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Extraction and Optical Fluorescence Method for the Measurement of Trace Beryllium in Soils

ANOOP AGRAWAL,* JOHN P. CRONIN, AKSHAY AGRAWAL, JUAN C. L. TONAZZI, AND LORI ADAMS
Beryllíant, Inc., 4541 East Fort Lowell Road, Tucson, Arizona 85712

KEVIN ASHLEY
National Institute for Occupational Safety and Health, Centers for Disease Control and Prevention, U.S. Department of Health and Human Services, Cincinnati, Ohio 45226

MICHAEL J. BRISSON
Washington Savannah River Company, Savannah River Site, Aiken, South Carolina 29808

BRANDY DURAN, GARY WHITNEY, ANTHONY K. BURRELL, AND T. MARK MCCLESKEY
Los Alamos National Laboratory, Los Alamos, New Mexico 87545

JAMES ROBBINS
National Energy Technology Laboratory, Albany, Oregon 97321

KENNETH T. WHITE
Consultive Services, Virginia Beach, Virginia 23462

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Beryllium metal and beryllium oxide are important industrial materials used in a variety of applications in the electronics, nuclear energy, and aerospace industries. These materials are highly toxic, they must be disposed of with care, and exposed workers need to be protected. Recently, a new analytical method was developed that uses dilute ammonium bifluoride for extraction of beryllium and a high quantum yield optical fluorescence reagent to determine trace amounts of beryllium in airborne and surface samples. The sample preparation and analysis procedure was published by both ASTM International and the National Institute for Occupational Safety and Health (NIOSH). The main advantages of this method are its sensitivity, simplicity, use of lower toxicity materials, and low capital costs. Use of the technique for analyzing soils has been initiated to help meet a need at several of the U.S. Department of Energy legacy sites. So far this work has mainly concentrated on developing a dissolution protocol for effectively extracting beryllium from a variety of soils and sediments so that these can be analyzed by optical fluorescence. Certified reference materials (CRM) of crushed rock and soils were analyzed for beryllium content using fluorescence, and results agree quantitatively with reference values.

Introduction

Occupational exposure to beryllium can lead to a deleterious and potentially fatal lung disease (*1*). Also, skin contact with beryllium has been associated with sensitization (*2, 3*). Consequently, limits for beryllium in the air and on surfaces have been established to reduce exposure risks to workers (*4*). Apart from airborne and surface dusts, the importance of analyzing soils for beryllium has arisen at several U.S Department of Energy (DOE) sites and other locations where the soil may have been contaminated with beryllium and/or beryllium compounds (*5*). Several DOE sites have buildings which may have been used for legacy beryllium work in the past and have been vacant for decades. Many of these legacy site buildings have thick layers of dust with unknown beryllium contamination built up over the years. It is desired that the analytical protocol used will distinguish between the natural beryllium background and the anthropogenic levels of beryllium in the wipe or bulk samples. This requires the establishment of background levels of beryllium in soils and dust around the buildings to assess whether there is an elevated level of beryllium collected from the building interior surfaces and to determine whether the beryllium detected is anthropogenic or not. It is desired that simple techniques be made available so that these measurements can be performed in the field as the samples are being taken and processed, enabling quick decision-making for hazard assessment purposes. Candidate techniques for beryllium field monitoring have included fluorescence (*6–8*), electroanalysis (*9*), laser-induced breakdown spectroscopy (*10*), and chemical spot tests (*11*).

Recently, a fluorometric method for beryllium analysis was developed by researchers at Los Alamos National Laboratory (LANL) (*12, 13*) and has been licensed commercially (*14*). The use of a novel fluorophore for Be^{2+} ion (*15*), hydroxybenzoquinoline sulfonate, resulted in the LANL method having significantly better limits of detection (LODs) for beryllium compared to other fluorometric reagents (*16*). Further, this fluorophore is specific to beryllium. The previous methods (*7, 17, 18*) relied on fluorescence reagents that demonstrate insufficient sensitivity for trace measurements of beryllium or interference from other elements. The newly developed fluorescence technique, for air filter wipe samples, was published as a standard test method by ASTM International (*19*) and by the National Institute for Occupational Safety and Health (NIOSH) (*20*). The method was shown to be effective for the determination of trace amounts (0.02−4 μg/sample) of beryllium metal, as well as refractory beryllium oxide (*13*), and steps have been taken for automating the process to analyze a large number of samples (*21*).

The fluorescence method has advantages of low capital cost, fast turnaround, high throughput, and use of weakly acidic ammonium bifluoride as a dissolution medium instead of concentrated acids. The objective of this work was to extend this technique to analysis for total beryllium in soils by investigating the utility of ammonium bifluoride as a soil, sand, dust, and sediment dissolution medium and establish whether beryllium content can be determined precisely using the fluorescence technique after ammonium bifluoride extraction.

