

# Validation of a standardized portable fluorescence method for determining trace beryllium in workplace air and wipe samples†‡§

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Beryllium is widely used in industry for its unique properties; however, occupational exposure to beryllium particles can cause potentially fatal disease. Consequently, exposure limits for beryllium particles in air and action levels on surfaces have been established to reduce exposure risks for workers. Field-portable monitoring methods for beryllium are desired in order to facilitate on-site measurement of beryllium in the workplace, so that immediate action can be taken to protect human health. In this work, a standardized, portable fluorescence method for the determination of trace beryllium in workplace samples, *i.e.*, air filters and dust wipes, was validated through intra- and inter-laboratory testing. The procedure entails extraction of beryllium in 1% ammonium bifluoride (NH<sub>4</sub>HF<sub>2</sub>, aqueous), followed by fluorescence measurement of the complex formed between beryllium ion and hydroxybenzoquinoline sulfonate (HBQS). The method detection limit was estimated to be less than 0.02 µg Be per air filter or wipe sample, with a dynamic range up to greater than 10 µg. The overall method accuracy was shown to satisfy the accuracy criterion ( $A \leq \pm 25\%$ ) for analytical methods promulgated by the US National Institute for Occupational Safety and Health (NIOSH). Interferences from numerous metals tested (in >400-fold excess concentration compared to that of beryllium) were negligible or minimal. The procedure was shown to be effective for the dissolution and quantitative detection of beryllium extracted from refractory beryllium oxide particles. An American Society for Testing and Materials (ASTM) International voluntary consensus standard based on the methodology has recently been published.

## Introduction

The unique properties of beryllium (Be) have led to many applications in the aerospace industry, the nuclear industry, manufacturing, electronics, and even sports equipment.<sup>1</sup> Beryllium metal is lightweight and has high strength, and alloying

beryllium with copper and aluminum results in materials with high corrosion resistance, stiffness and low stress relaxation.

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Trace beryllium is also often found in coal slag and aluminum ore. The high thermal conductivity of beryllium oxide, while also being electrically insulating, is a key component to the dissipation of heat in integrated circuits. Beryllium alloys are also used in high-end electrical connectors, springs, bearings and other components of a wide range of products.

Unfortunately, beryllium is a Class A EPA carcinogen, and its inhalation can cause an incurable and potentially fatal lung ailment, chronic beryllium disease (CBD).<sup>2,3</sup> Hence, monitoring of airborne beryllium in occupational environments is of vital importance. Further, it has also been reported that skin exposure may result in sensitization towards Be.<sup>4</sup> Thus, it is desirable to monitor and limit exposure of workers in industrial workplaces to particulate matter containing beryllium which can be inhaled or might come into contact with the skin. Beryllium metal (as metal or as a metal alloy) and beryllium oxide are the most important beryllium materials from an industrial perspective.

Widely used laboratory methods to measure beryllium in workplace atmospheres (*e.g.*, NIOSH 7102,<sup>5</sup> OSHA ID-125G<sup>6</sup> and ASTM D7035<sup>7</sup>) use atomic spectrometric instrumentation. Preparation of samples for such analysis involves the use of strong acids and high heat, and the necessary laboratory equipment can be expensive. This instrumentation also requires highly trained personnel and is not easily field deployable. To overcome these issues, a rapid, quantitative and sensitive test for the detection of beryllium has been developed using fluorescence. The method is based on the fluorescence of beryllium bound to hydroxybenzoquinoline sulfonate (HBQS),<sup>8</sup> and includes a dissolution technique using dilute ammonium bifluoride solution.<sup>9</sup> Dilute ammonium bifluoride has been proposed as a field extraction medium which is much less hazardous than the strong acids used ordinarily in digestion of beryllium samples in the laboratory. Also, portable fluorometers that can be hand-carried to the field and powered by battery are commercially available. Given these and other considerations, it is of interest to thoroughly evaluate the on-site extraction and fluorescence method for beryllium in workplace samples.

