

Interlaboratory evaluation of an extraction and fluorescence method for the determination of trace beryllium in soils

John P. Cronin,^a Anoop Agrawal,^a Lori Adams,^a Juan C. L. Tonazzi,^a Michael J. Brisson,^b Kenneth T. White,^c David Marlow^d and Kevin Ashley^{*d}

Received 14th March 2008, Accepted 25th June 2008

First published as an Advance Article on the web 14th July 2008

DOI: 10.1039/b804313b

Analytical methods for the determination of trace beryllium in soils are needed so that anthropogenic sources of this element can be distinguished from native (background) levels of beryllium. In this work, a collaborative interlaboratory evaluation of a new extraction and fluorescence-based procedure for determining beryllium in soil samples was carried out to fulfil method validation requirements for ASTM International voluntary consensus standard test methods. A Canadian reference material, CCRMP Till-1 soil, with a background beryllium concentration of $2.4 \mu\text{g g}^{-1}$, was selected for study. This certified reference material (CRM) was spiked and homogenized with varying levels of beryllium oxide in order to give batches of material with beryllium concentrations of 4.36 ± 0.69 , 11.5 ± 0.7 , 124 ± 7 and $246 \pm 16 \mu\text{g g}^{-1}$ (\pm values are standard deviations). In the interlaboratory study (ILS), which was carried out in accordance with an applicable ASTM International standard practice (ASTM E691), samples of these spiked soils were subjected to extraction in dilute ammonium bifluoride at $\sim 90^\circ\text{C}$ for 40 h. Fluorescence measurement of the extracted beryllium was carried out *via* detection using the high quantum yield fluorophore, hydroxybenzoquinoline sulfonate (HBQS). Interlaboratory precision estimates from six participating laboratories ranged from 0.048 to 0.103 (relative standard deviations) for the five different beryllium concentrations. Pooled bias estimates resulting from this ILS were between -0.049 and 0.177 for the various beryllium levels. These figures of merit support promulgation of the analytical procedure as an ASTM International standard test method.

Introduction

Measurement of beryllium in soil samples is important in environmental remediation projects involving beryllium contamination and for establishment of background levels of beryllium at and near sites where anthropogenic beryllium may have been generated.¹ The necessity of analyzing soils for their beryllium content has arisen at several US Department of Energy (DOE) sites and other locations where the soil may have been contaminated with beryllium. At these sites it is desired to assess whether there are elevated beryllium levels in soils and to distinguish between the natural background levels and anthropogenic beryllium so that corrective action (*e.g.*, remediation) can be undertaken, if deemed necessary.

Methods to determine beryllium in soil samples must be highly vigorous in order to dissolve refractory materials such as silicates and oxides of beryllium, and they need to have sufficient detection power so that trace beryllium levels can be accurately

measured. Historically, techniques to dissolve soil samples for subsequent beryllium determination have involved high-temperature fluoride fusions^{2,3} or digestions employing hydrofluoric acid.⁴⁻⁶ Subsequent analytical determination of the extracted beryllium is usually carried out by atomic spectroscopic methods such as electrothermal atomic absorption or inductively coupled plasma optical emission spectrometry.^{7,8} However, less hazardous sample preparation techniques are desired and, to that end, recent work has demonstrated the efficacy of total beryllium extraction from geologic materials such as soils in dilute ammonium bifluoride, NH_4HF_2 .⁹ Subsequent selective determination of beryllium in sample extracts from soils can then be performed by means of fluorescence detection using the high quantum yield fluorophore, hydroxybenzoquinoline sulfonate (HBQS),⁹⁻¹² which offers detection limits ($<2 \text{ ng Be per sample}^{11}$) that are lower than those attainable by atomic spectrometry ($>5 \text{ ng Be per sample}^{13}$).

