation of Beryllium Concentration in Samples*—From the calibration curve, obtain the solution concentration for each sample, C_s (µg/mL), and the average media field blank, C_b (µg/mL).

NOTE 18—Alternatively, the mass of beryllium per sample can be read directly from the calibration curve using the procedure described in 8.5, where W_s and W_b are the amounts of beryllium in micrograms on the sample and the blank filter, respectively.

9.2.1 *Air Filter Samples*—Using the solution volumes of sample, V_s (mL), and media blank, V_b (mL), calculate the concentration, C (µg/m^3) of Be in the air volume sampled, V (1 m^3 = 1000 L), while accounting for the dilution factor DF (assuming equal dilution factors for samples and blanks):

$$C = DF \times [C_s V_s - C_b V_b]/V, \text{ µg Be/m}^3 \quad (1)$$

NOTE 19—Alternatively, $C = (W_s - W_b)/V_m$, µg Be/m^3, where W_s and W_b are the amounts of beryllium in micrograms on the sample and the average blank filter, respectively, and V_m is volume of the air sampled in m^3 (1 m^3 = 1000 L).

9.2.2 *Surface Samples*—Using the solution volumes of sample, V_s (mL), and average media blank, V_b (mL), calculate the concentration, C (µg/100 cm^2) of Be in the sample obtained from wiping or vacuuming an area A (in dm^2 or 100 cm^2), while accounting for the dilution factor DF (assuming equal dilution factors for samples and blanks):

$$C = DF \times [C_s V_s - C_b V_b]/A, \text{ µg Be/100 cm}^2 \quad (2)$$

NOTE 20—Alternatively, $C = (W_s - W_b)/A$, µg Be/100 cm^2, where W_s and W_b are the amounts of beryllium in micrograms in the sample and the blank medium, respectively.

NOTE 21—Vacuum samples can also provide gravimetric information; that is, mass of beryllium per unit mass of sample collected; see Practice D7144 for details.

10. Quality Control

10.1 *Laboratory and Field Blanks*—Carry reagent blanks (water and reagents) and media blanks (unspiked filters or wipes, or both) throughout the entire sample preparation and analytical process to determine whether the samples are being contaminated from laboratory activities. Field blanks shall also be obtained. Process reagent blanks and field blanks at a frequency of at least one per 20 samples, minimum of one per batch.

10.2 *Quality Control Samples:*

10.2.1 Carry spiked media and spiked duplicate media throughout the entire sample preparation and analytical process to estimate the method accuracy on the sample batch, expressed as a percent recovery relative to the true spiked value. Spiked samples and spiked duplicate samples consist of filters or wipes, or both, to which known amounts of beryllium have been added. Process these quality control samples according to a frequency of at least 1 per 20 samples, minimum of one per batch.

10.2.2 Monitor the performance of the method by plotting control charts of the relative percent recoveries and of the relative percent differences between the spiked samples and spiked duplicate samples. If quality control results indicate that the methods is out of control, investigate the reasons for this, take corrective action, and repeat the analyses. See Guide E882 for general guidance on the use of control charts.

10.3 *Certified Reference Materials (CRMs)*—If available, certified reference materials (CRMs) for beryllium shall be analyzed prior to or during routine use of the sample preparation and analytical method to establish whether the percent recovery relative to the certified value is satisfactory.

NOTE 22—Typically, recoveries of 100 % ± 15 % from CRMs are desired. However, for certain sample matrices, wider performance limits may be deemed acceptable.

10.4 *External Quality Assessment*—If the laboratory carries out analysis of beryllium in workplace air or wipe samples, or both, on a regular basis, it is recommended to participate in relevant external quality assessment and proficiency testing schemes.

11. Records

11.1 Records shall be maintained in accordance with Test Method D7035 (for air samples), Practice D7144 (for vacuum samples), and Guide D7659 (for wipe samples), and shall include a copy of the field sample collection report.

11.1.1 *Laboratory Records*—Record all reagent sources (lot numbers and vendors) used for sample preparation and analysis in a laboratory notebook. Record any inadvertent deviations, unusual happenings and notable observations on a real-time basis as the samples are processed. Use these records to add supplemental information when reporting the results.

