Measurement of ultra-trace beryllium in occupational hygiene samples by extraction and fluorescence detection

Beryllium is widely used in industry and commercial products for its unique properties; however, occupational exposure to beryllium particles can cause dermal sensitization and a potentially fatal lung ailment, chronic beryllium disease (CBD). Consequently, exposure limits for beryllium particles in air and action levels on surfaces have been established in efforts to minimize exposure risks for workers. In recent research, a molecular fluorescence method for the determination of trace beryllium in workplace samples, i.e., air filters and dust wipes, was evaluated and validated through intra- and inter-laboratory testing. The procedure entails extraction of sampled beryllium in dilute ammonium bifluoride (aqueous), followed by fluorescence measurement of the complex formed between beryllium and hydroxybenzoquinoline sulfonate (HBQS). The estimated method detection limit is <1 ng Be per air filter or wipe sample, with a dynamic range up to greater than 10 μg per sample. Interferences from numerous metals tested (in >400-fold excess concentration compared to that of beryllium) are negligible or minimal. The procedure is effective for the dissolution and quantitative determination of beryllium extracted from refractory beryllium oxide particles, and was successfully modified for measuring beryllium content in large BeO particles and in soil samples. The method performance compares favorably with methods employing sample digestion in acid mixtures that include hydrofluoric acid, followed by inductively coupled plasma-mass spectrometry. ASTM International voluntary consensus standards and US National Institute for Occupational Safety and Health methods based on the methodology have been promulgated.

By Kevin Ashley

INTRODUCTION AND BACKGROUND

Beryllium is a lightweight metal (atomic number 4) with unique mechanical, electronic and thermal properties that make it ideal for use in many applications and industries including defense, aerospace, nuclear power, telecommunications, automobiles, sporting equipment and even dental prosthetics.[1] In nature beryllium is found in highest concentrations in beryl and bertrandite ores, from which the element is mined.[2] Beryllium-containing alloys and beryllium compounds have been produced commercially in the US since as early as 1920.[3] Production of calcined beryllium oxide, often referred to as "high-fired" BeO, which is subjected to heating at temperatures >1,500 °C, began in the late 1950s.[4] Unfortunately, beryllium exposures can cause adverse health effects in a percentage of those exposed, and may lead to the development of chronic beryllium disease (CBD).[5–8] CBD is believed to be triggered first by sensitization through dermal exposure to beryllium, which precedes a subsequent airborne exposure via inhalation.[9] Development of CBD has been documented in about half of those individuals who have been sensitized.[10] CBD is treatable but cannot be cured.[11] Beryllium and compounds have also been identified as suspect carcinogens.[12,13]

Preventing occupational exposures to beryllium particles via skin contact and/or inhalation requires the ability to measure this highly toxic element at extremely low levels on surfaces and in workplace air.[14] Occupational exposure limits for beryllium in air have been established in a number of countries[15] and a revised Threshold Limit Value (TLV) for beryllium has been established at 0.05 μg/m^3, which is the lowest TLV promulgated for any metal.[16] US Department of Energy regulations have set action levels for beryllium in air and on surfaces, with a lowest surface limit of 0.2 μg Be per 100 cm^2 sampling area for release of equipment or for non-beryllium work areas.[17] The above exposure limits require the use of highly sensitive analytical techniques in order to achieve

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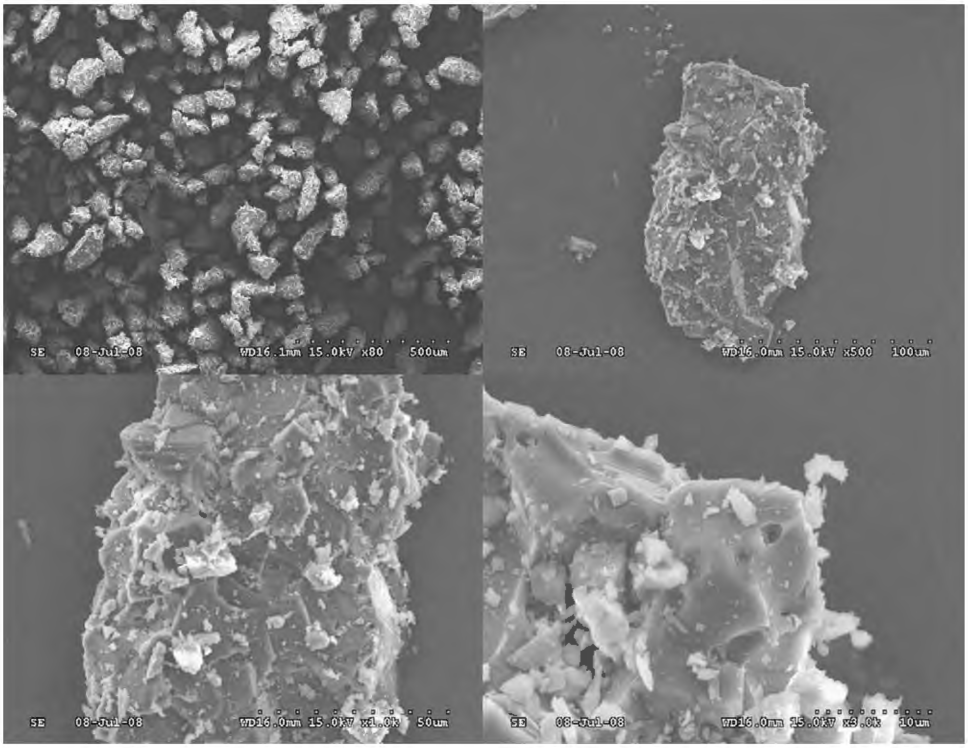