The aim of this work was to conduct an interlaboratory evaluation of the NH_4HF_2 extraction/HBQS detection method, with the goal of establishing estimates of method performance based on a collaborative round-robin trial. The method was previously found to be effective for the determination of total beryllium in geologic reference materials having a wide range of native beryllium concentrations ($0.3\text{--}21 \mu\text{g g}^{-1}$).⁹ The present interlaboratory evaluation was carried out in accordance with an applicable ASTM International standard pertaining to interlaboratory testing, ASTM E691.¹⁴ The method performance parameters estimated from interlaboratory analysis can be used

^aBerylliant, Inc, 4541 E. Fort Lowell Road, Tucson, AZ 85712, USA

^bWashington Savannah River Company, Savannah River Site 707-F, Aiken, SC 29808, USA

^cConsultive Services, 4428 Ironwood Drive, Virginia Beach, VA 23462, USA

^dUS Department of Health and Human Services, Centers for Disease Control and Prevention, National Institute for Occupational Safety and Health, 4676 Columbia Parkway, M.S. R-7, Cincinnati, OH, 45226-1998, USA. E-mail: KAshley@cdc.gov; Fax: +1(513)458-7189; Tel: +1(513)841-4402

to support a validated and ruggedized procedure that can be promulgated in the form of an ASTM International voluntary consensus standard test method.

Experimental

Materials and equipment

The certified reference material (CRM) used in this study was Till-1 Soil obtained from the Canadian Certified Reference Materials Project (CCRMP, Ottawa, ONT, Canada). The reported beryllium concentration of CCRPM Till-1 soil is $2.4 \mu\text{g g}^{-1}$,¹⁵ which represents a typical background soil beryllium concentration of less than $5 \mu\text{g g}^{-1}$. This CRM was fortified and homogenized by a contract laboratory (High-Purity Standards, Charleston, SC, USA) with varying levels of beryllium oxide powder (UOX-125, Brush-Wellman, Elmore, OH, USA) to produce batches of material with certified beryllium concentrations of 4.36 ± 0.69 , 11.5 ± 0.7 , 124 ± 7 and $246 \pm 16 \mu\text{g g}^{-1}$ (\pm values are standard deviations). These concentrations were chosen in order to produce materials with beryllium concentrations at approximately 2, 5, 50 and 100 times the background beryllium concentration, and represent materials having a wide range of anthropogenic beryllium contamination levels.

Beryllium certified standard solutions in dilute ammonium bifluoride, with beryllium concentrations of 0, 10, 40, 200 and $800 \mu\text{g l}^{-1}$ were obtained from Spex Certiprep (Metuchen, NJ, USA). Ammonium bifluoride extraction solution (3% w v⁻¹ NH_4HF_2 , aqueous) and fluorescence detection solution (1.1 mM hydroxybenzoquinoline sulfonate (HBQS), 1 mM ethylenediamine tetraacetic acid (EDTA) and 100 mM L-lysine monohydrochloride, aqueous) were provided by Berylliant, Inc. (Tucson, AZ, USA). The pH of the detection solution was adjusted to $12.85 (\pm 0.01)$ with 2.5 M NaOH (Sigma-Aldrich, Milwaukee, WI, USA) as monitored by an Orion model 710 pH meter equipped with a low sodium error electrode (Thermo-Fisher, Beverly, MA, USA). All aqueous solutions were made up in deionized water ($18 \text{ M}\Omega \text{ cm}^{-1}$) that was prepared using a MilliQ® purification system (Millipore, Billerica, MA, USA).

Polypropylene 15 ml centrifuge tubes and 60 ml flat-bottom polypropylene vials, 25 mm diameter nylon syringe filters (0.45 μm pore size), plastic 5 ml syringes, and low-fluorescence acrylic disposable cuvettes (10 mm path length) were obtained from Fisher Scientific (Waltham, MA, USA). Heating experiments using the 60 ml vials were carried out by transferring 0.5 g of CRM soil sample (weighed to the nearest 0.0001 g) into each vial, adding 50 ml of extraction solution, and then placing these for 40 h in a Precision model 45EG laboratory oven (Winchester, VA, USA) maintained at $90 \pm 2 \text{ }^\circ\text{C}$. Where applicable, precise weighing (to $\pm 0.0001 \text{ g}$) was performed using a Mettler Toledo model AT 261 analytical balance (Columbus, OH, USA).