A suite of experiments was carried out in order to validate the field method, which has been published as a new voluntary consensus standard by the American Society for Testing and Materials (ASTM) International. In this study, it was found that the intensity of fluorescence is linear with respect to beryllium concentration over several orders of magnitude. A detection limit of less than 0.02  $\mu\text{g Be}$  per sample has been achieved, which allows for detection of Be at an order of magnitude lower than the lowest applicable DOE regulatory levels. Interference studies have been carried out with a variety of commonly co-occurring metals, with minimal or no interferences found for the detection of trace beryllium in the presence of many-fold excess of the other metals. Specificity for beryllium has been achieved using a number of strategies, such as the use of (a) ethylenediaminetetraacetic acid (EDTA), which binds larger metals, (b) high pH in the detection solution, which causes unbound metals to precipitate, and (c) HBQS, which binds selectively with beryllium. Experiments conducted in support of the method validation are described in detail in the following sections.

## Experimental

### Reagents and solutions

Sources of beryllium in solid form included beryllium sulfate (99.99%  $\text{BeSO}_4 \cdot 4\text{H}_2\text{O}$ , Aldrich, Milwaukee, WI, USA), beryllium oxide (99.98%  $\text{BeO}$ , Aldrich; and 99.5+ % UOX-125  $\text{BeO}$ , Brush-Wellman, Elmore, OH, USA), and beryllium metal powder (99 + % Be, Matheson, Norwood, OH, USA). 1% (w/v) aqueous ammonium bifluoride ( $\text{NH}_4\text{HF}_2$ ) extraction solution was provided by Berylliant (Tucson, AZ, USA). The detection solution, also from Berylliant, contained 1.1 mM HBQS, 1 mM EDTA and 100 mM L-lysine monohydrochloride; the pH was adjusted to 12.8 ( $\pm 0.1$ ) with 10 M NaOH (Fisher Scientific, Hampton, NH, USA). Standard solutions consisting of  $\approx 1000 \mu\text{g mL}^{-1}$  metal (Al, Be, Ca, Co, Cu, Fe, Li, Ni, Pb, Sn, U, V, W, Zn) concentration were obtained from Inorganic Ventures (Lakewood, NJ, USA). Titanium dioxide ( $\text{TiO}_2$ ) came from Aldrich. Deionized water (18  $\text{M}\Omega \text{ cm}$ ) used for all experiments was prepared using a MilliQ<sup>®</sup> purification system (Millipore, Billerica, MA, USA).

### Materials and equipment

Mixed-cellulose ester (MCE) filters, 37 mm dia., 0.8  $\mu\text{m}$  pore size, and Whatman 541 filters, 47 mm dia., were obtained from SKC (Eighty-Four, PA, USA). Palintest and Ghost Wipe<sup>®</sup> dust sampling wipes were purchased from Palintest USA (Erlanger, KY, USA) and Environmental Express (Mt. Pleasant, SC, USA), respectively. Performance evaluation materials consisting of MCE and Whatman 541 filters spiked with beryllium sulfate to give levels between 0.05 and 0.5  $\mu\text{g Be}$  per filter were prepared at a contract laboratory (Environmental Resource Associates, Arvada, CO, USA). Beryllium oxide-spiked filters (MCE and Whatman 541) were prepared from aqueous  $\text{BeO}$  suspensions;<sup>10</sup> the spiking level was  $0.18 \pm 0.01 \mu\text{g Be}$  per filter. Plastic centrifuge tubes (15 and 50 mL), 0.45  $\mu\text{m}$  pore size, 25 mm dia., nylon plastic 5 mL syringe microfilters, and disposable fluorescence cuvettes (10 mm dia.) were obtained from Fisher. An analytical balance (Mettler Toledo AT261, Columbus, OH, USA) was used for high-precision weighing. Agitation was effected by using a rotator (Labquake<sup>®</sup>, Barnstead, Dubuque, IA, USA) or sonicator (Fisher FS110H). Sample heating was done using a VWR Digital Heatblock (VWR, West Chester, PA, USA). Where necessary, pH was measured using an Orion model 710 pH meter (Thermo, Beverly, MA, USA) that was calibrated with pH 4.0, 7.0 and 10.0 buffers (Fisher).