As a first step, it was necessary to investigate the dissolution process required for analysis of beryllium in soils. Soils can contain beryllium from natural and/or anthropogenic sources. It is primarily the latter that is of concern in DOE legacy sites and in other cleanup work involving contaminated soils. The lowest action level for a sample taken

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* Corresponding author phone: +1(520)321-7680; e-mail aagrawal@qwest.net.

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TABLE 1. Reference Materials Used

reference material	particle size	beryllium content (mg/kg)		iron (%)	silicon (%)
			uncertainty		
NIST SRM 2702, marine sediment	passed through 70 μm screen	3[a]	not known	7.91[b]	not known
NIST SRM 2710, Montana soil	passed through 74 μm screen	2.5[c]	±0.07	3.38[b]	28.97[b]
NIST SRM 1944, NY/NJ Waterway sediment	passed through 250 to 61 μm screens	1.6[d]	±0.3	3.53[b]	31[d]
NIST SRM 1633a, coal fly ash	less than 88 μm	12.1[a]	not known	0.0[b]	22.8[b]
GSJ JA-2, andesite	median 6.06 μm	2.05[d]	±0.44	4.34[d]	26.4[d]
GSJ JR-3, rhyolite	median 4.57 μm	7.6[d]	±0.831	3.3[d]	34[d]
GSJ JB-2, basalt volcanic rock	median 5.41 μm	0.27[e]	±0.043	9.97[d]	53.2[d]
CCRMP SY2 syenite	passed through 74 μm screen	22[e]	not known	4.42[d]	28.1[d]
CCRMP till-1 soil	passed through 74 μm screen	2.4[a]	not known	4.81[e]	28.5[e]

[a] Information value. [b] Certified Concentration. [c] Ref *24*. [d] Reference concentration. [e] Provisional value.

from an interior surface of a building used for beryllium work at any DOE site is 0.2 μg of beryllium/(100 cm^2 of surface area) (*4*). It is generally accepted that exposure to beryllium metal, alloys, and BeO causes beryllium sensitization and/or chronic beryllium disease (CBD), whereas exposure to naturally occurring forms, such as beryl and bertrandite, has not yet been associated with adverse health effects (*22, 23*). This also pertains to DOE legacy sites which may have been used for beryllium work. If the surface of concern is laden with thick dust, bulk samples are collected suspecting that a large fraction may have come from the surrounding geological environment. Depending on the surrounding geology, soils and rocks may have natural levels of beryllium in the range of 0.2−20 mg of beryllium/kg, with more typical numbers being from about 2 to 4 mg of beryllium/(kg of soil) (*24*). The naturally occurring beryllium content in collected samples can be greater than that added by human activity, and the total measurement may exceed the DOE action levels. It becomes important to be able to analyze these bulk samples in such a way that none of the natural beryllium is detected or to analyze samples so that all of the beryllium is and consistent with the natural levels in soil. For consistency it is necessary to use the same method to analyze bulk samples of the soil from the surrounding area to thereby establish the baseline beryllium level for each location.

Aqueous ammonium bifluoride (ABF) solutions are highly effective in the dissolution of refractory beryllium oxide (*25*) and are also known to react with silica (a significant component in all soils) according to the following reaction:

$$SiO_2 + 4NH_4HF_2 \rightarrow (NH_4)_2SiF_6 + 2NH_4F + 2H_2O$$

The above reaction rate depends on the concentration of ABF and the temperature (*26*). The kinetics of dissolution of silicates is low at 20 °C and not energetic enough for dissolution of refractory beryllium oxide. If a dissolution protocol is used that involves heating to ~80 °C, the natural beryllium from the soil silicate would be more likely to dissolve and thus be present in any subsequent analysis. To develop a simple dissolution protocol, it is desirable to employ a procedure that includes the extraction and analysis of all beryllium present, whether naturally occurring or anthropogenic.

According to the stoichiometry shown above, each mole of silica will consume 4 mol of ammonium bifluoride, which translates to about 3.8 g of ammonium bifluoride for each gram of pure silica. Since the kinetics of the process is dependent on the ABF concentration, as ABF is consumed in a typical dissolution scenario, the rate of silica dissolution will decrease (*26*). The reaction kinetics is particle size dependent, and in order to obtain high recoveries, there will be a limit on the soil particle size that can be effectively dissolved by any prescribed process.