Fluorometers used for in-house characterization prior to interlaboratory testing included: (1) a Turner Quantech® model FM 109515 instrument (Barnstead, Dubuque, IA, USA), which was equipped with a 460 nm emission filter having a bandpass of $\pm 20 \text{ nm}$; (2) a Synergy 4 plate reader (Biotek, Winooski, VT, USA), also with a 460 nm emission filter and bandpass of $\pm 20 \text{ nm}$; (3) a Modulus device (Turner Biosystems, Sunnyvale, CA, USA) with a 480 nm emission filter and bandpass of $\pm 5 \text{ nm}$; and

(4) a home-made instrument equipped with a 380 nm light-emitting diode (LED) optical source (Ocean Optics, Dunedin, FL, USA), a 377 nm filter for incident radiation with a bandpass of $\pm 25 \text{ nm}$, a 475 nm emission filter with a bandpass of $\pm 10 \text{ nm}$, and a Hamamatsu model H5784 photomultiplier tube detector (Bridgewater, NJ, USA).

The fluorometers were calibrated using cuvettes containing 1.9 ml of detection solution mixed with 0.1 ml each of the various aforementioned standard solutions. For measurement of soil samples, the samples were allowed to cool to room temperature after the oven heating step. Then 5 ml aliquots of each sample extract were filtered through 0.45 micron syringe filters into 15 ml centrifuge tubes. After this, 0.1 ml aliquots of the filtered extract solutions were added to 1.9 ml of the detection solutions in the fluorescence cuvettes. The amount of beryllium in each sample was calculated by using the calibration curve. All samples were measured within four hours of instrument calibration and, if the measured laboratory temperature drifted by more than $\pm 2 \text{ }^\circ\text{C}$, calibration was repeated to minimize errors due to thermal effects.

Interlaboratory analysis

Volunteer laboratories were solicited from participating members of the Sampling and Analysis Subcommittee of the Beryllium Health and Safety Committee, an *ad hoc* committee with member laboratories from the US, Canada and the United Kingdom.¹⁶ Five sets of the performance evaluation soil samples (one set for each beryllium concentration level) were supplied in triplicate to each participating laboratory. Beryllium concentrations in all samples were unknown (blind) to the participants in the interlaboratory study.

Volunteer laboratories were requested to prepare calibration solutions and to set up their fluorometers as outlined in NIOSH method 9110¹⁷ and/or ASTM D7202.¹⁸ The laboratories were asked to follow the following sample preparation protocol: (1) add 50 ml of extraction solution to each 60 ml polypropylene bottle containing 0.5 g of soil sample; (2) cap each bottle, shake to ensure complete sample wetting, and then place into a laboratory oven and heat at $90 \text{ }^\circ\text{C}$ for 40 h; (3) remove the samples from the oven and allow them to cool to room temperature; (4) take an aliquot (2–5 ml) of each extract and filter it through a nylon filter (0.45 μm pore size) using a 5 ml syringe; (5) for each sample extract, transfer the filtered aliquot into a 15 ml polypropylene centrifuge tube, cap the tube and store for analysis.

After preparing the samples, the participating laboratories were requested to perform analysis in accordance with the following steps: (1) pipette 100 μl of each filtered solution extract into a fluorescence cuvette, and to this add 1.9 ml of detection solution and mix well; (2) let the solution in each cuvette sit under quiescent conditions for two hours to allow for the solution to become colorless (yellowness may be observed initially due to the presence of iron,† which will precipitate out after a time period of two hours⁹); (3) re-filter each solution using a 5 ml syringe and 0.45 μm nylon filter, and empty the contents into a clean

† Titanium dioxide is another potential interferant;¹¹ however, insignificant levels of TiO_2 are present in the certified reference material used here.¹⁵

fluorescence cuvette; (4) measure the fluorescence and determine the beryllium concentration of each sample by comparison with the calibration curve established previously; (5) for samples that are off-scale due to excessively high beryllium concentration levels, dilute each filtered sample extract and measure the fluorescence, accounting for the dilution factor.