Figure 1. Scanning electron micrographs of ≈100 μm diameter high-fired BeO particles at 80× (top left), 500× (top right), 1000× (bottom left), and 3000× (bottom right) magnifications.

the method detection limits (MDLs) necessary for determining ultra-trace levels of beryllium. For example, in order to measure airborne beryllium at levels below the TLV, candidate analytical methods must be able to quantify beryllium at masses of nanograms per sample or less.[18]

Prior to analytical measurement of beryllium, effective dissolution techniques must be utilized in order to extract this element from challenging sample matrices.[19] These include refractory materials such as silicates and high-fired beryllium oxide[20] (Figure 1). In occupational hygiene chemistry applications, air filter and wipe samples containing collected refractory particulate matter historically have been subjected to acid digestions that include hydrofluoric or sulfuric acids.[19,21,22]

In other work, concentrated ammonium bifluoride, NH_4HF_2, has been employed in the dissolution of quartz silicate materials.[23] The rate of the reaction with silica

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

is concentration and temperature dependent. NH_4HF_2 has also been used to dissolve beryllium oxide, beryllium hydroxide and metallic beryllium.[24] The reaction with beryllium oxide can be expressed[25]

$$BeO + 2NH_4HF_2 \rightarrow (NH_4)_2BeF_4 + H_2O,$$

in analogous fashion to the reaction with beryllium hydroxide[20]:

$$Be(OH)_2 + 2NH_4HF_2 \rightarrow (NH_4)_2BeF_4 + 2H_2O.$$

For wipes and air filter samples, extraction of beryllium with dilute aqueous NH_4HF_2, is a useful alternative to digestion in concentrated acids.[26] NH_4HF_2 in diluted form has also been successfully employed in the dissolution of beryllium from soils, although long extraction times at elevated temperature are required.[27] This extraction medium offers a safe and facile alternative to the use of concentrated acids that have traditionally been used for dissolution of beryllium in challenging environmental samples.

Subsequent to dissolution, laboratory methods to measure beryllium in occupational hygiene samples have relied mainly on atomic spectrometric methods such as electrothermal atomic absorption and inductively coupled plasma optical emission spectrometry.[14,22] In order to obtain yet lower detection limits for beryllium, recent work has focused on the use of inductively coupled plasma mass spectrometry (ICP-MS)[28,29] and a new molecular fluorescence method[30] that relies on a high quantum yield fluorophore, hydroxybenzoquinoline sulfonate (HBQS).[31] When complexed with the beryllium dication in basic solution, HBQS offers much greater intensity of fluorescence than previously studied fluorophores, thereby enabling ultra-trace beryllium detection.[30]

Fluorescence spectra of trace levels of beryllium in the presence of HBQS are presented in Figure 2. Using excitation in the near ultraviolet ($\lambda = 365$–380 nm), unreacted HBQS reagent fluoresces at $\lambda_{max} \approx 590$ nm, while the intense fluorescence of the Be–HBQS adduct is blue-shifted to $\lambda_{max} \approx 475$ nm. With this fluorescence