### Fluorescence instrumentation

Portable fluorometers used were Turner Quantech<sup>®</sup> (Barnstead) and Ocean Optics S2000-FL (Dunedin, FL, USA) devices, respectively. The Turner Quantech instrument utilizes bandpass filters in the paths of incident and fluorescent beams, with excitation radiation of 360–390 nm and a detection spectral window of at least 440–490 nm. The Ocean Optics device employs a 380 nm light-emitting diode (LED) for excitation and a diode array detector for spectral measurements over a wavelength range of 300 to 800 nm; optical fibers

are used to transmit the excitation beam and the radiation detected at 90° to the incident 380 nm radiation.

## Experimental methods

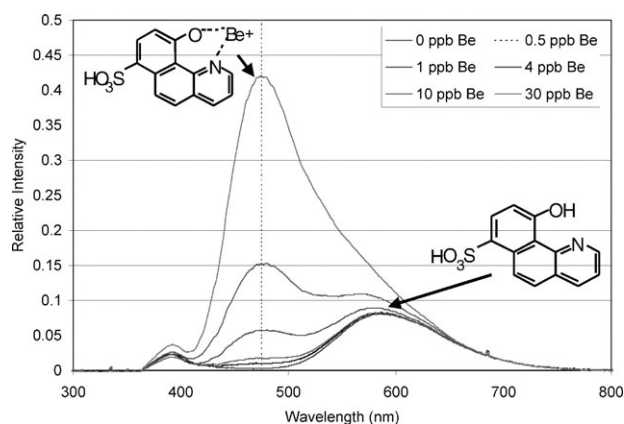
The objective of this work was to validate the field-portable fluorescence method in accordance with standard guidelines. Within-laboratory and field studies were carried out following strategies outlined by NIOSH for applications in workplace air sampling and analysis.<sup>11</sup> Interlaboratory collaborative testing was conducted as described in a pertinent ASTM International voluntary consensus standard.<sup>12</sup>

The overall analysis method<sup>13</sup> entailed the following steps: (1) Placement of filter or wipe samples into plastic centrifuge tubes of appropriate size. (2) Extraction of the samples in 1% (w/v) ammonium bifluoride solution for at least 30 minutes using agitation or heating. (3) Filtration of extract solutions through nylon plastic syringe microfilters. (4) Transfer of aliquots of sample extracts into disposable fluorescence cuvettes using mechanical micropipettes. (5) Reaction of the sample aliquots with detection solution containing the fluorescent dye (HBQS). (6) Measurement of fluorescence at  $\approx 475$  nm using a portable fluorometer.

Experiments were conducted to evaluate the analytical recovery, dynamic range, method detection limit, long-term sample stability; interferences, performance on field samples, and interlaboratory precision. For the purposes of this work, analysis results were ordinarily reported in units of mass of beryllium (in  $\mu\text{g}$ ) per sample. This required comparison of results for unknowns with calibration standards, along with consideration of appropriate dilution and correction factors, to convert fluorescence response to mass. Confirmatory analysis was carried out using acid digestion and atomic spectrometry by NIOSH method 7102,<sup>5</sup> OSHA method 125G,<sup>6</sup> or equivalent.

## Results

Representative solution fluorescence spectra for trace levels of beryllium in the presence of HBQS are shown in Fig. 1. Unreacted HBQS reagent fluoresces at  $\lambda_{\text{max}} \approx 590$  nm, while the intense fluorescence of the Be–HBQS adduct is blue shifted to  $\lambda_{\text{max}} \approx 475$  nm. With this fluorescence reagent, sub-ppb



**Fig. 1** HBQS ( $\lambda_{\text{max}} \approx 590$  nm) and Be–HBQS ( $\lambda_{\text{max}} \approx 475$  nm) fluorescence spectra.

concentrations of beryllium can be measured quantitatively. The HBQS fluorophore offers much higher sensitivity than do fluorescence reagents previously employed for beryllium detection.<sup>14–16</sup> Concentrations of less than 0.1 ppb Be can be determined using the HBQS reagent.