The participating laboratories were asked to report their results to the coordinator of the interlaboratory study. It was requested that each laboratory report their beryllium concentrations for each sample in units of $\mu\text{g g}^{-1}$. Volunteer laboratories were identified by number to ensure confidentiality.

Statistical analysis of interlaboratory data

Interlaboratory precision of analytical results reported by the participating laboratories was investigated using the statistical analysis described in ASTM E691.¹⁴ In accordance with this consensus standard practice, repeatability and reproducibility were calculated for each of the five beryllium CRMs that were analyzed by the volunteer laboratories.

Repeatability (r) is an estimate of within-laboratory variability, and this was computed by averaging the squares of the standard deviations of within-laboratory results for each sample having a given beryllium level and taking the square root of this average. Thus, the average within-laboratory standard deviation for each soil sample of a particular beryllium concentration is expressed by the repeatability standard deviation, s_r . Reproducibility (R) is an estimate of the variability of both within-laboratory and between-laboratory results. The reproducibility standard deviation s_R is given by the larger of $\{(s_x)^2 + [(s_r)^2 (n - 1) n^{-1}]\}^{1/2}$ and s_r , where s_x is the standard deviation of the mean value as estimated by the average of all interlaboratory study (ILS) results for a given CRM and n is the number of test results at a particular concentration level. Relative standard deviations for repeatability and reproducibility (RSD_r and RSD_R , respectively) are then calculated by dividing the repeatability and reproducibility standard deviations (*i.e.*, s_r and s_R) by the mean interlaboratory study result for a given beryllium-in-soil concentration level. The RSD for a particular test material can then be compared *versus* the precision that is desired (*e.g.*, $\text{RSD} < 0.20^{19}$) for the test method under evaluation.

Estimates of analytical bias were calculated by dividing the difference between the measured value and the reference value by the reference value: bias $B_i = (\mu_i - R_i) R_i^{-1}$, where B_i , μ_i and R_i are the bias, mean measured concentration and reference concentration, respectively, for the i^{th} laboratory-reported value for each beryllium-in-soil ILS material.

Results

Initial characterization

Prior to carrying out the collaborative interlaboratory investigation, initial work was performed on the soil performance evaluation materials in order to characterize these materials as obtained from the contract laboratory, and also to examine data obtained from different fluorometric instruments. Recall that these CRMs consisted of CCRMP Till-1 native soil, both unspiked as well as spiked, at four different levels with beryllium oxide. Four samples of each of these five CRMs were processed

Table 1 Beryllium concentrations ($\mu\text{g g}^{-1}$) measured in CCRMP Till-1 performance evaluation samples (unspiked and spiked with BeO at four different levels) by various fluorometers; \pm values are standard deviations from $n = 4$ results at each concentration level

Ref. [Be]/ $\mu\text{g g}^{-1}$	Fluorometer type and emission wavelength used			
	Turner Quantech (460 nm)	Synergy 4 (460 nm)	Modulus (480 nm)	Berylliant (475 nm)
2.4	2.8 ± 0.00	2.8 ± 0.03	2.3 ± 0.02	2.3 ± 0.09
4.36	5.17 ± 0.122	5.17 ± 0.088	4.83 ± 0.053	4.85 ± 0.061
11.5	12.7 ± 0.55	13.0 ± 0.91	12.5 ± 0.74	12.5 ± 1.10
124	136 ± 5.7	126 ± 5.2	132 ± 5.6	133 ± 5.3
246	253 ± 4.1	251 ± 19.3	254 ± 6.7	253 ± 4.4

using the NH_4HF_2 extraction procedure described above, and then measurements were carried out on each extracted sample using each of four different fluorometers *via* the HBQS detection method. Results from these experiments are shown in Table 1. It can be seen from these data that the measured beryllium concentrations are close to the reference values reported by the contract laboratory, and that measurements performed by different fluorometric instruments were comparable. Quantitative recoveries ($100\% \pm 15\%$) were, overall, obtained for all beryllium concentration levels. Although the measured values were (generally) slightly higher than the certified beryllium levels (Table 1), the measured means were, overall, statistically equivalent to the certified values. These results indicate that the extraction and fluorescence method is effective at quantitatively solubilizing and measuring beryllium in the soil CRMs.