The objective of this study was to develop a dissolution protocol so that soil samples could be effectively analyzed by optical fluorescence. Such an evaluation would also have to investigate the appropriate weight ratio of the sample to ABF of a given concentration and volume to ensure that beryllium recoveries remain high, in consideration that some ABF would be consumed by the background silica present in the soil. Soils contain a variety of metal compounds, some of which are present in high concentrations (such as iron, aluminum, and magnesium) and others to a lesser extent (such as manganese and titanium); the procedure must demonstrate their non-interference. The fluorophore used in this study is highly specific to beryllium, though the presence of excessive iron and/or titanium can cause the measurement solutions to be temporarily yellow in color (*27*). On standing in a high-pH environment, metals, such as iron and titanium, precipitate as hydroxides; subsequently, the solution can be filtered and the fluorescence measured. The protocol to analyze soils must also include a waiting period in which metal hydroxides are allowed to flocculate and can be removed via centrifugation or filtration prior to fluorescence measurement.

Experimental Section

Beryllium recovery tests were conducted using a number of soil, rock, dust, and sediment reference materials. Standard reference materials (SRMs) obtained from the National Institute of Standards and Technology (NIST, Gaithersburg, MD) were as follows: coal fly ash, SRM 1633a; Montana soil, SRM 2710; marine sediment, SRM 2702; and, NewYork/New Jersey Waterway sediment, SRM 1944. Certified reference materials (CRMs) obtained from the Geological Survey of Japan (GSJ, Tsukuba, Japan) were as follows: andesite, JA-2; rhyolite, JR-3; and basalt volcanic rock, JB-2. CRMs obtained from the Canadian Certified Reference Materials Project (CCRMP, Ottawa, ONT, Canada) were as follows: soil, till-1; and, syenite, SY2. The particle sizes and beryllium, iron, and silica content of these materials are shown in Table 1. Humic acid was purchased from Sigma-Aldrich Co. (Milwaukee, WI).

Beryllium certified standard solutions in dilute ammonium bifluoride with beryllium concentrations of 0, 10, 40, 200, and 800 μg/L were obtained from Spex Certiprep (Metuchen, NJ). Ammonium bifluoride extraction solution (aqueous) and fluorescence detection solution (aqueous) were provided by Berylliant, Inc. (Tucson, AZ). The detection solution was comprised of hydroxybenzoquinoline sulfonate (HBQS, 1.1 mM), ethylenediamine tetraacetic acid (EDTA, 1 mM), and L-lysine monohydrochloride (100 mM). The pH of the detection solution was adjusted to 12.85 ± 0.01 with 2.5 M NaOH using a low sodium error electrode.

Beryllium analysis was conducted using a Turner Quantech (Barnstead model FM109515) fluorometer fitted with bandpass filters to attenuate the excitation and detection beams, with source radiation of 360–390 nm and a detection spectral window of 460 nm with a bandpass of ±20 nm. Source radiation was provided by a quartz halogen lamp and fluorescence signal was detected using a photomultiplier tube.

Beryllium standards and samples were measured in 10 mm path length low-fluorescence acrylic cuvettes (4.5 mL). The fluorometer was calibrated using cuvettes with 1.9 mL of the detection solution mixed with 0.1 mL each of the various standard solutions. For measurement of soils, the samples were allowed to cool to room temperature after the dissolution step and filtered through a 0.45 μm syringe filter. Then 0.1 mL aliquots of the extract solutions were added to 1.9 mL of the detection solutions in cuvettes. The amount of beryllium was calculated using a fluorescence calibration curve, an example of which can be seen in the Supporting Information. If the laboratory temperature drifted by more than 2 °C from the initial calibration temperature, the fluorometer was recalibrated.

Analysis of beryllium via inductively coupled plasma—mass spectrometry (ICP-MS) was conducted on an Elan 9000 Instrument (Perkin-Elmer, Waltham MA) by a scanning method.

Absorption spectra were performed using a Shimadzu UV–vis−near-IR spectrophotometer UV-3100 (Pleasanton, CA).

Results and Discussion

Initial work was carried out using NIST SRM 2710 (Montana soil) to establish appropriate dissolution conditions. This soil SRM was chosen as representative in consideration not only of its inorganic content but also in view of its organic makeup. The potential for soil organic matter to interfere with the fluorescence signal of the beryllium−HBQS complex required investigation. SRM 2710 does not have a beryllium reference value provided by NIST; thus, the reference value is cited from a different source (*24*). Subsequent tests were performed using SRM 2710 to establish if dilute ammonium bifluoride was effective for beryllium dissolution and to investigate whether the fluorescence method would be subject to possible interferences found therein. These experiments were conducted in 15 mL centrifuge tubes at room temperature (23 °C) using a rotator as a mechanical agitator or using a hot block at 80 °C, both for 30 min. At the end of the dissolution step and filtering, the samples were evaluated immediately after mixing with the dye solution, and after leaving the mixed sample overnight and collecting measurements again after filtration. Overnight treatment was found to be effective in removing the yellowness due to iron or titanium content.

