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Ultra-trace determination of beryllium in occupational hygiene samples by ammonium bifluoride extraction and fluorescence detection using hydroxybenzoquinoline sulfonate[☆,☆☆]

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Abstract

A highly sensitive molecular fluorescence method for measuring ultra-trace levels of beryllium has been previously described. The method entails extraction of beryllium workplace samples by 1% ammonium bifluoride (NH_4HF_2, aqueous), followed by fluorescence detection using hydroxybenzoquinoline sulfonate (HBQS). In this work, modification of the existing procedure resulted in a significant improvement in detection power, thereby enabling ultra-trace determination of beryllium in air filter and surface wipe samples. Such low detection limits may be necessary in view of expected decreases in applicable occupational exposure limits (OELs) for beryllium. Attributes of the modified NH_4HF_2 extraction/HBQS fluorescence method include method detection limits (MDLs) of <0.8 ng to ≈2 ng Be per sample (depending on the fluorometer used), quantitative recoveries from beryllium oxide, a dynamic range of several orders of magnitude, and freedom from interferences. Other key advantages of the technique are field portability, relatively low cost, and high sample throughput. The method performance compares favorably with that of inductively coupled plasma-mass spectrometry (ICP-MS).
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1. Introduction

Beryllium is a lightweight but durable metal that has numerous industrial and defense materials applications, including in aerospace, nuclear energy and weapons, electronics and communications, and automobile manufacturing [1]. When beryllium is alloyed with copper, aluminum or other metals, high-performance materials with a variety of attributes can be fabricated. Beryllium oxide has high thermal conductivity and is electrically insulating, properties that enable heat to be effectively dissipated in microscale integrated circuits. However, human exposures to beryllium can cause an immune system response known as beryllium sensitization [2], and can lead to the development of chronic beryllium disease (CBD), an incurable and potentially fatal progressive lung ailment [3]. The prevention of occupational exposures to beryllium particles by inhalation and/or skin contact requires the ability to measure this element at extremely low levels in workplace air and on surfaces.

Analytical methods for determining trace levels of beryllium in occupational hygiene samples have been recently reviewed [4]. While a variety of analytical techniques have been applied to trace beryllium measurement in the workplace, atomic spectrometric methods such as graphite furnace atomic absorption

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spectrometry (GFAAS) and inductively coupled-plasma atomic emission spectrometry (ICP-AES) are the most widely used methodologies for industrial hygiene monitoring purposes [5]. In pursuit of greater analytical sensitivity, inductively couple plasma-mass spectrometry (ICP-MS) for environmental analysis [6] has recently become more widely used for beryllium measurements in the occupational hygiene field. Compared to GFAAS and ICP-AES, ICP-MS offers lower detection limits for beryllium (and other elements), enabling ultra-trace analysis that may be required for short-term measurements and/or reduced occupational exposure limits (OELs).

Because of the complexity and expense of atomic spectrometric instrumentation, alternative methodologies have been investigated for trace beryllium measurements, including portable techniques such as colorimetry [7], electroanalysis [8,9], and fluorescence [10]. Recently a portable extraction/fluorescence procedure with an estimated method detection limit (MDL) that is competitive with GFAAS and ICP-AES was standardized and validated [11]. The method entails extraction of beryllium using a dilute aqueous solution of ammonium bifluoride, followed by fluorescence detection of beryllium using hydrobenzoquinoline sulfonate [12]. In this work we report on the modification of the fluorescence technique, which has enabled achievement of an estimated MDL that is comparable to that of ICP-MS. The modified fluorescence method has been applied to the determination of ultra-trace quantities of beryllium in occupational hygiene samples.