Results of the interlaboratory study

As was mentioned previously, the interlaboratory study (ILS) was carried out in accordance with ASTM E691,¹⁴ which requires data from a minimum of six participating laboratories. While eight laboratories were invited to participate in the ILS, results were received from the minimum number of six participants. The volunteer laboratories were provided with all of the consumables necessary for carrying out extraction and analysis, and the beryllium concentrations in the performance evaluation materials were unknown to the participants. Detailed instructions on performing the NH_4HF_2 extraction and HBQS fluorescence analysis, as described in the Experimental section, were also provided to each volunteer laboratory.

Overall results reported by the collaborative laboratories participating in the ILS are summarized in Table 2. Each participant reported results after sample preparation and analysis of each of the soil CRMs, with sample preparation and analysis carried out in triplicate. Overall mean values were computed based on the pooled means for the average of the three results reported by each laboratory for each sample. Computed interlaboratory relative standard deviations (RSDs) ranged from less than 0.05 to slightly above 0.10 (Table 2, bottom row).

Results for repeatability and reproducibility for the ILS soil samples, determined in accordance with ASTM E691, are shown in Table 3. It is emphasized that all reported results were included in the statistical calculations leading to the values given in Tables 2 and 3. Although two statistical outliers (out of a total of 90

Table 2 Results from NH_4HF_2 extraction/HBQS fluorescence measurement of beryllium in unspiked and BeO-spiked CCRPM Till-1 performance evaluation samples, as reported by laboratories participating in the ILS. Listed values are laboratory means and standard deviations for $n = 3$ samples at each concentration level. Reference values for beryllium concentrations in the ILS samples are given in parentheses

Laboratory number	Unspiked ($2.4 \mu\text{g g}^{-1}$)	Low [Be] ($4.36 \mu\text{g g}^{-1}$)	Medium [Be] ($11.5 \mu\text{g g}^{-1}$)	High [Be] ($124 \mu\text{g g}^{-1}$)	Very high [Be] ($246 \mu\text{g g}^{-1}$)
1	2.26 ± 0.087	6.03 ± 2.65^a	12.2 ± 1.56	129 ± 8.3	241 ± 6.0
2	2.76 ± 0.000	5.17 ± 0.122	12.7 ± 0.55	136 ± 5.7	253 ± 4.1
3	2.25 ± 0.031	4.53 ± 0.042	11.5 ± 1.97	111 ± 3.1	219 ± 2.8
4	2.27 ± 0.081	4.85 ± 0.392	13.1 ± 0.60	133 ± 20.6^a	222 ± 4.0
5	2.62 ± 0.044	5.37 ± 0.522	12.1 ± 1.24	121 ± 1.7	217 ± 15.7
6	2.44 ± 0.079	4.84 ± 0.092	12.9 ± 0.75	124 ± 6.5	249 ± 10.1
$\mu^b \pm \text{SD}^c$	2.43 ± 0.215	5.13 ± 0.528	12.4 ± 0.59	126 ± 9.0	234 ± 16.1
RSD ^d	0.0885	0.103	0.0476	0.0714	0.0688

^a Results include statistical outlier. ^b Overall mean value. ^c Overall standard deviation. ^d Overall relative standard deviation.