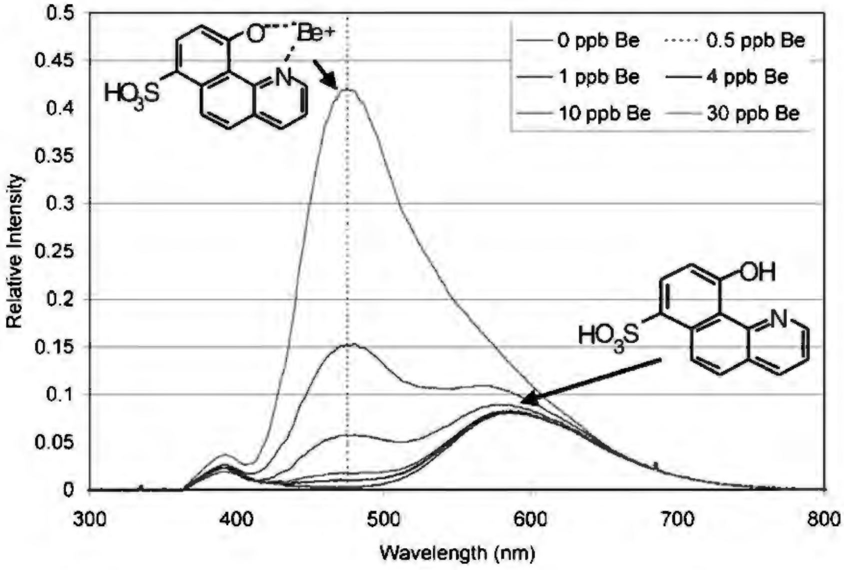

Figure 2. Fluorescence spectra of unreacted HBQS ($\lambda_{max} \approx 590$ nm) and Be–HBQS complex ($\lambda_{max} \approx 475$ nm).

reagent, beryllium concentrations in the sub-parts-per-billion range can be measured quantitatively,[26,32] thereby offering detection limits that are comparable with those attainable by ICP-MS.[30,33]

This paper briefly reviews the development and validation of the overall method that entails dissolution with NH_4HF_2 and ultra-trace detection of extracted beryllium by fluorescence measurement of the Be–HBQS complex. Applications to air filter samples, wipes, soils and other sample matrices are demonstrated.

LABORATORY PERFORMANCE

Evaluation of the overall NH_4HF_2 extraction and fluorescence measurement method[34,35] (schematized in Figure 3) has been carried out in accordance with published validation protocols.[36,37] The MDL of the procedure has been estimated using various fluorometers, with an optimum reported MDL of less than 0.8 ng per sample for filter media.[30] Still lower MDLs are attainable with longer fluorescence measurement times. By comparison, similar beryllium MDLs have been reported for environmental samples by ICP-MS.[33,38] The analytical range of the fluorescence detection method spans nearly five orders of magnitude.[32] Overall method uncertainty, as estimated through inter-laboratory testing, is better than ±20%.[39] This performance satisfies criteria for quantitative analysis established by voluntary consensus for occupational air monitoring in Europe[40] and also meets the criterion for accuracy of ±25% recommended by the U.S. National Institute for Occupational Safety and Health (NIOSH).[36,37]

Analytical recoveries of beryllium from beryllium sulfate, beryllium metal powder and high-fired beryllium oxide, and also sampling media spiked with these beryllium compounds, are presented in Table 1.[30,32] $BeSO_4$, Be metal powder and high-fired BeO represent water-soluble, water-insoluble and refractory materials, respectively. In these experiments, sample extraction in 1% NH_4HF_2 for a minimum of 30 min was performed with and without heating. Subsequent analysis of aliquots from extracted samples was carried out using the HBQS fluorescence technique. Recoveries from $BeSO_4$ and Be metal are satisfactory without the use of deliberate heating; however, BeO recoveries are higher when heating is used during extraction (Table 1). During extraction, the presence of active fluoride ions (from hydrofluoric acid (HF) by dissociation of NH_4HF_2 in aqueous acidic medium) enables dissolution of insoluble and refractory materials, notably high-fired BeO.

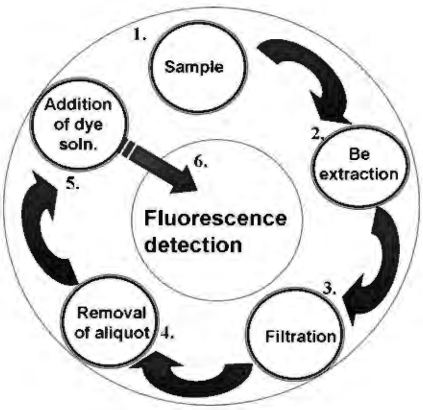

Figure 3. Scheme for sample preparation and analysis of occupational hygiene samples by means of NH_4HF_2 extraction and fluorescence detection using HBQS dye solution.