The method detection limit (MDL) was estimated according to the generalized NIOSH procedure.<sup>11</sup> An Ocean Optics S2000-FL portable fluorescence device (5 s signal integration time) was used for these trials. Low-level media spikes (MCE and Whatman 541 filters) corresponding to between 0.006 and 0.060  $\mu\text{g}$  Be per sample were analyzed (along with low-level calibration standards), and the mean results were obtained for replicate samples at each spiking level. From this treatment the MDL was estimated to be 4.2 ng Be per sample for each sampling medium. An alternative method for estimating MDL involves the measurement of multiple blanks.<sup>7</sup> MDLs estimated in this fashion were found to be comparable to those obtained using the NIOSH protocol.

The analytical range of the method was evaluated using an Ocean Optics fluorometer. With this device it was possible to quantitatively measure from the method quantitation limit,  $\approx 14$  ng Be, up to at least 6  $\mu\text{g}$  Be per sample without further dilution (fluorescence intensity  $y = 0.0696[\text{Be}] + 0.0115$ ;  $r^2 = 0.9998$ ; 2 s integration). Still greater masses, up to at least 10  $\mu\text{g}$  Be per sample, can be measured directly using the Turner Quantech device using the low sensitivity setting, which applies to higher beryllium concentrations.

Results for analytical recoveries of beryllium from beryllium sulfate or beryllium oxide, and sampling media spiked with these beryllium compounds at levels of  $\approx 0.02$ –2.0  $\mu\text{g}$  Be per sample, are summarized in Table 1. Mechanical agitation or heating at 80 °C was used during sample extraction in 1%  $\text{NH}_4\text{HF}_2$ . Reference values for samples containing beryllium oxide were established by using a combination of NIOSH 7102 (sample preparation by hotplate digestion in nitric/sulfuric acids) and NIOSH 7300 (Be measurement by inductively coupled plasma atomic emission spectrometry, ICP-AES).<sup>5</sup> Recoveries from BeO were found to be higher when heating was used during extraction (Table 1). Beryllium recoveries from samples with larger masses of material (5–20 mg), weighed on a high-precision analytical balance prior to

**Table 1** Beryllium recoveries from extraction in 1% ammonium bifluoride (> 30 min) and analysis by portable fluorometry; sampling media were spiked with beryllium sulfate (from solution) or beryllium oxide (Brush-Wellman UOX125 BeO in suspension) at masses of 0.02–2  $\mu\text{g}$  Be per sample

Sample/media	Extraction technique	Mean recovery (%)	Relative standard deviation (%)
$\text{BeSO}_4$ ( $n = 3$ )	Mechanical	102	4.4
$\text{BeSO}_4/\text{MCE}$ ( $n = 9$ )	Mechanical	105	6.1
$\text{BeSO}_4/\text{Whatman 541}$ ( $n = 12$ )	Mechanical	99.4	4.7
BeO ( $n = 6$ )	Mechanical	85.6	6.8
BeO ( $n = 3$ )	Heat	95.0	9.8
BeO/MCE ( $n = 12$ )	Mechanical	89.5	5.1
BeO/MCE ( $n = 3$ )	Heat	97.4	9.5
BeO/Whatman 541 ( $n = 12$ )	Mechanical	84.2	4.6
BeO/Whatman 541 ( $n = 3$ )	Heat	90.1	8.3

**Table 2** Summary of beryllium recoveries ( $\pm$  standard deviations) from extraction in 1% ammonium bifluoride and analysis by fluorometry, using mechanical rotation ( $>30$  min) or sonication (1 h). Masses treated were 10–20 mg for  $\text{BeSO}_4 \cdot 4\text{H}_2\text{O}$  and 5–10 mg for Be metal powder and BeO (Aldrich)

