

This article was downloaded by: [Goldcamp, Michael J.]

On: 5 November 2009

Access details: Access Details: [subscription number 916671224]

Publisher Taylor & Francis

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Occupational and Environmental Hygiene

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title-content=t713657996>

Extraction of Beryllium from Refractory Beryllium Oxide with Dilute Ammonium Bifluoride and Determination by Fluorescence: A Multiparameter Performance Evaluation

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First Published on: 01 December 2009

To cite this Article Goldcamp, Michael J., Goldcamp, Diane M., Ashley, Kevin, Fernback, Joseph E., Agrawal, Anoop, Millson, Mark, Marlow, David and Harrison, Kenneth(2009)'Extraction of Beryllium from Refractory Beryllium Oxide with Dilute Ammonium Bifluoride and Determination by Fluorescence: A Multiparameter Performance Evaluation',Journal of Occupational and Environmental Hygiene,6:12,735 — 744

To link to this Article: DOI: 10.1080/15459620903012044

URL: <http://dx.doi.org/10.1080/15459620903012044>

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Extraction of Beryllium from Refractory Beryllium Oxide with Dilute Ammonium Bifluoride and Determination by Fluorescence: A Multiparameter Performance Evaluation

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Beryllium exposure can cause a number of deleterious health effects, including beryllium sensitization and the potentially fatal chronic beryllium disease. Efficient methods for monitoring beryllium contamination in workplaces are valuable to help prevent dangerous exposures to this element. In this work, performance data on the extraction of beryllium from various size fractions of high-fired beryllium oxide (BeO) particles (from < 32 μm up to 212 μm) using dilute aqueous ammonium bifluoride (ABF) solution were obtained under various conditions. Beryllium concentrations were determined by fluorescence using a hydroxybenzoquinoline fluorophore. The effects of ABF concentration and volume, extraction temperature, sample tube types, and presence of filter or wipe media were examined. Three percent ABF extracts beryllium nearly twice as quickly as 1% ABF; extraction solution volume has minimal influence. Elevated temperatures increase the rate of extraction dramatically compared with room temperature extraction. Sample tubes with constricted tips yield poor extraction rates owing to the inability of the extraction medium to access the undissolved particles. The relative rates of extraction of Be from BeO of varying particle sizes were examined. Beryllium from BeO particles in fractions ranging from less than 32 μm up to 212 μm were subjected to various extraction schemes. The smallest BeO particles are extracted more quickly than the largest particles, although at 90°C even the largest BeO particles reach nearly quantitative extraction within 4 hr in 3% ABF. Extraction from mixed cellulosic-ester filters, cellulosic surface-sampling filters, wetted cellulosic dust wipes, and cotton gloves yielded 90% or greater recoveries. Scanning electron microscopy of BeO particles, including partially dissolved particles, shows that dissolution in dilute ABF occurs not just on the exterior surface but also via accessing particles' interiors due to porosity of the BeO material. Comparison of dissolution kinetics data shows that as particle diameter approximately doubles, extraction time is increased by a factor of about 1.5, which is consistent with the influence of porosity on dissolution.

Keywords beryllium oxide, dissolution, extraction, fluorescence analysis, surface samples

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Presented at the 3rd International Symposium on Beryllium Particulates and Their Detection, November 17–19, 2008, University of New Mexico, Albuquerque, New Mexico.

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INTRODUCTION

Beryllium (Be) has many applications as a constituent of materials in aerospace, nuclear energy, defense, electronics, circuitry, and machinery industries, owing to its light weight, high strength, and advantageous electrical insulating and alloying properties.^(1,2) However, exposures to beryllium-containing particulate materials can cause a number of serious deleterious health effects. In addition to being classified by the Environmental Protection Agency (EPA) as a carcinogen, skin contact may cause beryllium sensitization because the human immune system may respond to Be exposure.^(2–4) Of special concern is exposure by the inhalation of airborne beryllium-containing particles, which can cause the potentially

fatal respiratory condition known as chronic beryllium disease (CBD).^(5,6)

In view of these health effects, monitoring of beryllium exposures, particularly to airborne Be-containing particles, is important from an occupational health standpoint. In addition to traditional laboratory analytical techniques such as graphite furnace atomic absorption spectroscopy (GFAAS),⁽⁷⁾ inductively coupled plasma atomic emission spectrometry (ICP-AES),⁽⁸⁾ and inductively coupled plasma mass spectrometry (ICP-MS),⁽⁹⁾ a fluorescence method has recently been developed for trace Be detection.⁽¹⁰⁾

For highly sensitive detection of beryllium, this fluorescence method employs a solution of the high quantum yield fluorophore, hydroxybenzoquinoline sulfonate (HBQS).⁽¹⁰⁾ This method gives accurate and sensitive detection results after extraction of Be from Be metal, Be salts, and refractory BeO, as pure solids, spikes on filter media, and in soils.^(11–14) The fluorescence technique has the advantage of being field portable, which allows for efficient on-site evaluations of Be levels measured from a variety of sampling methods, while also offering detection limits comparable to ICP-MS methods.

Beryllium oxide sintered at very high temperatures (up to 2000°C) is a highly refractory material that (for analysis purposes) is typically digested using strong acid mixtures, notably those including sulfuric or hydrofluoric acid.⁽¹⁵⁾ Dilute ammonium bifluoride (ABF, 1–3% m/m) solutions effectively dissolve beryllium metal, beryllium sulfate, and “high-fired” beryllium oxide.^(11–16)

However, minimal performance data have been presented as to the effects of extraction and sample conditions on the recoveries of these Be extractions for particles with primary sizes (in terms of aerodynamic diameter) greater than $\sim 10\ \mu\text{m}$. The effect of BeO particle size on the effectiveness of extraction with dilute ABF has been questioned.⁽¹⁷⁾ Dissolution times for solute particles have been predicted by Mercer theory, where the percentage of the solute particles remaining undissolved is proportional to $[1-(t/d)]^3$, where t is time and d is the particle diameter.⁽¹⁸⁾ Thus, for increasing analyte particle size, this theory predicts that the extraction time will be proportional to the particle diameter.

Here, we have investigated the effects of BeO particle size on the rate of dissolution of BeO solids in dilute ABF solutions are presented. In addition to particle size, other extraction parameters were also examined, including BeO solid sample mass, extraction time and temperature, ABF extraction solution concentration and volume, and choice of sample tube. The extraction of BeO solids from a variety of sampling media (mixed cellulose ester filters, cellulosic filters, and cellulosic dust wipes) and cotton gloves, including those spiked with metalworking fluid as a possible interference, were examined. Nearly quantitative extraction of beryllium from BeO particles of a wide range of sizes ($<32\ \mu\text{m}$ up to $212\ \mu\text{m}$) was achieved in dilute ammonium bifluoride at mildly elevated temperatures (90°C). Also, the results demonstrated much faster dissolution rates than those predicted by Mercer theory.