Several of the Environmental Protection Agency (EPA) methods for preparation and analysis of soils and sludges (such as method 3051) (*28*) require a 0.5 g sample size which is large enough to sufficiently account for the heterogeneities present in these samples. Thus, a 0.5g sample size was chosen for the fluorescence method. On the basis of a 0.5 g sample and the chemistry discussed in the Introduction, it was decided to use 50 mL of 5% ABF solution to ensure that there was sufficient ABF to quantitatively solubilize beryllium in the presence of significant amounts of silica. The dissolution temperature was chosen as 80 °C on the basis of complete recovery of refractory beryllium oxide in previous studies (*13, 27*), and during optimization of the method, heating was more effective in extracting beryllium than mechanical agitation at room temperature.

TABLE 2. Effect of Extracted Solution Standing Time on [Be]

sample	[Be] (mg/kg) initial	2 h	4 h	6 h	24 h	reference [Be]
SRM 2702 (high Fe)	1.06	3.31	3.33	3.36	3.25	3[a]
SRM 1944 (lower Fe)	1.55	2.16	2.25	2.24	2.26	1.6 ± 0.3

[a] Information value from the certificate of analysis; NIST.

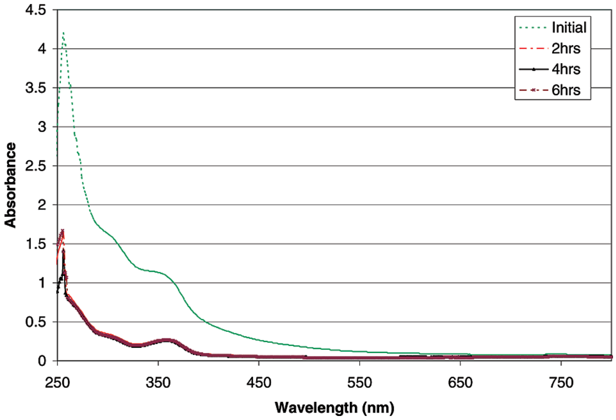

FIGURE 1. Absorption changes in the measurement solution due to precipitation of iron in the SRM 2702. The peak at 360 nm is due to the interaction of beryllium and the fluorescence dye.

Before establishing the time required for complete dissolution of beryllium, the time required for the measurement solution to settle out yellowness (due most likely to iron content) was investigated. For this work, two samples were investigated: SRM 2702 with high iron content and SRM 1944 with lower iron content (Table 1) and a dissolution time of 16 h at 80 °C was chosen. The dissolution was conducted in 50 mL of 5 wt % ABF using 0.5 g of soil. After cooling to room temperature, the dye solution was added to the sample and the solution was immediately analyzed after mixing, and then after 2, 4, 6 and 24 h of this mixing as seen in Table 2. Solutions were filtered through 0.45 μm pore filters after each waiting period.

These results show that after the dissolution solution is mixed with the dye, a waiting time of 2 h is sufficient for removing yellowness. Also, the change from the initial beryllium value to the measured result after 2 h was significantly higher for the high iron content sample. Thus, a 2 h waiting period for reduction of yellowness caused by iron content was used to conduct all of the remaining experiments.

Figure 1 shows changes in the SRM 2702 absorption measurement solution versus waiting time. High overall absorbance is dramatically reduced after ≥2 h of settling time, confirming the waiting time conclusion in Table 2.

As previously noted, the above experiments were conducted using sixteen-hour dissolution periods. Although the beryllium measurements shown in Table 2 were higher than the reference values, an optimum dissolution time to conduct these experiments had not yet been established. Further experiments were conducted wherein the dissolution time in 50 mL of 5% ABF solution at 80 °C (for each 0.5 g sample)

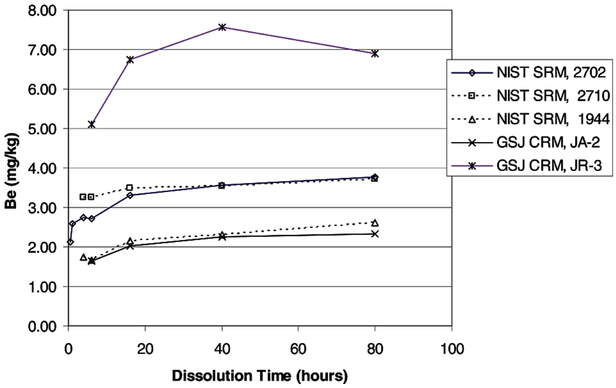

FIGURE 2. [Be] measured in soil, rock, and sediments recorded as a function of dissolution time in 50 mL of 5% ABF solution at 80 °C using 0.5 g samples.

was varied from 0.5 to 80 h. The results of these trials (recorded after a waiting period of 2 h as discussed above) are shown in Figure 2.