Sample/media ( $n = 3$ )	Mechanical rotation	Sonication
$\text{BeSO}_4 \cdot 4\text{H}_2\text{O}$ (no medium)	$99.8 \pm 4.4$	$106.6 \pm 12.0$
Be metal (no medium)	$96 \pm 3$	—
BeO (no medium)	$90 \pm 5$	$83 \pm 3$
$\text{BeSO}_4 \cdot 4\text{H}_2\text{O}$ /MCE	$98.6 \pm 1.6$	$110.4 \pm 4.7$
Be metal/MCE	$93 \pm 7$	—
BeO/MCE	$94 \pm 6$	$93 \pm 6$
$\text{BeSO}_4 \cdot 4\text{H}_2\text{O}$ /Whatman 541	$98.1 \pm 3.3$	$101.3 \pm 2.5$
Be metal/Whatman 541	$95 \pm 4$	—
BeO/Whatman 541	$86 \pm 8$	$96 \pm 5$
$\text{BeSO}_4 \cdot 4\text{H}_2\text{O}$ /Palintest	—	$87.6 \pm 2.5$
BeO/Palintest	—	$84 \pm 2$
$\text{BeSO}_4 \cdot 4\text{H}_2\text{O}$ /Ghost Wipe	—	$79.3 \pm 2.4$
BeO/Ghost Wipe	—	$40 \pm 4$

spiking, are shown in Table 2. Agitation by rotation or sonication was used in these trials. Analytical recoveries from these samples were computed after extraction and fluorescence measurement based on the mass of originally weighed material.

For 13 metals, interference studies were carried out by diluting the appropriate metal standard solution with 1%  $\text{NH}_4\text{HF}_2$ , such that the final concentration of the metal in the detection solution was 0.04, 0.4 or 2 mM. The potentially interfering metals were in  $\geq 400$ -fold molar excess to the beryllium that was present. The results from these trials, which were carried out using an Ocean Optics device (2 s integration), are shown in Table 3. Significant positive interference from iron which was measured initially (Table 3) disappeared several hours later, after allowing for precipitation to occur prior to reanalysis. Interference from titanium in the form of  $\text{TiO}_2$  was investigated in a separate experiment using a Turner Quantech fluorometer, where beryllium and  $\text{TiO}_2$  were spiked onto Whatman 541 filters at the levels shown in Table 4. Negative interference from titanium dioxide observed initially

**Table 3** Fluorescence measurements (a.u.) from interference study of 13 metals present in solution in many-fold excess compared to 0–1  $\mu\text{M}$  concentrations of beryllium

Metal, concentration	Fluorescence intensity (0 $\mu\text{M}$ Be)	Fluorescence intensity (0.1 $\mu\text{M}$ Be)	% difference	Fluorescence intensity (1 $\mu\text{M}$ Be)	% difference
(None)	0.005	0.112	—	1.078	—
0.4 mM Al	0.004	0.112	0.00	1.054	-2.22
0.4 mM U	0.004	0.110	-1.79	1.060	-1.67
2 mM Ca	0.004	0.112	0.00	1.057	-1.95
0.04 mM Li	0.004	0.112	0.00	1.060	-1.67
0.4 mM Pb	0.004	0.111	-0.89	1.105	2.50
0.4 mM Zn	0.003	0.112	0.00	1.103	1.02
0.4 mM Fe	0.003	0.101	-9.82	0.925	-14.2
0.4 mM V	0.003	0.114	1.79	1.083	0.46
0.4 mM Sn	0.003	0.113	0.89	1.105	2.50
0.4 mM W	0.003	0.116	3.57	1.103	2.32
0.4 mM Cu	0.003	0.114	1.79	1.062	-1.49
0.4 mM Ni	0.004	0.114	1.79	1.074	-0.37
0.4 mM Co	0.005	0.111	-0.89	1.030	-4.45