METHODS

Beryllium-containing materials are classified by the EPA as carcinogens. Contact of Be-containing materials with the skin may cause sensitization to beryllium. Inhalation of Be-containing materials can ultimately result in chronic beryllium disease. Appropriate care should be taken when handling Be-containing materials, including but not limited to the use of personal safety equipment, such as gloves, respirators, and appropriate laboratory ventilation.

Reagents and Solutions

BeO-containing solids were obtained as Thermalox BeO ceramic, produced by Brush Ceramics (Tucson, Ariz.) by sintering UOX powder at 1550°C for 4 hr. A ceramic piece was pulverized by impact grinding. The particles produced were size separated into various size fractions ranging from less than $32\ \mu\text{m}$ up to $212\ \mu\text{m}$. Ammonium bifluoride (ABF) solutions (1% and 3% m/m) were prepared by dissolving the appropriate amount of solid ammonium bifluoride (Sigma Aldrich, Milwaukee, Wis.) in deionized water (18 M Ω -cm resistivity; Milli-Q Water System, Millipore, Billerica, Mass.).

Beryllium calibration standard solutions were prepared by diluting a stock 1000-ppm Be standard solution (Fisher Scientific, Hampton, N.H.) with 1% ABF. The fluorescence detection solution was provided by Berylliant, Inc. (Tucson, Ariz.), and contained 1.1 mM hydroxybenzoquinoline sulfonate (HBQS), 2.5 mM ethylenediaminetetraacetic acid (EDTA), and 100 mM L-lysine monohydrochloride, with the pH adjusted to 12.8 ± 0.1 . Metalworking fluid (WS 6900; Wallover Oil Company, Strongsville, Ohio), both unused and used, was obtained from a copper-beryllium alloy foundry in the Midwestern United States. The metalworking fluid contained mineral oil ($<50\%$), with smaller percentages of water, emulsifiers, alkanolamines, and biocides.

MATERIALS AND INSTRUMENTATION

Equipment included 15-mL and 50-mL polypropylene “Falcon” sample tubes from Becton Dickinson (Franklin Lakes, N.J.) and 15-mL polystyrene sample tubes, 10-mL disposable syringes with nylon syringe filters (25 mm dia., $0.45\ \mu\text{m}$ pore size), and 10-mm \times 10-mm plastic fluorescence cuvettes from Fisher Scientific. Plastic 1.5-mL microcentrifuge tubes with snap caps were from Eppendorf (Hamburg, Germany). Mixed cellulose ester (MCE) filters ($0.8\ \mu\text{m}$, 37 mm diameter) and Whatman 541 cellulosic filters (55 mm diameter) were from SKC, Inc. (Eighty Four, Pa.). Cellulosic dust wipes (moistened with aqueous benzalkonium chloride) were from Palintest USA (Erlanger, Ky.).

BeO solid samples were weighed on a Mettler Toledo (Columbus, Ohio) model AB265-S analytical balance ($\pm 0.00001\ \text{g}$ readability). Mechanical pipettors and disposable plastic tips for dispensing small volumes were from Gilson (Middleton, Wis.). The calibrations of the analytical balance and mechanical pipettors were checked twice daily. Samples

were heated in an Econotemp Laboratory Oven Model 55G from Fisher Scientific (Hampton, N.H.).

Fluorescence measurements were performed on a Modulus 9200-000 fluorometer from Turner Biosystems (Sunnyvale, Calif.). The fluorometer was equipped with an LED source for excitation at 365 nm and an optical kit from the manufacturer with a bandpass filter for photomultiplier detection at wavelengths of 475–485 nm. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) analysis was performed using a Spectro Flame-EOP instrument (Spectro, Kleve, Germany) at a detection wavelength of 313 nm.

BeO Sample Preparation and Analysis

For samples without filter/wipe media, BeO solids (ranging from approximately 1 to 2 mg or 4.5 to 5.5 mg) were weighed out directly into clean polypropylene Falcon tubes on an analytical balance. For samples with smaller filter media (MCE and Whatman 541 filters), the BeO solids were dispersed on the filter inside the sample extraction tube (where the BeO was originally weighed out) so no BeO would be lost in transfer. For Palintest cellulosic wipes and cotton gloves, the BeO was weighed out in the extraction tube, then poured onto an open wipe or glove in a wide area (as widely dispersed on the wipe as possible); the wipe or glove was then loosely folded and placed back into the original tube (where the BeO was weighed out initially) for extraction.

Extraction Procedure

To each solid sample, 5.0 mL of ABF extraction solution (either 1% or 3% m/m) were added, and the lid of the tube was closed tightly. Samples were heated in a preheated oven at the prescribed temperature for the prescribed amount of time. If analyzing a sample at various time intervals, the sample tube was briefly removed (1–2 min) from the oven; a small aliquot (40–50 μ L) of the solution was then removed and placed in a plastic microcentrifuge-style tube for temporary storage. The original BeO sample tubes were replaced in the oven for continued heating. All sample aliquots to be analyzed were allowed to cool to room temperature before analysis. Reagent blanks were similarly prepared by heating ABF solutions in sample tubes.

Samples on filter or wipe media were prepared by spiking the media with 1–2 mg of the BeO solid (weighed to the nearest 0.01 mg). The media were then placed into sample containers: 50-mL polypropylene Falcon tubes for MCE filters, Whatman 541 filters, and Palintest wipes; 120-mL polypropylene sample jars for cotton gloves. A volume of 3% ABF solution (MCE and Whatman 541 filters: 10 mL; Palintest wipes: 15 mL; cotton gloves: 50 mL) was then added to the sample containers, the lids were closed tightly, and the samples were shaken for about 2 min. For Palintest wipes and cotton gloves, the lids were reopened and the media were pressed into the solution with clean glass stirring rods to submerge the media and to release trapped air bubbles. For cotton gloves, repeated pressing with stirring rods was necessary to completely release trapped air.

The samples were then capped and heated in the oven at $90\pm1^\circ\text{C}$ for 5 hr.

Fluorescence Analysis

The fluorescence spectrometer was calibrated using a reagent blank (0.10 mL 1% ABF + 1.9 mL HBQS-containing fluorescence dye solution) and five Be standards.⁽¹³⁾ The first calibration standard was prepared by mixing 0.10 mL of a stock 10 ppb Be solution (in 1% ABF) with 1.9 mL of the dye solution directly in a plastic disposable fluorescence cuvette. The contents of the cuvette were shaken gently to facilitate mixing. The remaining four standards were prepared identically, using the following Be stock concentrations: 50 ppb, 100 ppb, 200 ppb, and 500 ppb, all in 1% ABF.