The results in Figure 2 show that more than 83% (in some cases almost 98%) recovery is achieved after 16 h. But it was found best to use a dissolution time of at least 40 h for these types of samples, as the recovery for all 40 h dissolution samples was above 99% of the reference values. Since the dissolution process is a kinetic phenomenon, an increase in particle size may cause a shift toward longer dissolution periods. A minimum dissolution time of 40 h at 80 °C in 5% ABF solution was found to be best for particles considered in this study, which were all smaller than about 100 μm (see Table 1).

One of the important differences between soil and crushed rock is the presence of higher organic content in the former. Using the fluorescence method, it is important to ensure that when present these organics do not result in optical signals that may distort the analytical results. Since humic acid is the dominant organic material in most soils, it was decided to add humic acid (0.5–1.0 mg/g) in the proportions found in the soils (*29*) to samples of JA-2 material to investigate its impact. With 0.5 g samples of JA-2 and using a 40 h dissolution time at 80 °C in 50 mL of 5% ABF solution, a mean beryllium value of 2.25 mg/kg was determined. (Note: Experiments were run in triplicate.) These experiments were repeated by adding 2.5 and 5 mg of humic acid to the 0.5 g aliquots of JA-2 samples, which were then analyzed following the dissolution step. The results of these trials gave mean beryllium values of 2.19 and 2.23 mg/kg, respectively, indicating that humic acid in these concentrations did not interfere with the fluorescence measurements.

Using the dissolution protocol above (i.e., 40 h dissolution time at 80 °C in 50 mL of 5% ABF solution and a sample size of 0.5 g), the beryllium content of several other materials was determined and is presented as Table 3.

Aqueous ABF is a versatile and strong dissolution agent (in beryllium mining it is generally used following sintering) for beryllium; it can be used in lieu of more toxic concentrated acids used in a number of published digestion methods (*12, 13, 27, 30*). Initial results showed that even at low ABF concentrations and room temperature, the soils were attacked vigorously to enable extraction of beryllium from the matrix. To distinguish anthropogenic beryllium from natural background beryllium, it is desirable that the dissolution process used extracts all of the beryllium present.

The data in Figure 2 demonstrate that a dissolution time of 40 h is adequate by using a solution of 5 wt % ABF. Although this is a long duration for sample preparation, a simple laboratory convection oven is required for this treatment and several hundred vials can be processed simultaneously.

TABLE 3. Comparison of [Be] Values Determined by Fluorescence to Published Reference Values (Dissolution Using 50 mL of 5% Abf Solution for 40 h at 80 °C)

	beryllium content		
soil/rock type	reference value/ uncertainty[a] (mg/kg)	fluorescence value/uncertainty (SD) (mg/kg) ($N = 3$)	recovery (%)
NIST SRM 2702	3/nr	3.13/± 0.05	104
NIST SRM 2710	2.5/± 0.07	3.11/± 0.16	124
NIST SRM 1944	1.6/± 0.3	2.10/± 0.05	131
GSJ, JA-2	2.05/± 0.44	2.20/± 0.06	107
GSJ, JR-3	7.6/± 0.831	7.56/± 0.07	99
CCRMP SY2	22/nr	22.54/± 0.36	102
GSJ, JB-2	0.27/± 0.043	0.24/± 0.06	89
NIST SRM 1633a	12.1/nr	12.9/± 0.11	108
CCRMP till-1	2.4/nr	2.30/± 0.02	96

[a] nr = not reported.

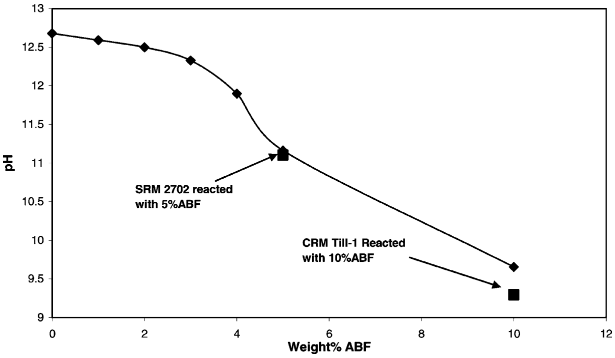

FIGURE 3. Change in pH of mixture of 0.1 mL of ABF solution mixed with 1.9 mL of detector solution.