Potential interferences from numerous commonly co-occurring metals in the presence of trace beryllium have been investigated.[32] Negligible interferences are obtained with the following elements in >400-fold molar excess to the beryllium present in solution: Al, Ca, Co, Cu, Li, Ni, Pb, Sn, U, V, W, and Zn. Significant interferences from Fe and TiO_2 are manifested in the form of observed yellowness or cloudiness in the extract solutions. These interferences are extremely rare in air samples but occur more commonly in wipe and especially bulk (e.g., soil or accumulated dust) samples. Interference from Fe or TiO_2 can be readily addressed by allowing for precipitation of hydroxides, followed by an additional filtering step to remove the precipitates. This treatment for interference correction does not adversely affect detection limits or analytical sensitivity for beryllium. Specificity for beryllium in the presence of potentially interfering elements is achieved by use of: (a) ethylenediamine-tetraacetic acid, which binds larger metals in solution; (b) a highly basic detection solution, which causes unbound metals to precipitate; and (c) HBQS, which binds selectively with beryllium dication.

Application of the HBQS fluorescence detection method to occupational hygiene samples collected in

Table 1. Beryllium Recoveries After Extraction in 1% NH_4HF_2 and Fluorescence Measurement Using HBQS.

Sample/Media	Be Mass Range	Extraction Temp. (°C)	Mean Recovery ± Std. Dev.
$BeSO_4$ (n[a] = 3)	0.02–2.0 μg	23	102 ± 4
$BeSO_4$ (n = 3)	5–10 mg	23	100 ± 4
$BeSO_4$/MCE[b] (n = 9)	0.02–2.0 μg	23	105 ± 6
$BeSO_4$/MCE (n = 3)	5–10 mg	23	99 ± 2
$BeSO_4$/cellulosic wipe (n = 12)	0.02–2.0 μg	23	99 ± 5
$BeSO_4$/cellulosic wipe (n = 3)	5–10 mg	23	98 ± 3
Be metal (n = 3)	5–10 mg	23	96 ± 3
Be metal/MCE (n = 3)	5–10 mg	23	93 ± 7
Be metal/cellulosic wipe (n = 3)	5–10 mg	23	95 ± 4
BeO (n = 6)	0.02–2.0 μg	23	86 ± 6
BeO (n = 3)	0.02–2.0 μg	85	95 ± 10
BeO (n = 3)	5–10 mg	23	90 ± 5
BeO (n = 3)	5–10 mg	85	97 ± 7
BeO/MCE (n = 20)	0.02–2.0 μg	23	86 ± 5
BeO/MCE (n = 15)	0.02–2.0 μg	85	99 ± 8
BeO/MCE (n = 7)	5–10 mg	23	86 ± 5
BeO/MCE (n = 9)	5–10 mg	85	96 ± 6
BeO/cellulosic wipe (n = 18)	0.02–2.0 μg	23	82 ± 5
BeO/cellulosic wipe (n = 15)	0.02–2.0 μg	85	90 ± 7
BeO/cellulosic wipe (n = 3)	5–10 mg	23	86 ± 7
BeO/cellulosic wipe (n = 3)	5–10 mg	85	96 ± 6

[a] Number of replicate samples.
[b] Mixed cellulose ester filters.

field sites demonstrated excellent correspondence with atomic spectrometric measurements.[26,32] Quantitative beryllium recoveries from surface wipe samples have been obtained from field samples by use of NH_4HF_2 extraction.[26] No interferences to beryllium determination were observed, even from samples known to contain significant levels of mineral oils and other organic and metallic contaminants.

For the determination of beryllium in soils, sediments, crushed rock, and coal fly ash samples, the NH_4HF_2/fluorescence method is modified in order to dissolve the trace beryllium that is present in these silicate matrices. 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. With the use of higher NH_4HF_2 concentration (3%) and longer extraction times (40 hr) at 90 °C, beryllium in geological reference materials can be extracted and measured with acceptable accuracy (Table 2).[27] After extraction, pH adjustment of sample aliquots is especially important given the higher acidity of the dissolution solution. As applied to geological samples, this procedure provides an effective, practical alternative to the use of high-temperature digestions employing HF and ICP-MS analysis.[19]

The NH_4HF_2 extraction and HBQS fluorescence detection methodology has been applied successfully to the quantitative determination of beryllium in high-fired BeO particles of larger aerodynamic diameter, that is, for size fractions of <32 μm up to ≈200 μm.[41] An NH_4HF_2 concentration of 3% with an extraction time of up to 5 hr at 80–90 °C yields quantitative determination of beryllium from samples of this refractory material, both alone and spiked onto various types of sampling media (Table 3). Scanning electron microscopic analysis of partially dissolved BeO particles (Figure 4) illustrates that dissolution in NH_4HF_2 solution occurs not just on the exterior surface of the particles, but also via accessing their interiors due to the inherent porosity of the BeO material.