Table 3 Precision statistics for beryllium measurements from ILS soil CRM samples, as computed using values reported by participating laboratories ($n = 6$) and presented in accordance with ASTM E691.¹⁴

Ref. [Be]/ $\mu\text{g g}^{-1}$	$\mu^a/\mu\text{g g}^{-1}$	s_x^b	s_r^c	s_R^d	r^e	R^f	RSD _r ^g	RSD _R ^h
2.4	2.43	0.215	0.0623	0.223	0.174	0.624	0.0256	0.0918
4.36	5.13	0.528	0.456	0.646	1.28	1.81	0.0889	0.126
11.5	12.4	0.594	1.05	1.05	2.95	2.95	0.0847	0.0847
124	126	8.98	9.85	12.1	27.6	33.7	0.0782	0.0960
246	234	16.1	8.39	17.5	23.5	48.9	0.0359	0.0748

^a Overall mean. ^b Overall standard deviation. ^c Repeatability standard deviation. ^d Reproducibility standard deviation. ^e Repeatability ($2.8 s_r$). ^f Reproducibility ($2.8 s_R$). ^g Relative standard deviation for repeatability. ^h Relative standard deviation for reproducibility.

Table 4 Bias estimates and recoveries for beryllium measurements from ILS soil CRM samples; reference values for beryllium concentrations are in parentheses

	Unspiked soil ($2.4 \mu\text{g g}^{-1}$)	Low [Be] ($4.36 \mu\text{g g}^{-1}$)	Medium [Be] ($11.5 \mu\text{g g}^{-1}$)	High [Be] ($124 \mu\text{g g}^{-1}$)	Very high [Be] ($246 \mu\text{g g}^{-1}$)
Est'd. bias	+0.013	+0.177	+0.078	+0.016	-0.049
% Recovery	103	118	108	102	95.1

individual analyses performed by the collaborating laboratories) were identified (Dixon's Q-test,²⁰ $P = 0.05$), they were not omitted from the calculations.

When using the ASTM E691 statistical protocol,¹⁴ if the computed value for repeatability standard deviation s_r is greater than that for the reproducibility standard deviation s_R , then the larger value is used and these two quantities are set to be equal. This situation applied for the instance of the ILS performance evaluation CRM spiked at the loading level of $11.5 \mu\text{g g}^{-1}$ (fourth row of Table 3).

Estimates of bias computed for each ILS soil performance evaluation sample are shown in Table 4; overall mean values used for these computations were taken from Tables 2 and 3. Bias estimates ranged from near -0.05 to almost $+0.18$, with consequent beryllium recoveries of between $\sim 95\%$ and $\sim 118\%$.

Discussion

The single-laboratory results shown in Table 1 demonstrate acceptable beryllium recoveries ($100 \pm 15\%$) as compared to the certified beryllium contents of the performance evaluation soil samples. These results also yield good agreement between results from different fluorimeters and helped to justify the subsequent

interlaboratory study. Acceptable intralaboratory repeatability ($\text{RSD} < 0.15$) is demonstrated by the data of Table 1, thereby illustrating the ruggedness of the NH_4HF_2 extraction/HBQS fluorescence measurement method for beryllium in soil samples. The results from these experiments confirmed related data pertaining to beryllium determination in a series of geologic CRMs having a wide range of reference beryllium concentrations (Fig. 1). Previous work yielded quantitative recoveries of beryllium in the CRMs and demonstrated comparability of the fluorescence detection technique with analysis by inductively coupled plasma mass spectrometry (ICP-MS).⁹

Further evidence of the ruggedness of the method under evaluation can be seen in the data of Table 2. The ILS interlaboratory precision estimates are acceptable in consideration that the highest overall RSD measured was slightly in excess of 0.10, which compares to a generally desired maximum RSD of 0.15–0.20 for environmental media of the kind investigated here.^{9,19,21} This highest RSD observed was obtained from the performance evaluation material having the lowest spike value ($[\text{Be}] = 4.36 \mu\text{g g}^{-1}$), which is not terribly surprising given the challenges in obtaining a homogeneous material in the concentration range near $5 \mu\text{g g}^{-1}$. Indeed, the uncertainty in the certified value ($\text{RSD} = 0.16$) is greater than that established through