From previously published data, it is evident that both temperature and ABF concentration are strong accelerators for dissolving refractories such as silica (*26*). Doubling the concentration accelerates the silica–ABF solution reaction by a factor of 2, which is equivalent to increasing the temperature by about 10 °C. For soils rich in silica, one may be able to shorten the dissolution time and accelerate the extraction, by increasing the temperature by 10 °C (to 90 °C) or by increasing the concentration of ABF. For safety considerations in the laboratory, temperatures were kept <95 °C to limit pressure buildup in the vials.

To check the above hypothesis, two CRMs, NIST SRM 2702 and Canadian till-1, were subjected to extraction in 5 wt % ABF at 90 °C for 20 h. Measured beryllium recoveries after this treatment were quantitative. Note that if the ABF concentration is too high (>5 wt %), then the pH of the resulting detection solution becomes too low (<12) and the quantum yield of fluorescence decreases, as observed for soils at 10 wt % ABF at 80 °C for 20 h. If the 10 wt % ABF solution is diluted with water after mixing with the dye solution, the pH increases and the fluorescence values give quantitative results consistent with 10-HBQS fluorophore sensitivity versus the concentration of fluoride ion. On the basis of these findings it was decided to look closer into the pH effect. Different concentrations of ABF solutions were prepared and 0.1 mL of these solutions added to 1.9 mL of the dye solution and the pH measured, as shown in Figure 3. The two soil samples SRM2702 and CRM till-1 were both dissolved in 5 and 10 wt % ABF solution, respectively, and 0.1 mL of these solutions were mixed with 1.9 mL of dye solution resulting in low pH, as shown in Figure 3.

In both cases, the pH change was found to approximate the pH of the ABF and the dye solution mixture. Since even

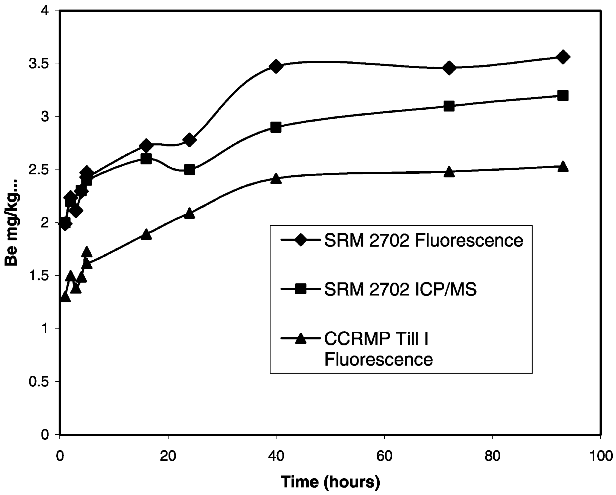

FIGURE 4. Analysis of [Be] in SRM 2702 and CCRMP Till-1. Dissolution was performed using 50 mL of 3% ABF for various times at 90 °C. The SRM 2702 sample was analyzed by both fluorescence and ICP-MS.

TABLE 4. [Be] Established by Fluorescence and ICP-MS Using 0.5 g of Soil Dissolved in 50 mL of 3% (w/w) ABF for 40 h at 90 °C

		fluorescence		
material type	reference value/uncertainty[a] [Be] (mg/kg)	[Be] (mg/kg)	std dev ($n = 8$)	ICP-MS[Be] (mg/kg)
NIST SRM 1944	1.6/± 0.3	2.37	0.05	1.7
GSJ, JR-3	7.6/± 0.831	7.10	0.18	7.1
NIST SRM 2710	2.5/± 0.07	3.35	0.10	2.4
CCRMP SY2	22/nr	21.35	0.60	23
GSJ, JA-2	2.05/± 0.44	2.11	0.02	2.30
GSJ JB-2	0.27/± 0.043	0.31	0.02	0.28
NIST SRM 1633a	12.1/nr	12.85	0.36	14.7
NIST SRM 2702	3/nr	3.50	0.06	3.0
CCRMP till-1	2.4/nr	2.53	0.03	2.4

[a] nr = not reported.

a 5% ABF solution causes a significant change in pH, it was decided to reevaluate the dissolution protocol.

The last set of conditions tested were 50 mL of 3% ABF solution at 90 °C with 0.5 g of soil. At 3% ABF there is still excess acid to dissolve other metals present and increasing the temperature by 10 °C will increase dissolution kinetics. After cooling, the dissolution solutions were filtered through 0.45 μm filters before mixing with the detection solution. All results were obtained using the standard procedure of mixing 0.1 mL of the dissolution solution with 1.9 mL of the detection solution. After mixing, the solutions were left for 2 h, filtered again through 0.45 μm filters, and then evaluated using fluorescence. For some of the solutions the second filtration was done through 0.1 μm media with similar results. The time versus Be concentration traces on the SRM 2702 and Canadian till-1 are shown in Figure 4.