INTER-LABORATORY STUDIES

Inter-laboratory data from application of the NH_4HF_2 extraction/HBQS fluorescence detection method on $BeSO_4$-spiked filters over a range of beryllium levels are reported in Table 4.[30,32] For beryllium loadings down to ultra-trace levels, these results demonstrate mean reported values that are close to the spike levels. Precision estimates, as measured by inter-laboratory relative standard deviations (RSDs), compare favorably with ICP-MS inter-laboratory data[28] and also with uncertainties typically reported in relevant proficiency testing programs.[42] The performance data shown in Table 4 were generated in support of

Table 2. Beryllium Measured in Geological Reference Materials (≈0.5 g samples) after 40-hr Extraction in 3% NH_4HF_2 and Fluorescence Measurement Using HBQS.

Reference Material[a]	Reference [Be] (μg/g)[b]	Measured [Be] (μg/g)[c]
GSJ JB-2 (basalt)	0.27 ± 0.043	0.31 ± 0.02
NIST SRM 1944 (waterway sediment)	1.6 ± 0.3	2.37 ± 0.05
GSJ JA-2 (andesite)	2.05 ± 0.44	2.11 ± 0.02
CCRMP Till-1 (soil)	2.4	2.53 ± 0.03
NIST SRM 2710 (soil)	2.5 ± 0.07	3.35 ± 0.10
NIST SRM 2702 (marine sediment)	3	3.50 ± 0.06
GSJ JR-3 (rhyolite)	7.6 ± 0.83	7.1 ± 0.18
NIST SRM 1633a (coal fly ash)	12.1	12.85 ± 0.36
CCRMP SY2 (syenite)	22	21.35 ± 0.60

[a] GSJ, Geological Survey of Japan; NIST, US National Institute of Standards and Technology; CCRMP, Canadian Certified Reference Materials Project.
[b] Uncertainty estimate given if reported by certifying organization.
[c] ±values are standard deviations (n = 8).

Table 3. Beryllium Recoveries from High-fired BeO Particles (1–2 mg) with and without Sampling Media After 90 °C Extraction in 3% NH_4HF_2 for 4-5 hr and Fluorescence Measurement Using HBQS.

BeO Particle Size Fraction (μm)	Percent Recoveries with and without Sampling Media[a]			
	No Sampling Media ($n=3$)	MCE[b] Filters ($n=3$)	Cellulosic Wipes ($n=6$)	Cotton Gloves ($n=3$)
<32	95 ± 5	92 ± 6	91 ± 5	111 ± 17
90–106	102 ± 12	100 ± 7	97 ± 4	98 ± 12
180–212	97 ± 5	92 ± 1	97 ± 4	90 ± 5

[a] ±values are standard deviations.

[b] Mixed cellulose ester.

Figure 4. Scanning electron micrographic images of BeO particles after partial dissolution in dilute NH_4HF_2 at 500× (left) and 3,000× (right) magnifications.

NIOSH methods[34] and a voluntary consensus standard[35] that have been promulgated which describe the determination of beryllium in occupational hygiene samples. The NH_4HF_2 extraction and HBQS fluorescence detection method can be used for the determination of beryllium in workplace air and surfaces at levels as low as a few nanograms per sample, and field-portable devices have been evaluated and validated.[43] Moreover, the NH_4HF_2/fluorescence methodology has been recognized as a specific field of testing under the laboratory accreditation programs of the American Industrial Hygiene Association.[44]

An inter-laboratory evaluation of the NH_4HF_2 extraction and fluorescence detection method for determining beryllium in soil samples[27] was carried out using a Canadian soil reference material, both unspiked and spiked with various concentrations of high-fired BeO.[45] The results from this study are summarized in Table 5. These challenging samples posed no problem for dissolution by means of heated extraction in dilute (3%, aqueous) NH_4HF_2 and measurement by fluorescence with HBQS dye solution, as evidenced by recoveries of 95–118% determined through inter-laboratory analysis. It is also noteworthy that the highest inter-laboratory RSDs were ≈10%, which is indicative of the ruggedness of the method. This work shows that beryllium extraction with dilute

Table 4. Inter-laboratory Analysis Results from Filter Samples Spiked with Beryllium Sulfate (0.002–0.40 μg Be/sample).

