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Standard Practice for
Separation of Beryllium from Other Metals in Digestion and Extraction Solutions from Workplace Dust Samples[1]

This standard is issued under the fixed designation D7441; 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 practice covers the separation of beryllium from other metals and metalloids in acid solutions, by extraction chromatography, for subsequent determination of beryllium by atomic spectroscopy techniques such as inductively coupled plasma atomic emission spectroscopy (ICP-AES).

1.2 This practice is applicable to samples of settled dust that have been collected in accordance with Practices D6966 or D7296.

1.3 This practice is compatible with a wide variety of acid digestion techniques used in digesting settled dust samples, such as those described in Test Method D7035.

1.4 This practice is appropriate for the preparation of settled dust samples where an unacceptable bias is suspected or known because of spectral interferences caused by other metals or metalloids present in the sample. This practice may also be appropriate for the analysis of other types of samples.

1.5 *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

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)

D7296 Practice for Collection of Settled Dust Samples Using Dry Wipe Sampling Methods for Subsequent Determination of Beryllium and Compounds

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

3. Terminology

3.1 For discussion of pertinent terms not discussed here, see Terminology D1356.

3.2 *Definitions:*

3.2.1 *digestion*—dissolution using a combination of acids and other reagents of solid materials into solution for subsequent instrumental analysis.

3.2.2 *eluate*—the effluent from a chromatography or resin column.

3.2.3 *extraction chromatography*—liquid chromatography applied to the separation of metal ions utilizing selective organic extractants as the stationary phase and the aqueous solution as the mobile phase (**1**)[3].

3.2.3.1 *Discussion*—Extraction chromatography resins consist of inert porous beads coated with selective extractants.

3.2.4 *spectral interference*—an interference caused by the emission from a species other than the analyte of interest. **D7035**

3.2.5 *surface wipe*—refers either to a wetted wipe, as defined in Practice D6966, or to a dry wipe, as defined in Practice D7296, used to gather material from a surface for subsequent analysis.

3.2.5.1 *Discussion*—The terms wipe sampling, swipe sampling, and smear sampling describe the techniques used to assess surface contamination on the skin, work surfaces, and PPE surfaces (for example, gloves, respirators, aprons, etc.)

3.2.6 *vacuum box*—container used to maintain a vacuum on a resin or column sample in order to increase the rate of flow

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[1] This practice 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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[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.

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

of liquid through the column. Other vacuum sources such as an aspirator may be used.

4. Summary of Practice

4.1 This practice is based on using extraction chromatography resin to separate beryllium ions from other metal ions in extracts and digestates of surface wipe samples.

4.2 Surface wipe samples are collected using Practice D6966 or Practice D7296, and are then digested or extracted into solution by mineral acids.

4.3 The pH of the solution is adjusted to between 1 and 2 with sodium acetate.

4.4 The sample is then loaded onto the extraction chromatography resin column, where beryllium is retained. Matrix interferences are rinsed from the column with 0.2 M nitric acid.

4.5 Beryllium is selectively eluted from the resin with 4 M nitric acid and is available for analysis using the spectroscopic techniques such as ICP-AES (See Test Method D7035).

5. Significance and Use

5.1 Beryllium is an important analyte in industrial hygiene because of the risk of exposed workers developing Chronic Beryllium Disease (CBD). CBD is a granulomatous lung disease that is caused by the body's immune system response to inhaled dust or fumes containing beryllium, a human carcinogen (**2**). Surface wipe samples and air filter samples are collected to monitor the workplace. This practice addresses the problem of spurious results caused by the presence of interfering elements in the solution analyzed. The practice has been evaluated for all elements having emission spectra near the 313.042 and 313.107 nm beryllium lines, as well as elements of general concern including aluminum, calcium, iron and lead. Below is a table listing each possible spectrally interfering element:

Cerium	Chromium	Hafnium	Molybdenum
Niobium	Thorium	Titanium	Thulium
Uranium	Vanadium	Uranium	

Measurement of beryllium on the order of 1 ppb (0.003 µg Be/100 cm^2 wipe sample) has been successfully accomplished in the presence of spectrally interfering elements on the order of hundreds of ppm. This method has been validated on matrices containing 10 mg of each of the above elements. In some cases including interferents such as chromium and calcium, the single 2 mL beryllium extraction chromatography resin can handle >100 mg of total dissolved solids and still deliver >90 % beryllium yield. Should the matrix contain greater amounts of contaminants, additional resin may be used or, more likely, a combination of different resins may be used. (**3**,**4**).