BeO sample extracts were used without filtration if all undissolved solids settled to the bottom of the sampling tube. Otherwise, samples with visible suspended particles were filtered using plastic, disposable 10-mL syringes equipped with nylon syringe filters. All sample extracts, filtered or unfiltered, were then diluted by mixing 10 μ L of the extract solution with 5.0 mL of 1% ABF solution in clean 15-mL polypropylene sample tubes.

For fluorescence analysis, 0.10 mL of diluted sample extract from each sample was mixed directly in a plastic, disposable fluorescence cuvette with 1.9 mL of the HBQS-containing fluorescence dye solution. The contents of the cuvette were shaken gently to facilitate mixing, and the samples were then analyzed using the fluorescence spectrometer.

ICP-AES Analysis

Inductively coupled plasma atomic emission spectroscopy (ICP-AES) analysis was performed on aliquots of samples (identical to those extracted for fluorescence analysis) in accordance with NIOSH Method 7300 (after extraction in 3% ABF at 90°C) at a detection wavelength of 313 nm.⁽¹⁹⁾

Scanning Electron Microscopy

BeO samples were mounted on conductive tape and then affixed to 15 mm diameter scanning electron microscopy (SEM) stubs (Ted Pella, Inc., Redding, Calif.). These mounts were then sputter coated with gold/palladium for 40 sec at 25 mA using a Denton model Desk 2 sputter coater (Denton Vacuum, Moorestown, N.J.). Analyses were performed using a Hitachi S-3000N (Tokyo, Japan) variable pressure scanning electron microscope. Both secondary and backscatter electron detectors were employed, with an accelerating voltage of 15 keV. Secondary electron images were obtained for each sample at $80\times$, $500\times$, $1000\times$ and $3000\times$ magnification.

RESULTS AND DISCUSSION

Effect of Concentration of Ammonium Bifluoride Extraction Solution

Dilute solutions of ammonium bifluoride (ABF) have been previously used to extract beryllium from BeO-containing materials. One percent ABF solutions have been effective for

TABLE I. Mesh Sizes and Their Corresponding BeO Solids Particle Size Fractions

BeO Particle Sizes	
Mesh	Particle Size (μm)
–500	< 32
–270 + 325	45 to 53
–140 + 170	90 to 106
–80 + 140	106 to 180
–70 + 80	180 to 212

quantitatively extracting small masses of pure solids and solids spiked on filter media.^(11,12) Also, 3% ABF solutions have been successfully used for quantitative BeO dissolution in soil samples.⁽¹³⁾

To examine the effect of the concentration of ammonium bifluoride on the rate of dissolution of BeO, samples (~1 mg) of BeO of various mesh sizes (Table I) were extracted in 50-mL polypropylene Falcon tubes at $90 \pm 1^\circ\text{C}$ using 5.0 mL of either 1% or 3% (m/v) ABF. Analysis of the extracts by fluorescence (Tables II and III) shows that, in general, 3% ABF solutions yield percent recoveries of 90% or greater approximately twice as quickly as do solutions of 1% ABF. For the smallest size fraction of BeO particles examined (< 32 μm), 89% of the material is extracted within 2 hr with 3% ABF. For the largest size particles examined (180–212 μm), quantitative recovery is reached in about 4 hr with 3% ABF. In contrast, to achieve 90% or greater recovery in 1% ABF, the smallest BeO particles require about 4 hr and the largest BeO particles require nearly 8 hr.

Effect of BeO Particle Size

BeO particle size significantly affected the rate of dissolution by ABF solutions, and previous work had used BeO solids of relatively small particle size.^(11,12) Few data previously existed comparing the dissolution of BeO particles of varying sizes using dilute ABF solutions. Results from this

TABLE II. Percent Recovery vs. Time for Various Particle Size Fractions of BeO after Dissolution in 5 mL 1% ABF Extraction Solution at 90°C

Time (hr)	Percent Recovery in 1% ABF BeO Particle Size (μm)			
	< 32	45 to 53	106 to 180	180 to 212
2	63 (2)	35 (3)	26 (1)	19 (1)
4	90 (6)	66 (8)	53 (1)	48 (1)
6		85 (1)	79 (8)	74 (5)
8		90 (5)	98 (2)	96 (3)

Note: N = 3 for all samples, relative standard deviation (RSD) in parentheses.

TABLE III. Percent Recovery vs. Time for Various Particle Size Fractions of BeO after Dissolution in 5 mL 3% ABF Extraction Solution at 90°C

Time (hr)	Percent Recovery in 3% ABF BeO Particle Size (μm)			
	< 32	45 to 53	106 to 180	180 to 212
2	89 (2)	64 (5)	55 (2)	41 (4)
4	95 (5)	106 (1)	102 (12)	97 (5)

Note: N = 3 for all samples, RSD in parentheses.

study comparing the percent recoveries from the extraction of BeO solids of varying mesh sizes are shown in Tables II and III. As would be predicted, the smallest size particles (< 32 μm) dissolved the most quickly, with rates decreasing as particle size increases. In 3% ABF, all of the BeO solids analyzed, including the largest (180–212 μm), were extracted with yields of 90% or greater within 4 hr under the conditions used.

Effect of Temperature

Extractions of BeO with fraction sizes of < 32 μm , 90 to 106 μm , and 180 to 212 μm were performed at temperatures of 90°C, 80°C, 60°C, and 25 (± 1)°C to investigate the effect of temperature on the rate of dissolution. Sample masses of approximately 1 mg were extracted using 5 mL 3% ABF in 50 mL polypropylene Falcon tubes. Results of these temperature-dependent studies are shown in Table IV.

Fluorescence analysis of the extracts at set time intervals shows that, as would be predicted, the BeO solids of each size fraction studied dissolved most quickly at the highest temperature (90°C) and most slowly at the lowest temperature (25°C). Samples of the 180 to 212 μm BeO size fraction (the largest sized particles) yielded quantitative recoveries after 4 hr at 90°C, but required 6 hr of heating at 80°C for near quantitative recovery ($\geq 90\%$) to occur. In samples extracted at room temperature (25°C), while BeO particles with sizes < 32 μm showed a considerably faster rate of extraction, none of the solids was dissolved above the level of 90% or greater within 24 hr, making room temperature extraction impractical for any of the size fractions of BeO studied.