As seen in Figure 4, a dissolution period of 40 h under the stated conditions is sufficient for beryllium extraction. To confirm that these beryllium values were not being affected by any other variables, aliquots of the dissolution solutions were sent for ICP-MS analysis at an independent laboratory. ICP-MS results are shown in Figure 4. Using this protocol (with 40 h as dissolution time), fresh samples were prepared and beryllium values determined for all the materials, as shown in Table 4.

Use of 3% ABF solutions at 90 °C for 40 h is an effective medium for dissolution of beryllium in various representative geologic reference materials. Higher ABF concentration can be used to lower the dissolution time; however, these solutions will have to be diluted or treated so that the pH of the measurement solution remains high, preferably above pH 12. Following extraction with ABF, optical fluorescence is an effective method to determine beryllium in CRM soils, sediments, rocks, and fly ash. Samples of all of these materials can be handled and analyzed using the same testing protocol. The protocol utilizes the advantages of established methods for other sample matrices (i.e., air and wipe samples) with the exceptions that dissolution requires higher ABF concentration and the extraction takes much more time.

Acknowledgments

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Supporting Information Available

Specifics about the Experimental Section, a plot of a typical calibration curve for the Be standards, and a figure showing a comparison of Be reference values to those determined by fluorescence and ICP-MS. This material is available free of charge via the Internet at http://pubs.acs.org.

Literature Cited

(1) Office of Health Security and Safety, Department of Energy, 2007; http://www.hss.energy.gov/HealthSafety/WSHP/be/index.html.

(2) Tinkle, S. S.; Antonini, J. M.; Rich, B. A.; Roberts, J. J.; Salmen, R.; DePree, K.; Adkins, E. J. Skin as a route of exposure and sensitization in chronic beryllium disease. *Environ. Health Perspect.* **2003**, *111* (9), 1202–1208.

(3) Day, G. A.; Dufresene, A.; Stefaniak, A. B.; Schuler, C. R.; Stanton, M. L.; Miller, W. E.; Kent, M. S.; Deubner, K. K.; Hoover, M. D. Exposure pathway assessment at a copper-beryllium alloy facility. *Ann. Occup. Hyg.* **2007**, *51* (1), 67–80.

(4) Chronic beryllium disease prevention program; Code of Federal Regulations, 10 CFR Part 850; U.S. Department of Energy: Washington, D.C., 1999; http://hss.energy.gov/healthsafety/wshp/be/docs/berule.pdf.

(5) U.S. Army Corps of Engineers. Luckey Site (Luckey, Ohio)—Record of Decision for Soils Operable Unit; Total Environmental Restoration Contract DACW27-7-D-0015, Task Order 0009,2006; http://www.lrb.usace.army.mil/fusrap/luckey/luckey-rod-soil-2006-07.pdf. See also: http://www.em.doe.gov/bemr/bemrsites/luck.aspx.

(6) Ruedas-Rama, M. J.; Medina, A. R.; Díaz, A. M. Implementation of flow-through multi-sensors with bead injection spectroscopy — fluorimetric renewable biparameter sensor for determination of beryllium and aluminum. *Talanta* **2004**, *62*, 879–886.

(7) Pal, B. K.; Baksi, K. Chromotropic acid as fluorogenic reagent. 1. Fluorometric determination of beryllium. *Mikrochim. Acta* **1992**, *108*, 275–283.

(8) Bhat, P. N.; Pillai, K. C. Beryllium in environmental air, water and soil. *Water, Air, Soil Pollut.* **1997**, *95*, 133–146.

(9) Wang, J.; Tian, B. M. Trace measurements of beryllium by adsorptive stripping voltammetry and potentiometry. *Anal. Chim. Acta* **1992**, *270*, 137–141.

(10) Millard, J. A.; Dalling, R. H.; Radziemski, L. J. Time-resolved laser-induced breakdown spectrometry for the rapid determi-

nation of beryllium in beryllium-copper alloys. *Appl. Spectrosc.* **1986**, *40*, 491–494.

(11) Tekleab, T. M.; Mihaylov, G. M.; Kirollos, K. S. Onsite direct-read system for semi-quantitative detection of traces of beryllium on surfaces. *J. Environ. Monit.* **2006**, *8*, 625–629.

(12) Minogue, E. M.; Ehler, D. S.; Burrell, A. K.; McCleskey, T. M.; Taylor, T. P. Development of a new fluorescence method for the detection of beryllium on surfaces. *J. ASTM Int.* **2005**, *2* (9), 10, (DOI: JA113161).