2. Experimental

2.1. Reagents, materials, and equipment

High-purity beryllium oxide powder (99.98% BeO) was obtained from Aldrich (Milwaukee, WI, USA). Beryllium metal (>99% Be) powder came from Matheson (Norwood, OH, USA). Ammonium bifluoride extraction solution (1% NH_4HF_2, aqueous), as well as fluorescence detection solution (aqueous) containing hydroxybenzoquinoline sulfonate (HBQS, 1.1 mM), ethylenediamine tetraacetic acid (EDTA, 1 mM), and L-lysine monohydrochloride (100 mM), were provided by Berylliant, Inc. (Tucson, AZ, USA). Low-concentration beryllium calibration standards (0–0.2 $\mu g\,mL^{-1}$) were prepared daily by dilution of aliquots from standard stock solutions (Berylliant). The pH of the detection solution was adjusted to 12.8 ± 0.1 with 10 M NaOH (Fisher Scientific, Hampton, NH, USA) with the aid of mechanical micropipets (Eppendorf, Hamburg, Germany) and an Orion model 710 pH meter (Thermo, Beverly, MA, USA) that was calibrated using pH 4.0, 7.0, and 10.0 buffers (Fisher Scientific). Deionized water (18 MΩ cm resistivity), prepared using a MilliQ® (Millipore, Billerica, MA, USA) water purification system, was used for all experiments.

Mixed-cellulose ester (MCE) filters (37 mm diameter, 0.8 μm pore size) and Whatman 541 cellulosic filters (47 mm diameter) were purchased from SKC, Inc. (Eighty-Four, PA, USA). Performance evaluation materials consisting of MCE and Whatman 541 filters spiked with extremely low levels of beryllium (0.002–0.05 μg Be per filter) were prepared by a contract labo-

ratory (Environmental Resource Associates, Arvada, CO, USA) from an aqueous 1000 $\mu g\,mL^{-1}$ beryllium standard solution (Inorganic Ventures, Lakewood, NJ, USA). MCE filters spiked with BeO (Aldrich) at levels of 0.2 and 0.5 μg per filter (±1%), prepared from aqueous suspensions [13], were provided by High-Purity Standards (Charleston, SC, USA). Where applicable, materials were weighed to the nearest 0.0001 g using a Mettler Toledo (Columbus, OH, USA) model AT 261 high-precision analytical balance.

Plastic 15 mL centrifuge tubes, 25 mm diameter nylon microfilters (0.45 μm pore size), plastic 5 mL syringes, and disposable fluorescence cuvettes (10 mm diameter) were obtained from Fisher Scientific. A Labquake® rotator (Barnstead, Dubuque, IA, USA) was used for mechanical extraction of some samples at room temperature (23 ± 1 °C), and a VWR Digital Heatblock (West Chester, PA, USA) was employed for sample heating at 85 ± 2 °C, where necessary.

Fluorometers used were Ocean Optics S2000-FL (Dunedin, FL, USA), Turner Quantech® (Barnstead), and Spex Fluorolog2 (Horiba Ltd., Tokyo, Japan) instruments. The Ocean Optics instrument utilizes a 380 nm light-emitting diode (LED) as an excitation source, and a diode array detector records the fluorescence signal over the range 300–800 nm; optical fibers transmit the source beam and the detected radiation at 90° to the incident source radiation. The Turner Quantech fluorometer employs bandpass filters to attenuate the excitation and detection beams, with source radiation of 360–390 nm and a detection spectral window of 440–490 nm. A quartz halogen lamp provides source radiation and a photomultiplier tube is used for detection. The Spex Fluorolog2 device utilizes a xenon arc lamp source (360–460 nm), monochromators for source and emission radiation (3 nm slit widths), and a photomultiplier tube detector (240–850 nm).

2.2. Electron microscopy

Scanning electron microscopy (SEM) [14] was performed using a Hitachi S-3000N instrument (Hitachi America, Brisbane, CA, USA). SEM images were obtained at 15 kV accelerating voltage and 300× magnification using a secondary electron detector.

2.3. Extraction and fluorescence measurement

To attain extremely low method detection limits for beryllium, and also to obtain quantitative recoveries from refractory beryllium compounds that are extremely difficult to dissolve, the procedure required significant modification of the published test method [15]. Specific differences entailed heating (versus mechanical agitation) to dissolve refractory BeO, and 1:5 dilution (versus 1:20) of extract solutions with the detection solution. Experiments on performance evaluation samples were carried out blind by analysts at four different laboratories, using one or more of the three fluorometric instruments.