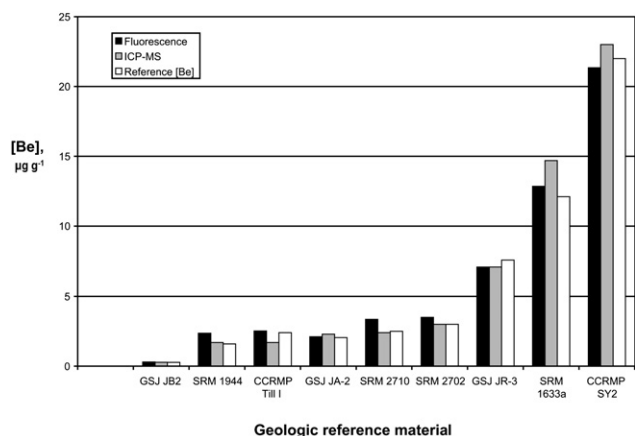


Fig. 1 Comparison of beryllium reference values for geologic CRMs to beryllium concentrations determined by HBQS fluorescence and inductively coupled plasma mass spectrometry (ICP-MS), after extraction of 0.5 g of material in 50 ml of 3% NH_4HF_2 solution for 40 h at 90 °C (data compiled from ref. 9).

interlaboratory testing. Interlaboratory RSDs obtained are lower for soils spiked at higher concentrations (Table 2), but no general trend in terms of precision either improving or getting worse with continued increases in beryllium concentration is observed.

Estimates of analytical bias based on the collaborative ILS data are presented in Table 4 and reveal a somewhat high apparent bias of +0.177 for the low-beryllium spiked soil CRM. However, the magnitude of this bias estimate is not statistically significant (*t*-test for independent means, 95% confidence limits²⁰), owing largely to the higher uncertainty in the certified beryllium concentration of this CRM (as discussed in the preceding paragraph).

It is especially noteworthy that the ILS samples were quite challenging in view of the requirement to completely solubilize refractory berylliosilicate and beryllia (BeO) matrices within the sample media. Silicate beryllium is represented by the native CCRMP Till-1 soil, which has a background beryllium concentration of 2.4 $\mu\text{g g}^{-1}$. Refractory beryllium oxide spiked into this soil at different levels represents an anthropogenic source of “high-fired” beryllia, *i.e.*, beryllium oxide prepared at temperatures in excess of 1500 °C.^{7,8} These challenging matrices posed no problem for dissolution by means of extraction in dilute NH_4HF_2 , as evidenced by beryllium recoveries of ~95% to ~118% determined through interlaboratory analysis (Table 4).

In conclusion, the results of this collaborative interlaboratory evaluation of the NH_4HF_2 extraction and HBQS fluorescence measurement procedure indicate that the method is effective for the quantitative determination of beryllium in unspiked native soil and in soils spiked with high-fired beryllium oxide. The method performance demonstrated acceptable intralaboratory and interlaboratory repeatability and reproducibility for performance evaluation soil samples (CRMs) over a two orders of magnitude range of beryllium concentrations. This study strongly suggests that beryllium extraction with dilute NH_4HF_2 can be used in lieu of fluoride fusions and/or HF digestions, thereby greatly simplifying sample preparation and enhancing overall safety of the laboratory procedure. Also, this work

indicates that the HBQS fluorescence technique can be employed as an alternative to ICP-MS detection of beryllium. The acceptable performance of the NH_4HF_2 extraction/HBQS fluorescence protocol has led to its being developed as an ASTM International standard test method for the determination of beryllium in samples of geologic media.

Disclaimers

This article was prepared by US Government employees and contractors as part of their official duties and legally may not be copyrighted in the United States of America. Mention of company names or products does not constitute endorsement by the Centers for Disease Control and Prevention. The findings and conclusions in this paper are those of the authors and do not necessarily represent the views of the National Institute for Occupational Safety and Health.

Acknowledgements

We thank Eve Bauer and Brandy Duran (Los Alamos National Laboratory), Paul Lee (University of Arizona), and Tim Oldham (Oak Ridge National Laboratory) for their invaluable assistance with this project. Ronnee Andrews, Amy Feng and Bob Streicher (CDC/NIOSH) kindly reviewed the draft manuscript.