Be Spike Level (μg/sample)	Average Reported Be ± Std. Dev. (μg/sample)	Inter-laboratory RSD[a] (%)	Estimated Bias
Mixed cellulose ester filters			
0.002 ($n=4$)	0.0023 ± 0.00030	13	+0.15
0.005 ($n=4$)	0.0052 ± 0.00012	2.3	+0.040
0.020 ($n=4$)	0.021 ± 0.00055	2.6	+0.050
0.050 ($n=12$)	0.051 ± 0.0027	5.3	+0.020
0.10 ($n=9$)	0.10 ± 0.0048	4.8	0.00
0.20 ($n=9$)	0.21 ± 0.018	8.6	+0.050
0.40 ($n=9$)	0.42 ± 0.040	9.5	+0.050
Cellulosic wipes			
0.002 ($n=4$)	0.0025 ± 0.00048	19	+0.25
0.005 ($n=4$)	0.0056 ± 0.00035	6.3	+0.12
0.020 ($n=4$)	0.0209 ± 0.00049	2.3	+0.045
0.050 ($n=12$)	0.052 ± 0.0044	8.5	+0.040
0.10 ($n=9$)	0.11 ± 0.011	10.0	+0.10
0.20 ($n=9$)	0.21 ± 0.0094	4.5	+0.050
0.40 ($n=9$)	0.41 ± 0.025	6.1	+0.025

Beryllium data (μg/sample) were reported by participating laboratories after extraction in 1% NH_4HF_2 and fluorescence measurement with HBQS.

[a] Relative standard deviation.

Table 5. Inter-laboratory Analysis Results (n = 6) for Reference Material Soil Samples Spiked with BeO (40-hr extraction in 3% NH_4HF_2 at 90 °C with subsequent HBQS fluorescent measurement).

[Be] Reference, Value (μg/g)	Average Reported [Be] ± Std. Dev. (μg/g)	Inter-laboratory RSD[a] (%)	Estimated Bias
2.4[b]	2.43 ± 0.215	8.85	+0.013
4.36	5.13 ± 0.528	10.3	+0.177
11.5	12.4 ± 0.59	4.76	+0.078
124	126 ± 9.0	7.14	+0.016
246	234 ± 16.1	6.88	−0.049

[a] Relative standard deviation.

[b] Unspiked material (CCRMP Till-1 soil).

NH_4HF_2 can be used in lieu of fusion techniques and/or HF digestions, thereby greatly simplifying sample preparation and enhancing overall safety of the laboratory procedure. Additionally, the HBQS fluorescence technique can be employed as an alternative to ICP-MS measurement of beryllium in soil samples. The excellent performance of the NH_4HF_2 extraction/HBQS fluorescence protocol led to its development as an international voluntary standard test method for the determination of beryllium in samples of geological origin.[46]

SUMMARY

Beryllium exposures are of particular concern in the industrial hygiene arena, and recent efforts to improve beryllium sampling and analysis methodologies have resulted in significant advances and improvements.[47,48] Research summarized in this paper has demonstrated that trace and ultra-trace determination of beryllium in occupational hygiene samples such as air filters and surface wipes can be effectively carried out by means of extraction in dilute NH_4HF_2 and detection using HBQS dye. The method performance compares favorably with more traditional methods entailing acid digestions involving HF and subsequent ICP-MS measurement of beryllium. Additionally, the method performs well on challenging sample matrices such as silicate materials (e.g., soils, fly ash) and refractory beryllium oxide particles. It is noted that the NH_4HF_2 extraction/HBQS fluorescence protocol can be carried out at a fraction of the cost of methods requiring acid digestion and atomic spectrometric measurement of beryllium by ICP-MS. High-throughput, automated laboratory instrumentation is available, as well as field-portable equipment (Figure 5). Analytical attributes include: (1) estimated MDLs of 1 ng Be per sample or less; (2) high specificity for beryllium; (3) quantitative beryllium recoveries from geological materials and from refractory BeO; and (4) a dynamic range of up to five orders of magnitude. Standardized procedures based on the NH_4HF_2 extraction/HBQS fluorescence method have been promulgated by CDC/NIOSH and by ASTM International. Also, an accrediting organization in the US has recognized the methodology as a new field of testing for industrial hygiene chemistry laboratories that conduct beryllium analyses.[44]

Figure 5. Equipment for (a) automated laboratory analysis and (b) field-portable measurement of beryllium by NH_4HF_2 extraction and fluorescence measurement using HBQS.

DISCLAIMERS

Mention of company names or products does not constitute endorsement by the Centers for Disease Control and Prevention. The findings and conclusions in this article are those of the author and do not necessarily represent the views of the National Institute for Occupational Safety and Health.