6. Reagents and Materials

6.1 *Equipment:*

6.1.1 50-mL polypropylene centrifuge tubes,

6.1.2 2-mL cartridges of beryllium extraction chromatography resin[4],

6.1.3 Syringe barrel (or similar size reservoir),

6.1.4 Vacuum box, with fittings compatible with the cartridges,

6.1.5 Delivery pipet, 5 mL or 10 mL,

6.2 *Reagents:*

(See Note 1.)

6.2.1 Deionized Water, Type I or Type II in accordance with Practice D1193,

6.2.2 Nitric Acid (HNO_3), concentrated, ρ~1.42 g/mL (~70 % m/m),

6.2.3 Boric Acid (H_3BO_3),

6.2.4 Ammonium Oxalate monohydrate ($NH_4C_2H_4O$),

6.2.5 Sodium acetate trihydrate ($C_2H_3O_2Na\cdot{}_3H_2O$),

6.2.6 Methyl Violet (indicator grade).

NOTE 1—*Purity of Reagents*—Reagent grade chemicals shall be used in all tests. 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.

6.3 *Solutions:*

6.3.1 3.4 M Sodium acetate + 0.2 M Ammonium oxalate + (0.2 M Boric acid): To a l-L volumetric flask, add 500 mL of deionized water. Add 12.37 grams of Boric acid and mix until dissolved. Add 28.42 grams of Ammonium oxalate monohydrate and mix until dissolved. Add 462.68 grams of Sodium acetate trihydrate and mix. Fill to 1 L with deionized water and mix until dissolved.

NOTE 2—Boric acid is added to combat the effect of HF used in digestion. If HF is not used, the Boric acid may be omitted.

6.3.2 *Ammonium Oxalate, 0.25 M:* To a l-L volumetric flask, add 500 mL of deionized water. Add 35.53 grams of Ammonium oxalate monohydrate and mix until dissolved. Fill to 1 L with deionized water and mix until dissolved.

6.3.3 *Nitric Acid, 0.2 M:* To a 1-L volumetric flask, add 200 mL of deionized water. Add 12.5 mL of concentrated (70%) nitric acid (trace metal grade) and mix. Fill to 1 L with deionized water and mix thoroughly.

6.3.4 *Nitric Acid, 4.0 M:* To a 1-L volumetric flask, add 200 mL of deionized water. Add 250 mL of concentrated (70 %) nitric acid (trace metal grade) and mix. Fill to 1 L with deionized water and mix thoroughly.

6.3.5 *Methyl Violet, 0.1 % solution, in deionized water:* 0.1 gm Methyl Violet per 100 mL of water.

7. Procedure

7.1 *Wipe Digest Preparation:*

7.1.1 Prepare resin load solution in accordance with the chemical reagents normally used to digest beryllium surface wipes.

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[4] Beryllium extraction chromatography resin cartridge: 2 mL bed volume, 50-100 micron beads, bis (2-ethylhexyl) methanediphosphonic acid sorbed onto acrylic ester beads (**3**, **4**, **5**). Quality control parameters for the resin are stated in subsection 8.6.

NOTE 3—Example methods for sample preparation may be found in Test Method D7035.

7.1.2 Transfer extract from digested filter or wipe to a 50 mL polypropylene centrifuge tube (see 6.1.1). The volume should be less than 20 mL at this point. If a larger volume is required to adequately digest the sample, check beryllium yield with a suitable matrix spike solution to verify acceptable yield, or consider increasing the amount of resin used. The digested filter solution may be slightly yellow, but should be free of any fine solids. If the solution appears cloudy or if solids remain following the digestion, filtration is required to remove fine particulate matter which can impede the flow of solution through the cartridge and may cause poor chromatographic performance.