12. Report

12.1 Data to report shall include, at a minimum, the following:

12.1.1 All sample receipt and chain-of-custody information, if applicable;

12.1.2 All sample analysis results;

12.1.3 Applicable quality assurance and quality control data;

12.1.4 Information on instrumentation and equipment used;

12.1.5 Instrument parameters used;

12.1.6 Identity of laboratory and analyst(s); and

12.1.7 Any other information deemed appropriate.

13. Precision and Bias[4]

13.1 *Beryllium Solution Spikes*—An interlaboratory evaluation of the method was carried out using mixed cellulose ester (MCE) membrane filters and Whatman 541 filters (cellulosic filters used as wipe sampling media) that were spiked with beryllium standard solutions so that the filters spanned the range ≈0.05 to ≈0.5 µg Be per sample (**8**). Beryllium nitrate standard calibration solutions were used for spikes.

13.1.1 Data for interlaboratory precision (in terms of repeatability and reproducibility) were processed in accordance with Practice E691. Repeatability was calculated by averaging the squares of the standard deviations of within-laboratory results for each beryllium level, hence the average within-laboratory variance is given by the repeatability variance, $(S_r)^2$. Reproducibility variance is expressed by $(S_R)^2 = (S_r)^2 + (S_L)^2$, where S_L is the sample standard deviation of the mean value estimated from the average of reported interlaboratory test results for a given performance evaluation material. Relative standard deviations ($RSDs$) for repeatability and reproducibility (RSD_r and RSD_R, respectively) are then computed by dividing the standard deviations S_r and S_R by the mean interlaboratory test result for a particular performance evaluation material. Precision data from the interlaboratory study are summarized in Table 2.

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[4] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D22-1034. Contact ASTM Customer Service at service@astm.org.

TABLE 2 Repeatability and Reproducibility for Beryllium Measurements from Performance Evaluation MCE and Whatman 541 Filters, as Computed Using Values Reported by Laboratories (n = 8) Participating in an Interlaboratory Evaluation

Media Beryllium Level	Average (µg Be)	S_r	S_R	RSD_r	RSD_R
MCE Filters					
Low	0.052	0.0034	0.0051	0.065	0.098
Medium Low	0.10	0.0052	0.0071	0.052	0.071
Medium High	0.21	0.012	0.020	0.057	0.095
High	0.43	0.0080	0.033	0.019	0.077
Whatman 541 Filters					
Low	0.054	0.0027	0.0039	0.050	0.072
Medium Low	0.11	0.0068	0.012	0.062	0.11
Medium High	0.21	0.012	0.014	0.057	0.067
High	0.41	0.012	0.025	0.029	0.061

13.1.2 Estimates of analytical bias, B, were computed by simply dividing the difference between the measurand and the reference value by the reference value, $B = (\mu_i - R_i) / R_i$, where μ_i and R_i are the mean and reference beryllium contents, respectively, for the ith beryllium loading level in each performance evaluation sample. Bias data from the interlaboratory study are summarized in Table 3(**8**).

13.1.3 In a separate study, MCE filters and cellulosic (wiping) filters spiked with ultra-low levels of beryllium (0.002–0.05 µg Be per sample) were analyzed by four laboratories (**7**). Measured Be amounts were very close to the spike values, and RSDs were ≈2 to 6 % for levels of 0.005–0.05 µg Be, to ≈13 to 19 % for MCE and cellulosic filters spiked at 0.002 µg Be.

13.2 *Beryllium Oxide Spikes*—Evaluations of the method were carried out using MCE membrane filters, cellulosic filters, and polyvinyl alcohol (PVA) wipes spiked with BeO prepared from slurries. Beryllium levels ranged from ≈0.03 to ≈18 µg Be per sample (**3**, **7**, **9-12**).

13.2.1 Laboratory studies of the method have obtained beryllium recoveries of 85–100 % from filter and wipe media spiked with BeO (**3**, **9**), and estimated method quantitation limits of less than 1 ng Be per sample and about 14 ng Be per sample with 5× (**7**) and 20× (**3**) dilution of filtered extracts with detection solution, respectively. BeO particles of larger physical diameter may require the use of higher concentrations of ammonium bifluoride and longer extraction periods (**10**); see Test Method D7458.