It is noteworthy that for samples extracted at elevated temperatures in this work, a preheated gravity convection oven was used. The temperature of the samples during the initial period of extraction using this method was measured by placing thermocouples inside sealed 50-mL Falcon sample tubes containing 5 mL or 10 mL of water (to mimic sample extraction volumes). Comparison of oven temperature to sample temperature during the first 2 hr of heating, as shown in Figure 1, shows a significant delay in samples reaching their intended extraction temperatures: a time period of 45–60 min was required for samples to reach temperatures of 80°C in an oven that was preheated to 90°C. Thus, for samples extracted

TABLE IV. Percent Recovery vs. Time for Various Particle Size Fractions of BeO after Dissolution in 5 mL 3% ABF Extraction Solution at Four Different Temperatures

Time (hr)	Percent Recovery BeO Particle Size (μm)											
	< 32				90 to 106				180 to 212			
	25°C	60°C	80°C	90°C	25°C	60°C	80°C	90°C	25°C	60°C	80°C	90°C
2	19 (2)	52 (1)	81 (4)	89 (2)	3.9 (0.1)	23 (1)	55 (5)	55 (2)	2.6 (0.8)	16 (2)	28 (2)	41 (4)
4	26.5 (0.2)	75 (2)	93 (2)	95 (5)	6.8 (0.8)	47 (5)	91 (6)	102 (12)	5.8 (0.6)	31 (3)	61.3 (0.2)	97 (5)
6	34 (1)	83 (2)			9.8 (0.1)	65 (8)			7.9 (0.5)	46 (3)	91 (1)	
8	45 (3)	90 (2)			13.4 (0.2)	84 (3)			9.6 (0.8)	67 (3)		
10						95 (4)				84 (5)		
12	57 (1)				19.3 (0.2)				13 (1)	91 (5)		
24	72 (3)				29 (1)				22 (2)			

Note: N = 3 for all samples, RSD in parentheses.

using other heating methods such as forced air convection ovens, extraction times may be shortened.

Effects of Sample Mass, Extraction Solution Volume, and Sample Tube

Samples of the largest size fraction of BeO particles (180 to 212 μm) were extracted in 3% ABF at 90°C under multiple variations of the following conditions: Sample mass: ~1 mg vs. ~5 mg; Extraction solution volume: 5 mL vs. 10 mL; and Sample tube: 15-mL polypropylene Falcon tube vs. 50-mL polypropylene Falcon tube. The results are summarized in Tables V and VI. In general, ~1 mg samples were more

quickly extracted than ~5 mg samples, with ~5 mg samples at best reaching only 73% recovery after 5 hr in 3% ABF solution.

The volume of the extraction solution had no statistically significant effect on the rate of extraction (t-test at 95% confidence level). Examination of the rate of heating of deionized water inside sealed 50-mL polypropylene Falcon tubes (to mimic the same heating conditions as for the BeO samples) showed that 10-mL samples are about 2–5°C cooler than samples of 5-mL for about the first 80 min of heating. Thus samples extracted with larger volumes may require more time to reach BeO recovery levels of those extracted in smaller volumes.

The choice of sample tube had a significant effect on the rate of extraction. The 15-mL polypropylene Falcon tubes, which have a pointed bottom, showed slower rates of extraction as compared with the 50-mL polypropylene Falcon tubes, which have a significantly flatter bottom at the tip of the tube. In the

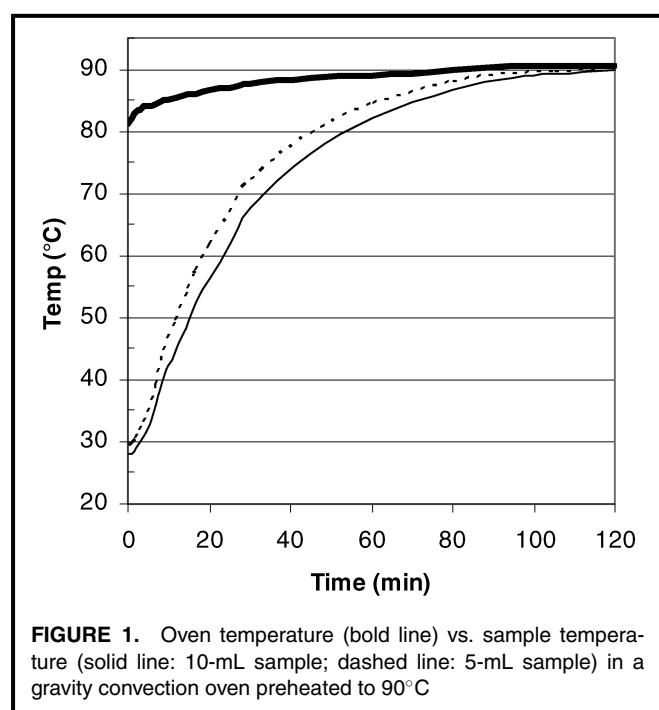


TABLE V. Percent Recovery vs. Time for BeO (particle sizes 180 to 212 μm) Extracted in 15-mL Polypropylene Falcon Tubes Under Varying Combinations of BeO Mass (~1 mg vs. ~5 mg) and ABF Extraction Solution Volume (5 mL vs. 10 mL)

Time (hr)	Extraction Solution: Mass of BeO:	Percent Recovery: 15-mL Tubes			
		5 mL 3% ABF		10 mL 3% ABF	
		~1mg	~5mg	~1mg	~5mg
2		36 (4)	11 (1)	29 (3)	12 (2)
4		67 (5)	25 (4)	71 (13)	25 (3)
5		71 (5)	29 (2)	69 (11)	29 (9)

Note: Samples were extracted in 3% ABF at 90°C; N = 3 for all samples, RSD in parentheses.

TABLE VI. Percent Recovery vs. Time for BeO (particle sizes 180 to 212 μm) Extracted in 50-mL Polypropylene Falcon Tubes Under Varying Combinations of BeO Mass (~ 1 mg vs. ~ 5 mg) and ABF Extraction Solution Volume (5 mL vs. 10 mL)

Time (hr)	Extraction Solution: Mass of BeO:	Percent Recovery: 50-mL Tubes			
		5 mL 3% ABF		10 mL 3% ABF	
		~ 1 mg	~ 5 mg	~ 1 mg	~ 5 mg
2		48 (3)	29 (2)	27 (3)	31 (5)
4		94 (9)	55 (6)	78 (3)	56 (11)
5		92 (6)	73 (5)	82 (5)	71 (12)

Note: Samples were extracted in 3% ABF at 90°C; N = 3 for all samples, RSD in parentheses.