7.1.3 Add 5-10 drops of 0.1 % methyl violet (see 6.3.5). For large numbers of samples, the methyl violet can be added directly to the 3.4 M sodium acetate solution. For each 100 mL of 3.4 M sodium acetate prepared add 4 mL of 0.1 % methyl violet in deionized water or 4 mg of solid methyl violet (see 6.2.6).

7.1.4 Adjust the digested filter solution to a pH target of 1.5 with 3.4 M sodium acetate + 0.2 M ammonium oxalate (+ 0.2 M boric acid) (see 6.3.1). Upon the addition of methyl violet, the diluted digested filter solution should appear yellow. Addition of the sodium acetate solution will increase the pH and the solution will turn green (pH 0.5), blue-green (pH 1), blue (pH 2) and dark violet (pH > 2.5). The pH of the solution should be adjusted with the sodium acetate solution and 4 M HNO_3 until a blue-green or blue color is obtained. An appropriate standard solution should be made for color comparison.

NOTE 4—If HF is used in the digestion process, 0.2 M boric acid will be needed to sequester any remaining fluoride ion. Without the boric acid, beryllium will form fluoride complexes which will not be retained by the beryllium extraction chromatography resin. The boric acid is added to the stock sodium acetate-ammonium oxalate solution.

NOTE 5—If hydrogen peroxide persists in the filter or wipe solution following digestion, the color of the pH indicator may fade, making it difficult to monitor the pH effectively. If this happens, simply add 3-5 drops of 0.1 % methyl violet indicator (see 6.3.5). For highly colored solutions, pH paper or a pH meter may be more effective for pH measurement than methyl violet.

7.2 *Beryllium Separation:*

7.2.1 Mount the 2 mL beryllium extraction chromatography resin cartridge (see 6.1.2), equipped with a 20-30 mL reservoir to a vacuum source and container large enough to capture the column effluent. Steps 7.2.2–7.2.4 may be collected into the same container (either a liner or 50-mL centrifuge tubes) and discarded as waste.

7.2.2 Add the neutralized digested filter solution to the reservoir and pass the solution through the 2 mL beryllium extraction chromatography resin cartridge at 2 mL/min. Discard the eluate.

7.2.3 Rinse the beryllium extraction chromatography resin cartridge with 15 mL of 0.25 M ammonium oxalate (see 6.3.2) at 2 mL/min. Discard the eluate.

7.2.4 Rinse the beryllium extraction chromatography resin cartridge with 15 mL of 0.2 M HNO_3 (see 6.3.3) at 2 mL/min. Discard the eluate.

7.2.5 Equip the vacuum box (see 6.1.4) with a 50-mL polypropylene centrifuge tube for each beryllium extraction chromatography resin cartridge.

7.2.6 Elute the beryllium with 15 mL of 4.0 M HNO_3 (see 6.3.4) at 1 mL/min. Collect the eluate in a 50-mL polypropylene centrifuge tube. A greater volume of 4 M nitric acid may be used to increase beryllium yield, but will result in a more dilute beryllium solution.

7.2.7 Analyze the eluate for beryllium by ICP-AES in accordance with Test Method D7035.

NOTE 6—Other analysis methods may be suitable, for example, ICP-MS.

8. Quality Control

8.1 *Laboratory Blanks*—Carry reagent blanks (water and reagents) and media blanks (unspiked filters) throughout the entire sample preparation and analytical process to determine whether the samples are being contaminated from laboratory activities. Process reagent blanks at a frequency of at least 1 per 20 samples, minimum of one per batch.

8.2 *Quality Control Samples:*

8.2.1 Carry spiked filters and spiked duplicate filter 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 to which known amounts beryllium have been added. Process these quality control samples in accordance with a frequency of at least 1 per 20 samples, minimum of one per batch.

8.2.2 Monitor the performance of the method by plotting control charts of the relative percent recoveries and of the relative percent difference between spiked samples and spiked duplicate samples. If quality control results indicate that the method 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.

8.3 *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 7—Typically, recoveries of 100 ± 15 % are desired. However, for certain sample matrices, wider performance limits may be deemed acceptable.