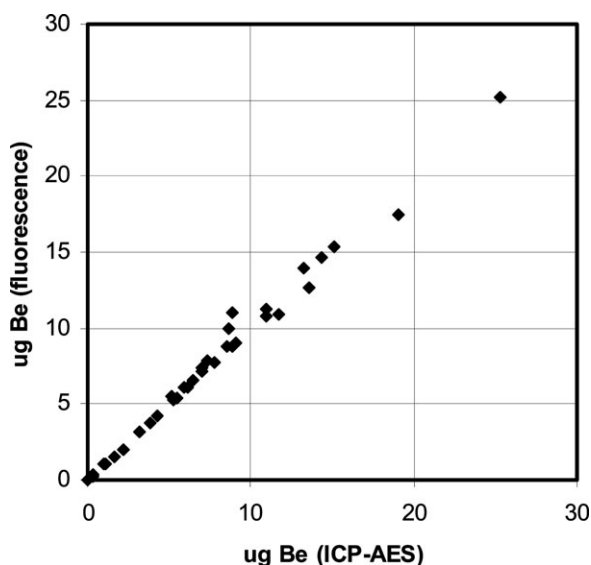
**Table 4** Interference study of beryllium fluorescence measurement (a.u.) in presence of titanium dioxide

Mass of Be on filter/ $\mu\text{g}$	Mass of $\text{TiO}_2$ on filter/mg	Beryllium/ $\mu\text{g}$ , determined by fluorescence	
		Initial intensity measurement	Measurement after additional filtration step
0.20	0.00	0.20	0.20
2.00	0.00	2.02	2.03
0.20	10.00	0.17	0.20
2.00	10.00	1.64	2.02
0.20	20.00	0.17	0.21
2.00	20.00	1.65	2.04

in fluorometric measurement was alleviated after a second filtration step was performed using nylon filters (Table 4).

Long-term sample stability studies of beryllium on MCE filters have been conducted in previous work to support NIOSH methods 7102 and 7300.<sup>5</sup> To supplement those data, an investigation of long-term stability was carried out whereby Whatman 541 filters were spiked with beryllium in solution form at 0.1  $\mu\text{g}$  Be per sample, and analyses were carried out for up to 30 days, as per NIOSH guidelines.<sup>11</sup> Samples were stored at room temperature, and HBQS fluorescence measurements were conducted using an Ocean Optics instrument (2 s integration time) after mechanical extraction in 1%  $\text{NH}_4\text{HF}_2$ . Results from these experiments showed no significant change in fluorescence intensity over the 30 day period. In a related study, long-term stability of the HBQS detection solution was investigated. Standard curves of beryllium concentration *versus* fluorescence intensity were obtained for freshly prepared detection solution and for the solution stored in a dark bottle at room temperature for a 12 week period. An Ocean Optics fluorometer (2 s integration time) was employed for these experiments. Fluorescence results from trace beryllium (0–30 ppb) with freshly prepared HBQS detection solution *vs.* 12 week old solution were essentially identical.

Field wipe samples (using Whatman 541 filters wetted with deionized water) were obtained from a machine shop and from a firing range at Los Alamos National Laboratory. These samples, which were taken from a variety of surfaces, were first processed and analyzed using the 1%  $\text{NH}_4\text{HF}_2$  extraction/portable fluorescence method.<sup>13</sup> The remaining extract solution was subsequently analyzed using ICP-AES.<sup>5,6</sup> Only 100  $\mu\text{L}$  of the 5 mL sample extract is required for the fluorescence measurement, so 98% of the remaining solution is available for subsequent confirmatory analysis. Results from this comparison, which consisted of the paired analysis of results from 50 wipe samples taken in the field, are shown in Fig. 2. The plot is very close to linear (slope = 1.007) and the correlation is extremely close to unity ( $r^2 = 0.9958$ ). For paired results above the respective method detection limits (*i.e.*,  $\approx 0.02 \mu\text{g}$  Be sample<sup>-1</sup>), the average relative percent difference between data obtained using the portable extraction/fluorescence method *vs.* ICP-AES analysis was 4.7% ( $n = 39$ ). For a subset of the field samples treated by extraction in 1%  $\text{NH}_4\text{HF}_2$  (*i.e.*,  $n = 19$ ), the remaining, undissolved wipe material was digested and analyzed by OSHA method 125-G.<sup>6</sup> No beryllium was detected in these samples: all results were below the MDL.