15-mL tubes, the sample solid becomes compacted and does not interface well with the extraction solution, as opposed to in the more open 50-mL tubes, which provides for good exposure of the undissolved solid to the extraction solution. Additional evidence for this was noted when separately utilizing different 15-mL polystyrene tubes that had a rounded bottom, but were otherwise similar in shape and size to the 15-mL Falcon tubes with the pointed bottom. The extraction and analysis of samples of BeO particles of size fraction 180 to 212 μm using these round-bottom tubes yielded statistically identical results to those when using the 50-mL polypropylene Falcon tubes. This suggests that the pointed bottom of the 15-mL polypropylene Falcon tube was retarding the rate of BeO extraction.

Overall, the most effective set of parameter conditions of those tested for sample mass, extraction solution volume, and sample tube were: ~ 1 mg solid sample, 5 mL extraction solution, and 50-mL polypropylene Falcon tube (or another comparable tube that does not have a "pointed" tip).

Extraction of BeO on Filter and Wipe Media

Sampling in occupational settings can be achieved using a variety of methods, most of which utilize a filter or wipe medium to collect particulate matter for analysis.^(7,20–22) Examples of typical media include MCE filters for air samples and Whatman 541 cellulosic filters and dust wipes such as Palintest wipes for surface sampling. To test the performance of the extraction and fluorescence method under typical sampling conditions, samples of BeO solid (~ 1 – 2 mg of < 32 μm , 90 to 106 μm , or 180 to 212 μm size fractions) were spiked onto these media.

In addition, samples of BeO solid spiked onto cotton gloves were examined. These samples included those with spikes of metalworking fluid (both unused and used) added, as well as those without metalworking fluid added. All of these BeO samples on various media were then extracted in 3% ABF solution in an oven at 90°C for 5 hr. Sample tubes and solution volumes

were varied to contain the chosen medium and to completely submerge the medium in the extraction solution. Filters and wipes were placed into 50-mL polypropylene Falcon tubes and extracted with 10 mL or 15 mL of 3% ABF solution, respectively, to completely submerge the filter in the extraction solution; gloves were placed into 120-mL polypropylene sample jars with lids and extracted with 50 mL of 3% ABF solution to completely submerge the glove in the extraction solution.

The results for the extraction and analysis of BeO on various media are shown in Table VII. In nearly every case the extractions yielded nearly quantitative recoveries greater than or equal to 90%. Thus, the extraction of beryllium from BeO particles under these conditions (3% ABF solution, 90°C, 5 hr) is effective for a wide range of BeO particle sizes and on a variety of media.

Samples of BeO solid (size fraction 90 to 106 μm) on cotton gloves in the presence of metalworking fluid were also investigated. Two types of metalworking fluid spikes were utilized: 1 mL of unused metalworking fluid and 1 mL of used metalworking fluid (obtained from a Cu-Be foundry in the midwestern United States). Blanks of the extractions of the metalworking fluids on cotton gloves were also examined: the unused metalworking fluid contained no detectable Be, while the used fluid contained a trace of Be. The results for BeO on cotton gloves with spikes of the used metalworking fluid added are presented with the Be amounts from the blanks subtracted. The presence of metalworking fluid showed a slight decrease in recoveries (spiked with unused metalworking fluid: $92 \pm 3\%$, $n = 3$; spiked with used metalworking fluid: $91 \pm 4\%$, $n = 3$) vs. samples containing no metalworking fluid ($98 \pm 12\%$, $n = 3$), but the recoveries were all still greater than 90% and the decrease was not statistically significant.

To confirm these results, Be from BeO spikes on gloves (with metalworking fluid spikes) was determined by both

TABLE VII. Percent Recovery of BeO Solids of Varying Size Fractions on Several Filter/Wipe Media Types

BeO Particle Size (μm)	Percent Recovery on Sampling Media Filter / Wipe Medium			
	MCE	Whatman 541	Palintest	Cotton Glove
< 32	92 (6)	92 (5)	89 (6)	111 (16)
90 to 106	100 (7)	99 (2)	94 (5)	98 (12)
180 to 212	92 (1)	96 (3)	98 (5)	90 (6)

Notes: All samples were extracted in 3% ABF solution at 90°C for 5 hr. Samples with MCE and Whatman 541 filters were extracted in 10 mL ABF solution in 50-mL polypropylene Falcon tubes; samples with Palintest dust wipes were extracted in 15 mL ABF solution in 50-mL polypropylene Falcon tubes; samples with cotton gloves were extracted with 50 mL ABF solution in 120-mL polypropylene sample cups with lids. N = 3 for all samples, RSD in parentheses.

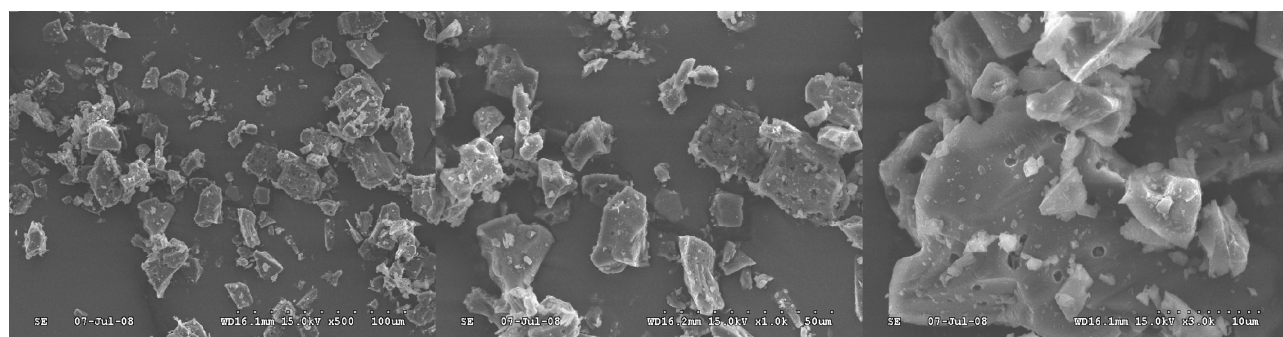


FIGURE 2. SEM images of Thermalox BeO ceramic of particle size fraction $<32\ \mu\text{m}$ at 500 \times (left), 1000 \times (center), and 3000 \times (right) magnifications

the fluorescence method and ICP-AES for comparison. After fluorescence analysis, Be was determined on different aliquots of the same samples by ICP-AES in accordance with NIOSH Method 7300 (after extraction in 3% ABF at 90°C). Results

from the fluorescence method vs. the ICP-AES analysis show Be recoveries greater than 90% for all samples analyzed by both methods. The average relative deviation between determinations (fluorescence vs. ICP-AES) of identical samples