References

- 1 US Department of Energy, 10 CFR Part 850, *Chronic Beryllium Disease Prevention Program. Code of Federal Regulations*, Washington, DC, 1999.
- 2 K. J. Eisenbraun, D. J. Greist and R. E. Sievers, *Anal. Chem.*, 1971, **43**, 2003–2007.
- 3 J. Stone, *Geochim. Cosmochim. Acta*, 1998, **62**, 555–561.
- 4 J. R. Merrill, M. Honda and J. R. Arnold, *Anal. Chem.*, 1960, **32**, 1420–1428.
- 5 W. F. Schmidt and F. Dietl, *Fresenius' Z. Anal. Chem.*, 1987, **326**, 40–42.
- 6 S. Dudka and B. Markert, *Sci. Total Environ.*, 1992, **122**, 279–290.
- 7 M. J. Brisson, K. Ashley, A. B. Stefaniak, A. A. Ekechukwu and K. L. Creek, *J. Environ. Monit.*, 2006, **8**, 605–611.
- 8 *Beryllium – Sampling and Analysis*, ASTM STP 1473. ASTM International, ed. K. Ashley, West Conshohocken, PA, USA, 2006.
- 9 A. Agrawal, J. P. Cronin, A. Agrawal, J. C. L. Tonazzi, L. Adams, K. Ashley, M. J. Brisson, B. Duran, G. Whitney, A. K. Burrell, T. M. McCleskey, J. Robbins and K. T. White, *Environ. Sci. Technol.*, 2008, **42**, 2066–2071.
- 10 H. Matsumiya, H. Hoshino and T. Yotsuyanagi, *Analyst*, 2002, **126**, 2082–2086.
- 11 A. Agrawal, J. Cronin, J. Tonazzi, T. M. McCleskey, D. S. Ehler, E. M. Minogue, G. Whitney, C. Brink, A. K. Burrell, B. Warner, M. J. Goldcamp, P. C. Schlecht, P. Sonthalia and K. Ashley, *J. Environ. Monit.*, 2006, **8**, 619–624.
- 12 K. Ashley, A. Agrawal, J. Cronin, J. Tonazzi, T. M. McCleskey, A. K. Burrell and D. S. Ehler, *Anal. Chim. Acta*, 2007, **584**, 281–286.
- 13 US National Institute for Occupational Safety and Health (NIOSH), Beryllium and Compounds, as Be; Elements by ICP-AES (Method Nos. 7102 & 7300); in *NIOSH Manual of Analytical Methods*, 4th edn, NIOSH, Cincinnati, OH, 1994; www.cdc.gov/niosh/nmam.
- 14 *ASTM E691*, Standard Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method, ASTM International, West Conshohocken, PA, USA, 2005.
- 15 Canadian Certified Reference Materials Project (CCRMP), *Certificate of Analysis: Till-1, Till-2, Till-3 and Till-4 Geochemical Soil and Till Reference Materials*, Natural Resources Canada, Ottawa, 1995, www.ccrmp.ca.
- 16 Beryllium Health and Safety Committee, <http://www.sandia.gov/BHSC>.

-
- 17 NIOSH, Beryllium in Surface Wipes by Field-Portable Fluorometry (Method No. 9110), in *NIOSH Manual of Analytical Methods*, 5th edn, NIOSH, Cincinnati, OH, 2007, www.cdc.gov/niosh/nmam.
- 18 *ASTM D7202*, Standard Test Method for the Determination of Beryllium in the Workplace using Field-based Extraction and Fluorescence Detection, ASTM International, West Conshohocken, PA, USA, 2006, www.astm.org.
- 19 K. Ashley, T. M. McCleskey, M. J. Brisson, G. Goodyear, J. Cronin and A. Agrawal, *J. ASTM Int.*, 2005, **2**(9), 8, DOI: JAI13156; <http://www.astm.org/>.
- 20 J. C. Miller and J. N. Miller, *Statistics for Analytical Chemistry*, Ellis Horwood, Ltd., Chichester, UK, 1984, ch. 3.
- 21 K. Ashley, R. Song, C. A. Esche, P. C. Schlecht, P. A. Baron and T. J. Wise, *J. Environ. Monit.*, 1999, **1**, 459–464.