(13) Agrawal, A.; Cronin, J.; Tonazzi, J.; McCleskey, T. M.; Ehler, D. S.; Minogue, E. M.; Whitney, G.; Brink, C.; Burrell, A. K.; Warner, B.; Goldcamp, M. J.; Schlect, P. C.; Sonthalia, P.; Ashley, K. Validation of a portable fluorescence method for the measurement of trace beryllium in work place air and wipe samples. *J. Environ. Monit.* **2006**, *8*, 619–624.

(14) Beryllíant, Inc. Manual for procedures and kit description for determination of beryllium (BeFinder). Berylliant, Inc.: Tucson, AZ, 2007; http://www.beryllium.com.

(15) Matsumiya, H.; Hoshino, H.; Yotsuyanagi, T. A novel fluorescence reagent, 10-hydroxy-benzo[h]quinoline-7-sulfonate, for selective determination of beryllium(II) ion at pg cm^{-3} levels. *Analyst* **2001**, *126*, 2082–2086.

(16) Matsumiya, H.; Hoshino, H. Selective determination of beryllium(II) ion at picomole per deciliter cubed levels by kinetic differentiation mode reversed-phase high-performance liquid chromatography with fluorometric detection using 2-(2′-hydroxyphenyl)-10-hydroxybenzo[*h*]quinoline as precolumn chelating reagent. *Anal. Chem.* **2003**, *75*, 413–419.

(17) Donascimento, D. B.; Schwedt, G. Off-line and on-line preconcentration of trace levels of beryllium using complexing agents with atomic spectrometric and fluorometric detection. *Anal. Chim. Acta* **1993**, *283*, 909–915.

(18) Morana, S. J.; Simmons, F. G. Beryllium extracted by the fluoride process. *J. Met.* **1962**, *14*, 571–574.

(19) ASTM International. ASTM D7202, Standard test method for determination of beryllium in the workplace using field-based extraction and fluorescence detection; ASTM International: West Conshohocken, PA,2006; http://www.astm.org.

(20) NIOSH. Methods 7704 and 9110. *NIOSH Manual of Analytical Methods*, 5th ed.; National Institute for Occupational Safety and Health: Cincinnati, OH,2007; http://www.cdc.gov/niosh/nmam/new.html.

(21) Spencer, W.; Ekechukwu, A. Automated digestion and fluorescence analysis of beryllium filter and swipe samples, Savannah River National Laboratory. Presented at Southeastern Regional Meeting of the American Chemical Society (SERMACS), Nov 1–4, 2006.

(22) Wegner, R.; Heinrich-Ramm, R.; Nowak, D.; Olma, K.; Poschadel, B.; Szadkowski, D. Lung function, biological monitoring, and biological effect monitoring of gemstone cutters exposed to beryls. *Occup. Environ. Med.* **2000**, *57*, 133–139.

(23) Brisson, M. J.; Ashley, K.; Stefaniak, A. B.; Ekechukwu, A. A.; Creek, K. Trace-level beryllium analysis in the laboratory and in the field: State of the art, challenges and opportunities. *J. Environ. Monit.* **2006**, *8*, 605–611.

(24) Briggs, P. The determination of forty elements in geological and botanical samples by inductively coupled plasma-atomic emission spectrometry. U.S. Geological Survey Open File Report. 02-223-G, 2001.

(25) *NIOSH Backup Data Report for NMAM Analytical Methods 7704 and 9110*; National Institute for Occupational Safety and Health: Cincinnati, OH, 2007; http://www.cdc.gov/niosh/docket/pdfs/NIOSH-077/0077-072805-backup%20data.pdf.

(26) Timokhin, A. R.; Komarova, L. A. Chemical reaction of ammonium bifluoride with quartz glass. *Glass Ceram.* **1985**, *42*, 267–270.

(27) Ashley, K.; Agrawal, A.; Cronin, J.; Tonazzi, J.; McCleskey, T. M.; Burrell, A. K.; Ehler, D. S. Ultra-trace determination of beryllium in occupational hygiene samples by ammonium bifluoride extraction and fluorescence detection using hydroxybenzoquinoline sulfonate. *Anal. Chim. Acta* **2007**, *584*, 281–286.

(28) U.S. Environmental Protection Agency. Method 3051 Microwave Assisted Acid Digestion of Sediments, Sludge's, Soils, and Oils; EPA SW846; U.S. Environmental Protection Agency: Washington, D.C., 2007.

(29) Huthison, K. J.; Heterberg, D.; Chou, J. W. Stability of reduced organic sulfur in humic acid as affected by aeration and pH. *Soil Sci. Soc. Am. J.* **2001**, *65*, 704–709.

(30) Everest, D. A. *The Chemistry of Beryllium*. Elsevier: Amsterdam, 1964; 3, 38−39, 114, and 118.

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