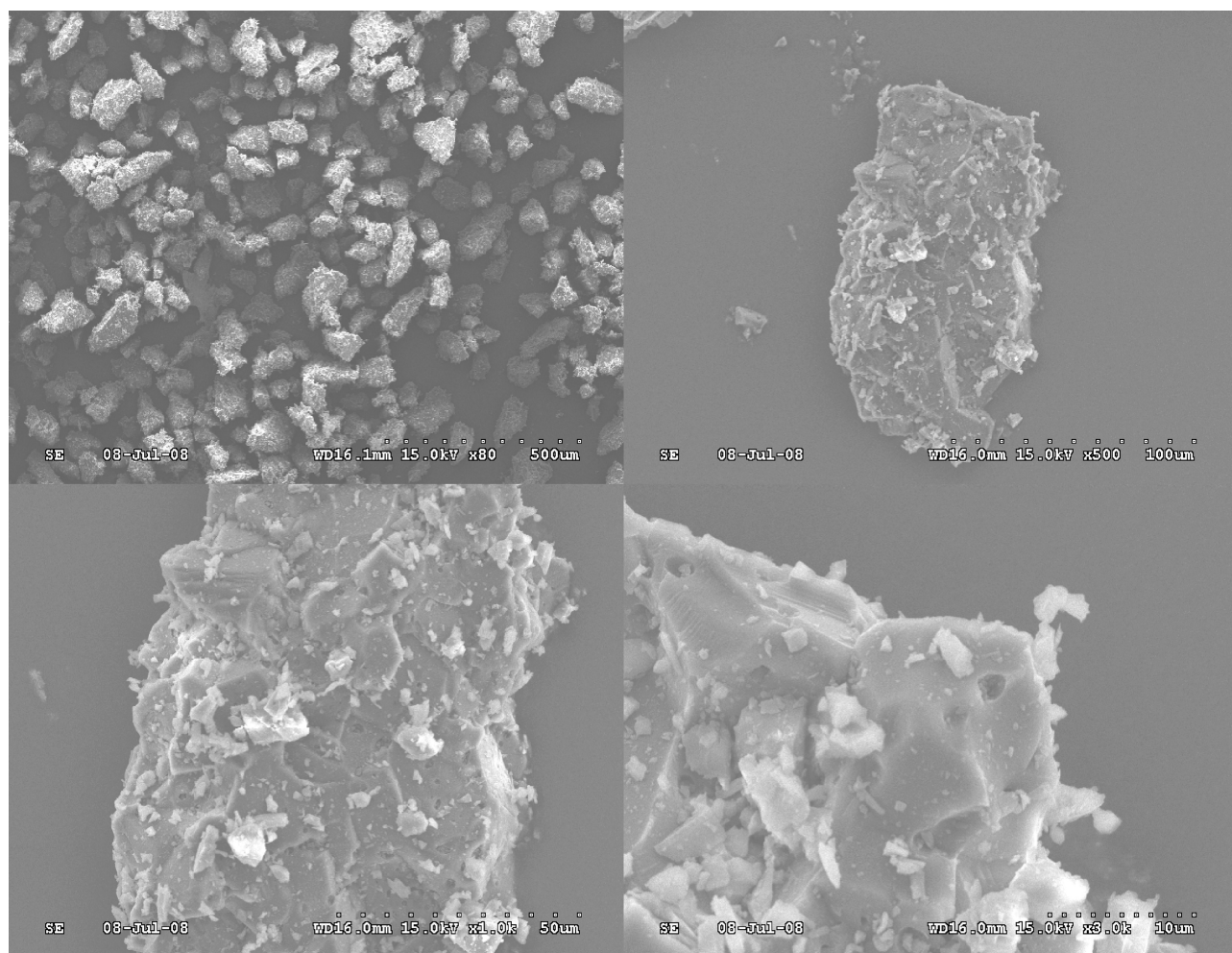


FIGURE 3. SEM images of Thermalox BeO ceramic of particle size fraction 90 to 106 μm at 80 \times (top left), 500 \times (top right), 1000 \times (bottom left), and 3000 \times (bottom right) magnifications

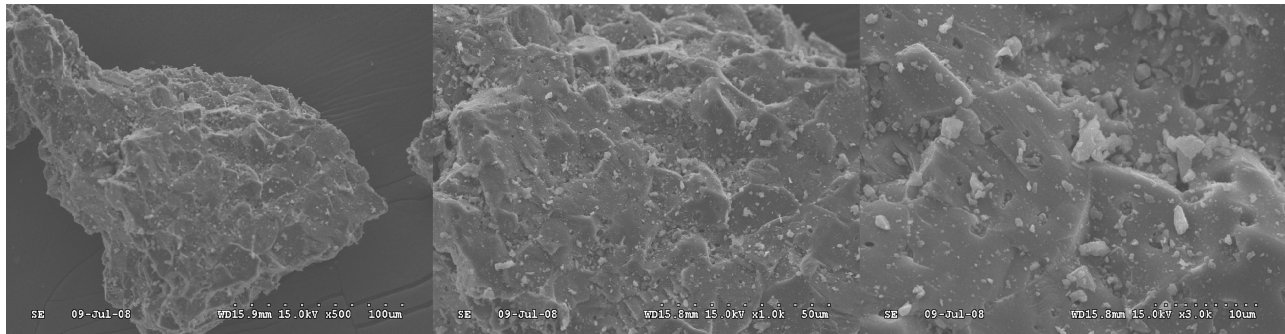


FIGURE 4. SEM images of Thermalox BeO ceramic of particle size fraction 180 to 212 μm at 500 \times (left), 1000 \times (center), and 3000 \times (right) magnifications

was 1.8%, with the lowest deviation being 0% and the highest 7.6%.

Scanning Electron Microscopy

Figures 2, 3, and 4 show scanning electron micrographs (SEMs) of the “as-received” particles at various magnifications. Figure 2 shows the smallest sized particles studied (<32 μm size fraction), Figure 3 shows particles of an intermediate size fraction (90–106 μm size fraction), and Figure 4 shows the largest sized particles studied (180–212 μm size fraction). Because these particles are produced by an impact process, they have irregular shapes with sharp edges.

Furthermore, at larger magnifications (i.e., 3000 \times magnification), a fine powder with sharp edges is observed to adhere onto the particle surfaces. This powder does not appear to be nonsintered UOX material, which typically is comprised of cube-shaped particles (0.1 to 0.2 mm in size) strung together as a loose network to form larger particles.^(12,18) In addition, some of the porosity left behind by the sintering process is also

evident. The theoretical density of BeO is 3.01 g/cm³; however, the typical density of Thermalox 995 (which is the material examined in this study) is 2.88 g/cm³, where the difference is ascribed to porous vs. nonporous particles. Porosity in BeO ceramics can be reduced but not eliminated (e.g., BW 3250 from Brush Ceramics can reach a maximum density of 2.95 g/cm³).