**Fig. 2** Field data from wipe samples: Comparison of extraction and portable fluorescence measurement vs. ICP-AES measurement of extract solutions.

Interlaboratory round-robin analysis results from nine participating laboratories that returned results are summarized in Table 5 (data are updated from ref. 17). The volunteer laboratories were requested to carry out the field extraction/fluorescence method for beryllium, and to report the results in terms of  $\mu\text{g Be}$  per sample. Results were reported for MCE and Whatman 541 filters spiked with beryllium (from beryllium sulfate solution) at levels between 0.05 and 0.5  $\mu\text{g Be}$  per sample. Overall mean values were computed based on the pooled mean values (if applicable) reported by each laboratory for each sample. Results from blank measurements were all below the reported method detection limit ( $<0.02 \mu\text{g Be}$  per sample). Interlaboratory relative standard deviations (RSDs) were found to range from  $\approx 5\%$  to  $\approx 10\%$ . Bias estimates of overall means were calculated vs. the reference values listed in the first column of Table 5.

## Discussion

It is pertinent to consider applicable action levels for beryllium in workplace air and on surfaces in view of the MDL estimated for the portable fluorescence method. Generally, in order to ensure that quantitative measurements can be achieved at the limit value of concern, it is desired that the MDL be at least an order of magnitude less than the applicable action level.<sup>11</sup> Several action levels for beryllium that have been established by government agencies in the US and in Europe are summarized in Table 6. The lowest applicable action levels for beryllium have been promulgated by the US Department of Energy (DOE).<sup>18</sup> For full-shift air samples and for surface dust samples of  $100 \text{ cm}^2$  area, it can be seen that an estimated MDL of  $\approx 0.004 \mu\text{g Be}$  per sample is more than 10 times less than all of the action levels listed in Table 6. Therefore, the portable fluorescence method can be used to quantitatively measure beryllium at the trace levels required (see, e.g., Fig. 1).

**Table 5** Interlaboratory round-robin analysis results ( $n = 9$ ) from MCE and Whatman 541 filters spiked with beryllium sulfate

Beryllium level/ $\mu\text{g Be sample}^{-1}$	Reported average $\pm$ std. dev./ $\mu\text{g Be sample}^{-1}$	Inter-laboratory RSD <sup>a</sup> (%)	Estimated bias
MCE filters			
0.050	$0.052 \pm 0.0034$	6.5	0.040
0.10	$0.10 \pm 0.0048$	4.8	0.00
0.20	$0.21 \pm 0.018$	8.6	0.050
0.40	$0.42 \pm 0.040$	9.5	0.050
Whatman 541 filters			
0.050	$0.053 \pm 0.0054$	10.2	0.060
0.10	$0.11 \pm 0.011$	10.0	0.10
0.20	$0.21 \pm 0.0094$	4.5	0.050
0.40	$0.41 \pm 0.025$	6.1	0.025

<sup>a</sup> (Relative standard deviation).