13.2.2 An interlaboratory study (ILS) of certified BeO-spiked polyvinyl alcohol (PVA) wipes meeting the specifications of Specification D7707 was performed. The ILS was carried out in accordance with Practice E691 on PVA media (Ghost Wipes) fortified at beryllium levels ranging from 0.03 to 5.6 µg Be per wipe. PVA wipes wetted with 0.5 ml of deionized water, and dry PVA wipes, were spiked with BeO from slurries to yield Be-spiked media at the desired levels. Duplicates of the BeO-spiked PVA materials, plus media blanks, were distributed to eight participating laboratories; spiking levels were unknown to the volunteer laboratories. Each participant was requested to carry out extraction and fluorescence measurement in accordance with the procedure described in this standard, and to report their results in units of µg Be per wipe sample.

13.2.2.1 *Repeatability Limit (r)*—Two test results obtained within one laboratory shall be judged not equivalent if they differ by more than the "*r*" value for that material; "*r*" is the interval representing the critical difference between two test results for the same material, obtained by the same operator using the same equipment on the same day in the same laboratory. Repeatability limits for the ILS are listed in Tables 4 and 5 for wetted and dry PVA wipes, respectively.

13.2.2.2 *Reproducibility Limit (R)*—Two test results shall be judged not equivalent if they differ by more than the "*R*" value for that material; "*R*" is the interval representing the critical difference between two test results for the same material, obtained by different operators using different equipment in different laboratories. Reproducibility limits for the ILS are listed in Tables 4 and 5 for wetted and dry PVA wipes, respectively.

13.2.2.3 The above terms (repeatability limit and reproducibility limit) are used as specified in Practice E177. Any judgment in accordance with statements 13.2.2.1 and 13.2.2.2 would have an approximate 95 % probability of being correct.

13.3 *Analytical Recovery*—The ILS data yielded beryllium recoveries of 87 % to 93 % for wetted PVA wipes (after results were corrected for moisture content), and 90 % to 99 % for dry PVA wipes (**11**).

14. Keywords

14.1 air; beryllium; filter; fluorescence; wipe; workplace

TABLE 3 Bias Estimates for Beryllium Measurements from Performance Evaluation MCE and Whatman 541 Filters, Computed Using Mean Values from Table 2 Reference Values for Beryllium Loadings on the Filters are Given in Parentheses

Media	Low (0.05 µg Be)	Medium low (0.10 µg Be)	Medium high (0.20 µg Be)	High (0.40 µg Be)
MCE filters	0.040	0.00	0.050	0.075
Whatman 541 Filters	0.080	0.10	0.050	0.025

TABLE 4 Repeatability and Reproduciblity for Beryllium Measurements from Interlaboratory Study of Wetted PVA Wipes (Micrograms Beryllium per Sample; $n = 8$)

Material ID	Average[A] $\bar{x}$	Repeatability Standard Deviation S_r	Reproducibility Standard Deviation s_R	Repeatability Limit r	Reproducibility Limit R
Wet-Blank	0.0080	0.0155	0.0168	0.0435	0.0470
Wet-0.030	0.024	0.0022	0.0046	0.0061	0.0129
Wet-0.16	0.126	0.0054	0.0121	0.0150	0.0339
Wet-0.32	0.259	0.0228	0.0228	0.0638	0.0638
Wet-1.8	1.43	0.238	0.276	0.0665	0.773
Wet-2.8	2.30	0.115	0.330	0.322	0.924
Wet-5.6	4.53	0.212	0.214	0.593	0.600

[A] The average of the laboratories' calculated averages.

TABLE 5 Repeatability and Reproduciblity for Beryllium Measurements from Interlaboratory Study of Dry PVA Wipes (Micrograms Beryllium per Sample; $n = 8$)

Material ID	Average[A] $\bar{x}$	Repeatability Standard Deviation S_r	Reproducibility Standard Deviation s_R	Repeatability Limit r	Reproducibility Limit R
Dry-Blank	0.0018	0.0009	0.0025	0.0026	0.0069
Dry-0.030	0.0298	0.0146	0.0146	0.0409	0.0409
Dry-0.16	0.143	0.0056	0.0178	0.0157	0.0498
Dry-0.32	0.292	0.0160	0.0251	0.0449	0.0703
Dry-1.8	1.71	0.0361	0.0821	0.101	0.230
Dry-2.8	2.73	0.122	0.328	0.343	0.918
Dry-5.6	5.33	0.109	0.593	0.305	1.66

[A] The average of the laboratories' calculated averages.

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