Partially dissolved particles that are shown in Figure 5 were examined by SEM after a measured Be recovery of about 15% using 1% ABF at 90°C (as determined by fluorescence analysis). For the particles shown in Figure 6, the recovery was near 20% after extraction using 3% ABF at 90°C. The SEMs presented in both of these figures (particularly at 3000 \times magnification) show that the dissolution process is influenced by the porosity that remains after the sintering process. The implication is that the dissolution solution accesses the interior of the particles via the pores and the exposed grain boundaries of the particles to cause their disintegration into smaller particles (Figures 5 and 6).

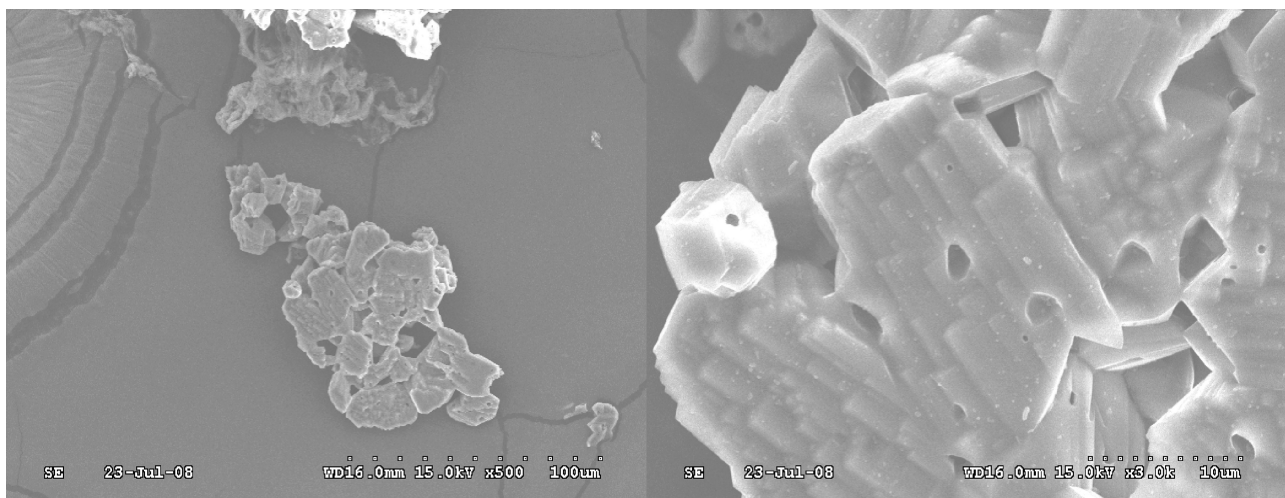


FIGURE 5. SEM images of Thermalox BeO ceramic (particle size fraction 45 to 53 μm) after partial dissolution in 1% ammonium bifluoride solution at 500 \times (left) and 3000 \times (right) magnifications

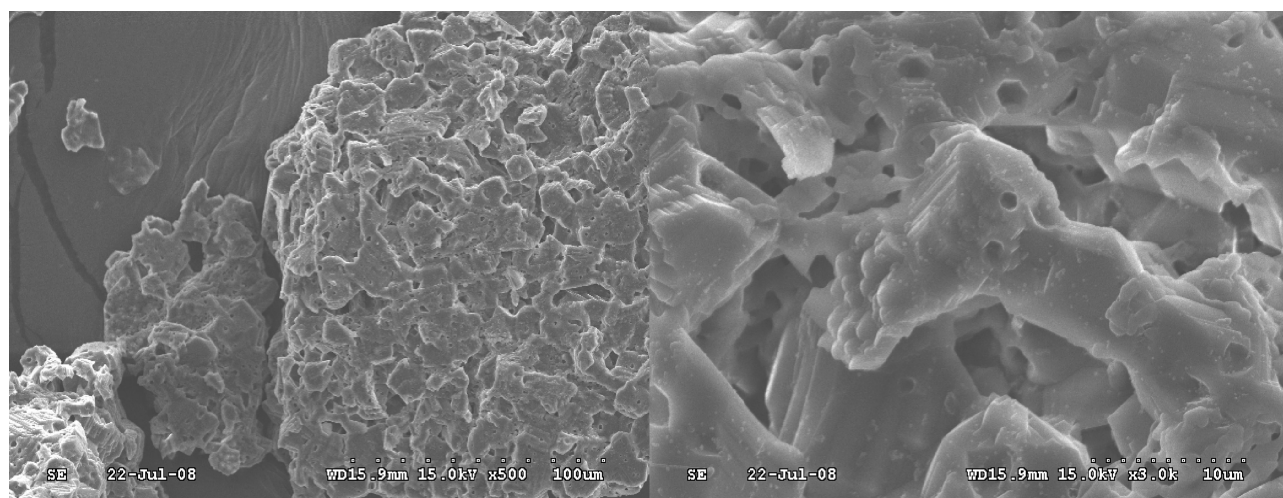


FIGURE 6. SEM images of Thermalox BeO ceramic (particle size fraction 180 to 212 μm) after partial dissolution in 3% ammonium bifluoride solution at 500 \times (left) and 3000 \times (right) magnifications

Data presented in Table II (for 1% ABF) and Table III (for 3% ABF) also show that the dissolution time is quite rapid for large particles and that it does not have a directly proportional dependence on particle diameter as suggested by Mercer's theory and adapted by Stefaniak et al.⁽¹⁸⁾ In our work, a particle that is nearly twice as large in aerodynamic diameter (180–212 μm size fraction vs. 90–106 μm size fraction) requires only about 1.5 \times as much time to dissolve. Using data for the these two particle size fractions (at temperatures of 25°C and 60°C) and assuming a pseudo first-order model for the dissolution kinetics, the ratio of rate constants for dissolution for these size fractions increased by factors of 1.4 and 1.6, respectively.

In Mercer's theory, which assumes that the particles (modeled as solid spheres) dissolve uniformly from the outside only, the rate should decrease by a factor of 2 when doubling the particle diameter, which is not the case here. This would also suggest that the larger particles of this type of ceramic, if ingested, may disintegrate more rapidly in the human body than as suggested by the above model. The higher surface roughness in Figure 6 as compared with that in Figure 5 also shows the enhanced aggressiveness of the 3% ABF solution as compared with extraction in 1% ABF solution.