Beryllium recoveries from a representative soluble compound (*i.e.*, beryllium sulfate) are quantitative, as indicated by recovery values close to 100% (Tables 1 and 2). Beryllium oxide, which is highly refractory, is more difficult to extract, as evidenced by somewhat lower recoveries from BeO obtained by mechanical extraction (Tables 1 and 2). BeO recoveries are improved to 90% and better if heating is applied during extraction (Table 1). Recoveries of beryllium from spiked MCE and Whatman 541 filters are quantitative for both sampling media (Tables 1 and 2); this is true for beryllium sulfate, beryllium metal powder and beryllium oxide (especially if heating is used in extraction of BeO). However, somewhat lower recoveries are obtained from Palintest wipes spiked with beryllium sulfate or beryllium oxide, and beryllium recoveries from Ghost Wipes are unacceptably low, presumably due to matrix interferences (Table 2). The results shown in Tables 1 and 2 indicate that 1% ammonium bifluoride is an effective medium for the quantitative extraction of beryllium, even from challenging matrices such as high-fired beryllium oxide. The data of Table 2 indicate that large masses of beryllium can be quantitatively extracted and measured, thereby demonstrating the robustness of the method for

**Table 6** European and US action levels for beryllium in workplace air and in surface dust

Country (organization)	8 h TWA <sup>a</sup> action level (air)
Austria, France, Germany, Spain, Sweden, UK, US (OSHA)	$2.0 \mu\text{g m}^{-3}$
Denmark	$1.0 \mu\text{g m}^{-3}$
US (NIOSH)	$0.5 \mu\text{g m}^{-3}$
Ceiling action level (air)	
Austria	$8.0 \mu\text{g m}^{-3}$
US (OSHA)	$5.0 \mu\text{g m}^{-3}$
Denmark	$2.0 \mu\text{g m}^{-3}$
US (DOE)	$0.2 \mu\text{g m}^{-3}$
Surface action level	
US (DOE)	$3.0 \mu\text{g}/100 \text{ cm}^2$ (housekeeping)
US (DOE)	$0.2 \mu\text{g}/100 \text{ cm}^2$ (equipment release)

<sup>a</sup> Time-weighted average.

samples that may contain beryllium in extremely high excess with respect to the action levels summarized in Table 6.

The data presented in Tables 3 and 4 show that, with the exception of iron and titanium dioxide, the portable fluorescence method does not suffer from interferences from other metals that are present in significant excess. Moreover, interferences from Fe and TiO<sub>2</sub>, which can be detected visually (by yellowish color or by turbidity, respectively), are effectively eliminated through further sample processing. Sample stability and the stability of the detection solution are excellent, as indicated by experimental results (not shown).

Results from field samples (Fig. 2) and from interlaboratory round-robin analysis (Table 5) offer further evidence of the robustness of the fluorescence method. The agreement observed for extracts of wipe samples between the portable fluorescence method and ICP-AES is outstanding (Fig. 2). Also, interlaboratory agreement when using the extraction/portable fluorescence method is excellent (Table 5). For air filter samples, pooled estimates of precision and bias (for the range 0.05–0.40 µg Be sample<sup>-1</sup>) were 0.074 (±0.021) and 0.035 (±0.024), respectively. Based on the interlaboratory data, the overall method performance for air filter samples yielded an analytical accuracy estimate of 16% (±5%), which meets NIOSH criteria for method accuracy.<sup>11</sup> For wipe samples, pooled estimates of precision and bias were 0.077 (±0.028) and 0.059 (±0.031), respectively. Based on the interlaboratory results, the overall method performance for wipe samples gave an analytical accuracy estimate of 19% (±6%), which also meets NIOSH accuracy criteria.

In conclusion, the fluorescence method described has been demonstrated to operate successfully under various operating conditions, including the detection of beryllium both in laboratory settings and in field trials. The procedure fulfills the requirements for a fast, inexpensive, field-deployable method for the determination of beryllium in workplace samples. There are several advantages of the system: it is rapid (test results within one hour); high throughput; beryllium-specific; low capital cost (≈\$10,000); field or laboratory deployable; detection limit less than 0.02 mg Be per sample; uses less hazardous solutions; uses only a fraction of material collected, an advantage for re-verification; does not require highly trained laboratory personnel.

The method described has been published as an ASTM International voluntary consensus standard,<sup>13</sup> and has also been submitted for publication as a NIOSH analytical method.

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