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REFERENCES

1. World Health Organization (WHO). *Beryllium and Beryllium Compounds*; Concise International Chemical Assessment Document No. 32. WHO; Geneva, 2001.
2. Walsh, K. A.; Vidal, E. E. Sources of beryllium, In K. A. Walsh (Ed.), *Beryllium Chemistry and Processing.* ASM International: Materials Park, OH, 2009 Chapter 3.
3. Taylor, T. P.; Ding, M.; Ehler, D. S.; Foreman, T. M.; Kaszubaand, J. P.; Sauer, N. N. *J. Environ. Sci. Health A,* **2003**, *38*, 439–469.
4. Kolanz, M. E. *Appl. Occup. Environ. Hyg.* **2001**, *16*, 559–567.
5. Agency for Toxic Substances and Disease Registry (ATSDR). *Toxicological Profile for Beryllium*; ATSDR; Atlanta, 2002.
6. Hong-Geller, E. *J. Occup. Environ. Hyg.* **2009**, *6*, 727–731.
7. Silva, S.; Ganguly, K.; Fresquez, T. M.; Gupta, G.; McCleskey, T. M.; Chaudhary, A. *J. Occup. Environ. Hyg.* **2009**, *6*, 775–782.
8. McCleskey, T. M.; Scott, B. L. *J. Occup. Environ. Hyg.* **2009**, *6*, 751–757.
9. Tinkle, S. S.; Antonini, J. M.; Rich, B. A.; Roberts, J. R.; Salmen, R. *Environ. Health Persp.* **2003**, *111*, 1202–1208.
10. Kreiss, K.; Mroz, M.; Newman, L.; Martyny, J.; Zhen, B. *Am. J. Ind. Med.* **1996**, *30*, 16–25.
11. Sood, A. *J. Occup. Environ. Hyg.* **2009**, *6*, 762–765.
12. International Agency for Research on Cancer (IARC). *Summaries and Evaluations–Beryllium and Compounds, Monograph Vol. 58,* IARC; Lyon, 1994.
13. US National Toxicology Program (NTP). *Report on Carcinogens, 11th Ed.* NTP; Research Triangle Park, NC, 2005.
14. Brisson, M. J. Overview of beryllium sampling and analysis, In M. J. Brisson, & A. A. Ekechukwu (Eds.), *Beryllium–Environmental Analysis and Monitoring.* Royal Society of Chemistry (RSC): Cambridge, 2009 Chapter 1.
15. Institut für Arbeitsschutz der Deutschen Gesetzlichen Unfallversicherung (IFA). *GESTIS International Limit Values for Chemical Agents–Occupational Exposure Limits*; IFA; Sankt Augustin, Germany, 2010, http://www.dguv.de/ifa/en/gestis/limit_values (updated annually; accessed 28 October 2010).
16. American Conference of Governmental Industrial Hygienists (ACGIH). *Threshold Limit Values for Chemical Substances and Physical Agents & Biological Exposure Indices*; ACGIH; Cincinnati, 2010, (updated annually).
17. US Department of Energy (DOE). *Chronic Beryllium Disease Prevention Program*; 10 CFR Part 850. Code of Federal Regulations; Washington, 1999.
18. Brisson, M. J.; Ashley, K. *J. Occup. Environ. Hyg.* **2005**, *2*, D97–D99.
19. Ashley, K.; Oatts, T. J. Sample dissolution reagents for beryllium, In M. J. Brisson, & A. A. Ekechukwu (Eds.), *Beryllium–Environmental Analysis and Monitoring.* RSC: Cambridge, 2009 Chapter 4.
20. Gupta, C. K.; Saha, S. *Min. Pro. Ext. Met. Rev.* **2001**, *22*, 413–451.
21. Brisson, M. J.; Ekechukwu, A. A.; Ashley, K.; Jahn, S. D. *J. ASTM Int.* **2006**, *3*(2)10.1520/JAI13157.
22. Brisson, M. J.; Ashley, K.; Stefaniak, A. B.; Ekechukwu, A. A. *J. Environ. Monit.* **2006**, *8*, 605–611.
23. Timokhin, A. R.; Komarova, L. A. *Steklo Keram.* **1985**, *6*, 13–15.
24. Everest, D. A. *The Chemistry of Beryllium*; Elsevier; Amsterdam, 1964, pp. 3, 38, 39.
25. McCleskey, T. M. Heating sources for beryllium sample preparation, In M. J. Brisson, & A. A. Ekechukwu (Eds.), *Beryllium–Environmental Analysis and Monitoring.* RSC: Cambridge, 2009 Chapter 5.
26. Minogue, E. M.; Ehler, D. S.; Burrell, A. K.; McCleskey, T. M.; Taylor, T. P. *J. ASTM Int.* **2005**, *2*(9)10.1520/JAI13168.
27. Agrawal, A.; Cronin, J. P.; Agrawal, A. ; Tonazzi, J. C. L.; Adams, L.; Ashley, K.; Brisson, M. J.; Duran, B.; Whitney, G.; Burrell, A.; McCleskey, T. M.; Robbins, J.; White, K. T. *Environ. Sci. Technol.* **2008**, *42*, 2066–2071.
28. Ashley, K.; Brisson, M. J.; Howe, A. M.; Bartley, D. L. *J. Occup. Environ. Hyg.* **2009**, *6*, 745–750.
29. Ashley, K.; Brisson, M. J.; Howe, A. M. *Anal. Methods,* **2010**, *2*, 1823–1826.
30. Ashley, K.; Agrawal, A.; Cronin, J.; Tonazzi, J.; McCleskey, T. M.; Burrell, A. K.; Ehler, D. S. *Anal. Chim. Acta,* **2007**, *584*, 281–286.
31. Matsumiya, H.; Hoshino, H.; Yotsuyanagai, T. *Analyst,* **2002**, *126*, 2082–2086.
32. 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.; Schlecht, P. C.; Sonthalia, P.; Ashley, K. *J. Environ. Monit.* **2006**, *8*, 619–624.
33. US Environmental Protection Agency (EPA). *Trace Elements in Water & Wastes–ICP-MS*; Method No. 200.8. EPA; Washington, 1994.
34. US National Institute for Occupational Safety and Health (NIOSH). *NIOSH Manual of Analytical Methods*; Method Nos. 7704 & 9110. NIOSH; Cincinnati, 2007.
35. ASTM International. *ASTM D7202. Standard Test Method for the Determination of Beryllium in the Workplace Using Ammonium Bifluoride Extraction and Fluorescence Detection*; ASTM International; West Conshohocken, PA, 2006.
36. Kennedy, E. R.; Fischbach, T. J.; Song, R.; Eller, P. M.; Shulman, S.; Hull, R. D. *Development and evaluation of methods*; NIOSH Manual of Analytical Methods. NIOSH; Cincinnati, 1998, Chapter E.
37. Kennedy, E. R.; Fischbach, T. J.; Song, R.; Eller, P. M.; Shulman, S. *Guidelines for Air Sampling and Analytical Development and Evaluation*; NIOSH Publ. No. 95-117. NIOSH; Cincinnati, 1995.
38. Hasegawa, S.; Yamaguchi, H.; Yamada, K.; Kobayashi, T. *Mater. Trans.* **2004**, *45*, 925–929.
39. Ashley, K.; McCleskey, T. M.; Brisson, M. J.; Goodyear, G.; Cronin, J.; Agrawal, A. *J. ASTM Int.* **2006**, *3*(2)10.1520/JAI13156.
40. Comité Européen de Normalisation (CEN). *EN 482, Workplace Atmospheres–General Requirements for the*