CONCLUSIONS

A number of parameters have been examined in the extraction of beryllium from high-fired BeO particles using dilute ammonium bifluoride (ABF) solutions. Three percent ABF solution demonstrates significant increases in the rates of dissolution of BeO over 1% ABF, with medium to large size particles dissolving nearly twice as quickly in the 3% ABF solution. The rate of dissolution is also significantly affected by the choice of sample tube used in the extraction, as samples in 15-mL tubes with pointed bottoms exhibited slower rates of dissolution, probably due to hindered interaction of the solid with the extraction solution. Elevated temperatures

increased the rate of extraction, with temperatures of 90°C giving sufficiently fast dissolution of all BeO solids tested. Thus the use of 3% ABF with heating has been shown to be of practical use for analytical applications in the field.

Several different particle sizes of BeO solids were examined, representative of those that would be expected to be collected by typical sampling methods used in occupational settings. Using the optimal conditions found in this work (3% ABF, 90°C), even the largest particles dissolved to give quantitative yields (> 90%) within 4 hr. Scanning electron microscopy images of partially dissolved BeO particles suggest that the porosity of the BeO particles has a significant influence on their dissolution in dilute ammonium bifluoride solution. Extraction of BeO on a variety of filter and wipe media showed nearly quantitative yields under the similar extraction conditions (3% ABF, 90°C, 5 hr) for all sizes of BeO particles examined.

ACKNOWLEDGMENTS

This work was partially supported by the U.S. Department of Energy (DOE contract DE-FG02-06ER84587). We thank Robert Streicher for critical review and helpful discussions.

REFERENCES

1. U.S. Agency for Toxic Substances and Disease Registry (ATSDR): *Toxicological Profile for Beryllium*. Atlanta: ATSDR, 2002.
2. Kolanz, M.E.: Introduction to beryllium—Uses, regulatory history, and disease. *Appl. Occup. Environ. Hyg.* 16:559–567 (2001).
3. Tinkle, S.S., J.M. Antonini, B.A. Rich, et al.: Skin as a route of exposure and sensitization in chronic beryllium disease. *Environ. Health Persp.* 111:1202–1208 (2003).
4. Day, G.A., A. Dufresne, A.B. Stefaniak, et al.: Exposure pathway assessment at a copper-beryllium alloy facility. *Ann. Occup. Hyg.* 51:67–80 (2007).

5. **Kreiss, K., M.M. Mroz, B. Zhen, J.W. Martyny, and L.S. Newman:** Epidemiology of beryllium sensitization and disease in nuclear workers. *Am. Rev. Resp. Dis.* 148:985–991 (1993).
6. **Schuler, C.R., M.S. Kent, D.C. Deubner, et al.:** Process-related risk of beryllium sensitization and disease in a copper-beryllium alloy facility. *Am. J. Ind. Med.* 47:195–205 (2005).
7. **National Institute for Occupational Safety and Health (NIOSH):** Method 7102, beryllium and compounds, as Be. In *NIOSH Manual of Analytical Methods (NMAM)*. Cincinnati, Ohio: NIOSH, 2003.
8. **ASTM International:** *Standard Test Method for the Determination of Metals and Metalloids by Inductively Coupled Plasma Atomic Emission Spectrometry* (ASTM D7035). [Standard] West Conshohocken, Pa.: ASTM International, 2004.
9. **U.S. Environmental Protection Agency (USEPA):** SW-846 Method No. 6020. In *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods*. Washington, D.C.: USEPA, 1996.
10. **Matsumiya, H., H. Hoshino, and T. Yotsuyanagi:** A novel fluorescence reagent, 10-hydroxybenzo[h]quinoline-7-sulfonate, for selective determination of beryllium(II) ion at pg cm^{-3} levels. *Analyst* 126:2082–2086 (2001).
11. **Agrawal, A., J. Cronin, J. Tonazzi, et al.:** Validation of a standardized portable fluorescence method for determining trace beryllium in workplace air and wipe samples. *J. Environ. Monit.* 8:619–624 (2006).
12. **Ashley, K., A. Agrawal, J. Cronin, et al.:** Ultra-trace determination of beryllium in occupational hygiene samples by ammonium bifluoride extraction and fluorescence detection using hydroxybenzoquinoline sulfonate. *Anal. Chim. Acta* 584:281–286 (2007).
13. **ASTM International:** *Standard Test Method for Determination of Beryllium in the Workplace Using Field-Based Extraction and Fluorescence Detection* (ASTM D7202). [Standard] West Conshohocken, Pa.: ASTM International, 2005.
14. **Agrawal, A., J.P. Cronin, A. Agrawal, et al.:** Extraction and optical fluorescence method for the measurement of trace beryllium in soils. *Environ. Sci. Technol.* 42:2066–2071 (2008).
15. **Brisson, M. J., A.A. Ekechukwu, K. Ashley, and S.D. Jahn:** Opportunities for standardization of beryllium sampling and analysis. *J. ASTM Int.* Vol. 3, Issue 1, 2006.
16. **Brisson, M.J., K. Ashley, A.B. Stefaniak, A.A. Ekechukwu, and K.L. Creek:** Trace-level beryllium analysis in the laboratory and in the field – State of the art, challenges and opportunities. *J. Environ. Monit.* 8:605–611 (2006).
17. **Stefaniak, A.B., G.C. Turk, R.M. Dickerson, and M.D. Hoover:** Size-selective poorly soluble particulate reference materials for evaluation of quantitative analytical methods. *Anal. Bioanal. Chem.* 391:2071–2077 (2008).
18. **Stefaniak, A.B., C.A. Brink, R.M. Dickerson, et al.:** A theoretical framework for evaluating analytical digestion methods for poorly soluble particulate beryllium. *Anal. Bioanal. Chem.* 387:2411–2417 (2007).
19. **National Institute for Occupational Safety and Health (NIOSH):** Method 7300, elements by ICP. In *NIOSH Manual of Analytical Methods (NMAM)*. Cincinnati, Ohio: NIOSH, 1994.
20. **Creek, K.L., G. Whitney, and K. Ashley:** Vacuum sampling techniques for industrial hygienists, with emphasis on beryllium dust sampling. *J. Environ. Monit.* 8:612–618 (2006).
21. **ASTM International:** *Standard Practice for Collection of Surface Dust by Micro-Vacuum Sampling for Subsequent Metals Determination* (ASTM D7144). [Standard] West Conshohocken, Pa.: ASTM International, 2005.
22. **Dufay, S.K., and M. Archuleta:** Comparison of collection efficiencies of sampling methods for removable beryllium surface contamination. *J. Environ. Monit.* 8:630–633 (2006).