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

8.5 *Measurement Uncertainty*—It is recommended that the laboratory estimate and report the uncertainty of their measurements in accordance with ISO guidelines (**6**). This entails first constructing a cause and effect diagram to identify the individual sources of random and systematic error in the overall sampling and analytical method. These are then estimated, or determined, or both, experimentally and combined in what is referred to as an uncertainty budget. The combined uncertainty is ultimately multiplied by an appropriate coverage factor to produce and expanded uncertainty. A coverage factor of 2 is ordinarily recommended, as this gives a confidence level of approximately 95 % in the calculated value.

NOTE 8—Application of cause and effect analysis to analytical methods has been described in the published literature (7). Terms that contribute to the random variability on an analytical method are generally accounted for in the measurement precision, which can be estimated from quality control data. Errors associated with instrumental drift can be estimated, assuming a rectangular probability distribution, by dividing the allowable drift before recalibration by $\sqrt{3}$. Systematic errors include, for example, those associated with analytical recovery, sampling recovery, preparation of working standard solutions, dilution of test solutions, and so forth.

8.6 *Representative Quality Control Parameters*—Beryllium extraction chromatography resin quality control parameters are as follows:

Parameter	Limit	Result
Be Mass Balance	95–105 %	Pass/Fail
Be Breakthrough	<5 % in Load/Rinse	Pass/Fail
Be Recovery	>90 % in 12 BV	Pass/Fail
Cr Impurity	<1 % in Strip	Pass/Fail
Al Impurity	<1 % in Strip	Pass/Fail
V Impurity	<1 % in Strip	Pass/Fail

All six parameters shall yield a "pass" result for data acceptance. The method is as follows: Spike a 5.5 centimetre diameter piece of cellulose ashless filter paper with 140 µg of Be, Al, V and Cr and digest with 2 mL of concentrated H_2SO_4 and 3 mL of concentrated HNO_3 on a hot plate at 150°C. 5-10 drops of 35 % H_2O_2 are added to complete the digestion and the sample is diluted to 10 mL with deionized water and neutralized to pH 1-2 with sodium acetate. The diluted, neutralized digestion solution is then loaded onto a 2-mL beryllium extraction chromatography resin cartridge at 2 mL/min. The cartridge is rinsed with 0.2 M HNO_3 at 2 mL/min and stripped with 4 M HNO_3 at 1 mL/min. Aliquots of the eluate are collected into tared polypropylene centrifuge tubes, diluted to 5 mL with deionized water and analyzed for Be, Al, Cr, and V by ICP-AES using the 234.861, 396.152, 267.716 and 292.402 nm peaks, respectively.

The results in the chromatogram of Fig. 1 are representative of the performance of acceptable beryllium extraction chromatography resin. The nomenclature of 'Be Resin' is an abbreviation for beryllium extraction chromatography resin.