Performance of Procedures for the Measurement of Chemical Agents; CEN; Brussels, 2006.

41. Goldcamp, M. J.; Goldcamp, D. M.; Ashley, K.; Fernback, J. E.; Agrawal, A.; Millson, M.; Marlow, D.; Harrison, K. *J. Occup. Environ. Hyg.* **2009**, *6*, 735–744.
42. Grunder, F. I. *Am. Ind. Hyg. Assoc. J.* **2001**, *62*, 736–738.
43. Ashley, K. *J. Chem. Health Safety,* **2010**, *17*(3), 22–28.
44. American Industrial Hygiene Association (AIHA). *Laboratory Accreditation Programs*; AIHA; Fairfax, VA, 2010, http://www.aiha.org (accessed 23 November).
45. Cronin, J. P.; Agrawal, A.; Adams, L. ; Tonazzi, J. C. L.; Brisson, M. J.; White, K. T.; Marlow, D.; Ashley, K. *J. Environ. Monit.* **2008**, *10*, 955–960.
46. ASTM International. *ASTM D7458, Standard Test Method for Determination of Beryllium in Soil, Rock, Sediment, and Fly Ash using Ammonium Bifluoride Extraction and Fluorescence Detection*; ASTM International; West Conshohocken, PA, 2008.
47. Ashley, K. (Ed.). *Beryllium–Sampling and Analysis.* ASTM STP No. 1473. ASTM International: West Conshohocken, PA, 2005.
48. Brisson, M. J., & Ekechukwu, A. A. (Eds.). *Beryllium–Environmental Analysis and Monitoring.* RSC: Cambridge, 2009.