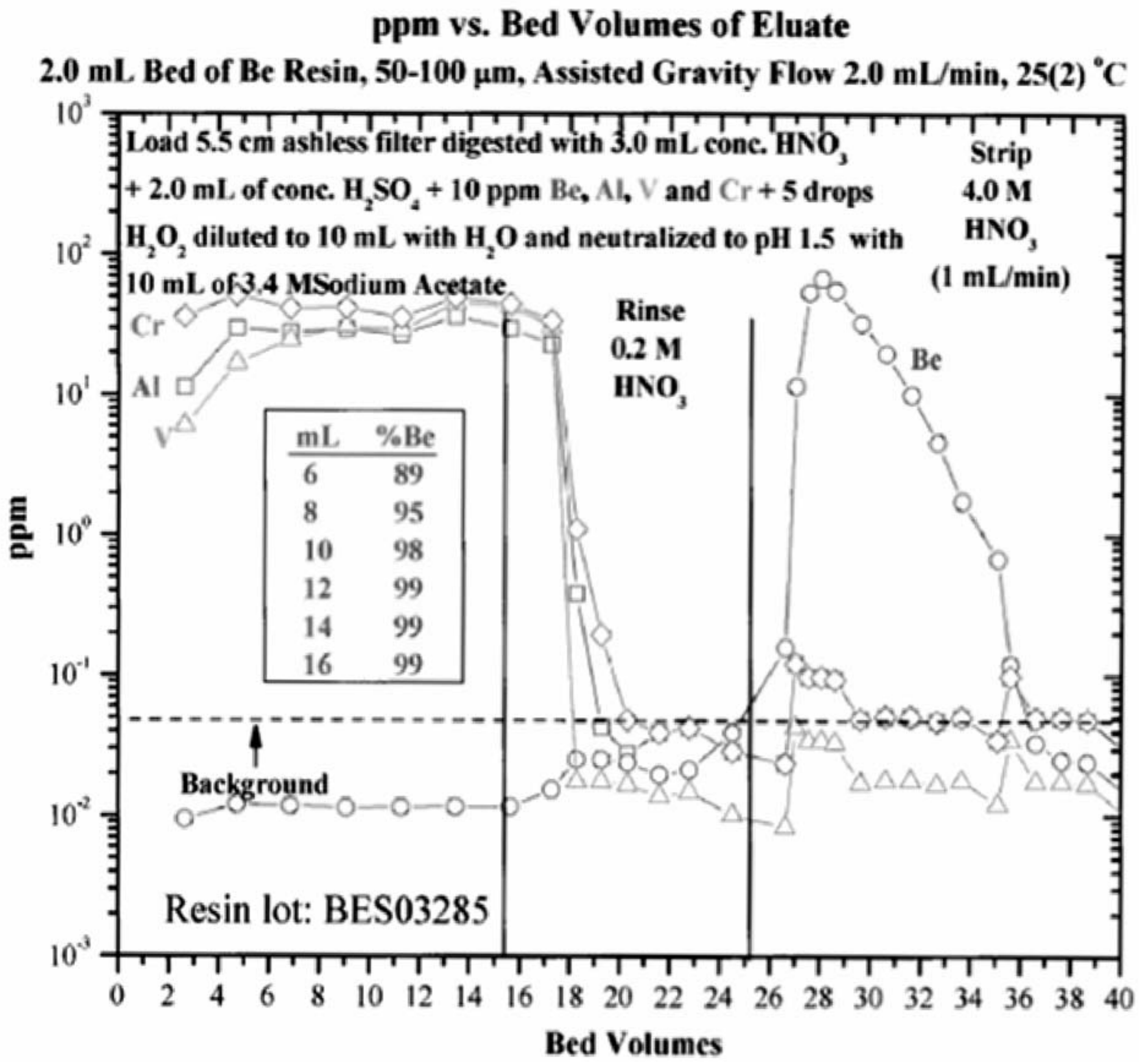

FIG. 1 PPM vs. Bed Volume of Eluate

9. Keywords

9.1 beryllium; extraction chromatography; sample preparation; separation

REFERENCES

(1) Horwitz, E.P., Delphin W.H., Bloomquist C.A.A. and Vandergrift G. F., "Radiochemical and Isotope Separations By High-Efficiency Liquid-Liquid Chromatography," *Journal of Chromatography*, Vol. 125 1976, pp. 203-218.

(2) Department of Energy, "Chronic Beryllium Disease Prevention Program," *Federal Register*, Vol. 64 (235), 1999, 68854-68914 managed per Title 10 Part 850 of the Code of Federal Regulations, Chronic Beryllium Disease Prevention Program.

(3) Horwitz, E. P. and McAlister, D. R., "Separation of Beryllium from Selected Elements Using the Dipex Extraction Chromatographic Resin," *Solvent Extraction and Ion Exchange*, Vol. 23(5), 2005, pp. 611-629.

(4) McAlister, D. R. and Horwitz, E. P., "A Method for the Separation of Beryllium from Spectral Interfering Elements in Inductively Coupled Plasma-Atomic Emission Spectroscopic Analysis," *Talanta*, Vol. 67(5), 2005. pp. 873-879.

(5) Horwitz, E. P et al. "Method for Chromatographic Separations of Cations from Aqueous Samples". US Patent #: 5,651,883, Jul 29, 1997.

(6) International Organization for Standardization (ISO), *Guide to the Expression of Uncertainty in Measurement*, ISO, Geneva, 1993.

(7) Ellison, S. L. R., and Barwick, V. J., "Estimating Measurement Uncertainty-Reconciliation Using Cause and Effect Approach," *Accreditation and Quality Assurance*, Vol 3, 1998, pp. 101-105.

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