First, the MCE and Whatman 541 filter samples containing trace beryllium were placed into 15 mL plastic centrifuge tubes. Then 5 mL of 1% NH_4HF_2 (aqueous) was added to each

centrifuge tube containing the filter sample, and each tube was capped securely. If necessary, a clean stirring rod was used to push the filter to the bottom of the centrifuge tube to ensure that the filter was completely immersed in the extraction solution. Extraction was carried out for 30 min either by mechanical agitation at room temperature using the rotator, or by heating at 85 °C using the hot block. (Samples containing soluble beryllium or beryllium metal were treated using mechanical extraction, while filters spiked with BeO were subjected to heating to facilitate dissolution.) After extraction (and cooling of sample extracts to room temperature, if necessary), sample extracts were filtered using the nylon microfilters attached to 5 mL syringes. Then 0.4 mL of extract solution was pipetted into a fluorescence cuvette, to which 1.6 mL of detection solution containing the fluorescence reagent (HBQS) was added. (The reaction between dissolved beryllium and HBQS to form the fluorophore adduct is instantaneous.) The fluorescence of the Be-HBQS complex was subsequently measured ($\lambda_{max} \approx 475$ nm) using one of the three fluorometers.

3. Results

Fluorescence spectra of extremely low concentrations of beryllium in the presence of HBQS, obtained using the Ocean Optics device, are presented in Fig. 1. Unreacted HBQS yields a fluorescence band with $\lambda_{max} \approx 590$ nm, while the fluorescence of the Be-HBQS complex is blue-shifted, with $\lambda_{max} \approx 475$ nm. Beryllium concentrations of less than 0.2 ng mL^{-1} were measured quantitatively using the HBQS fluorescence reagent with 1:5 dilution, offering a dramatic increase in sensitivity over beryllium fluorophores investigated previously [16–21]. This technique also offers a significant improvement in detection power compared to the method employing 1:20 dilution of the sample with detection solution [22]. For calibration standards in the range of a few parts-per-billion and below (i.e., 0.0, 0.2, 0.5, 0.8, 2.0, and 4.0 µg mL^{-1}), the measured coefficient of estimation $r^2 = 1.00$.

Recovery data from samples of beryllium metal and BeO in the absence and presence of sampling media (i.e., MCE

Table 1
Beryllium recoveries from beryllium metal and BeO in the absence and presence of sampling media

Sample/media ($n = 3$)	Extraction	Mean recovery (%)	R.S.D.[a] (%)
Be (no media)	Rotator	96	3.1
Be/MCE	Rotator	93	7.3
Be/Whatman 541	Rotator	95	4.2
BeO (no media)	Rotator	86	6.8
BeO (no media)	Heat block	97	6.6
BeO/MCE	Rotator	86	5.9
BeO/MCE	Heat block	99	7.7
BeO/Whatman 541	Rotator	86	7.8
BeO/Whatman 541	Heat block	96	6.2

Masses treated were 5–10 mg per sample.
[a] Relative standard deviation.

and Whatman 541 filters) are shown in Table 1. Recoveries were computed after extraction of 5–10 mg samples in 5 mL of 1% NH_4HF_2 and HBQS fluorescence measurement at 475 nm. These results show that mechanical extraction at room temperature (using the laboratory rotator) is effective for obtaining near quantitative (>90%) recoveries of beryllium metal. However, heating (at $\approx$85 °C by means of the heating block) is required in order to yield quantitative recoveries of BeO. The presence of active fluoride ions (from HF by dissociation of NH_4HF_2 in acidic medium) enables dissolution of refractory materials such as BeO.

Follow-up experiments were carried out to investigate the NH_4HF_2 extraction/HBQS fluorescence method from MCE filters spiked with low levels of BeO prepared from slurries. An SEM image from a representative filter fortified with BeO in this manner is shown in Fig. 2, and performance data from the BeO-spiked filters are presented in Table 2. The BeO particle in the SEM image consists of an agglomerate of a few micrometers in average diameter, comprised of primary particles of about 200 nm diameter. The results of Table 2 indicate that mechanical agitation of BeO-spiked MCE filter samples at room temperature yields beryllium recoveries of about 70%, while heating block extraction at $\approx$85 °C gives recoveries near 100%.
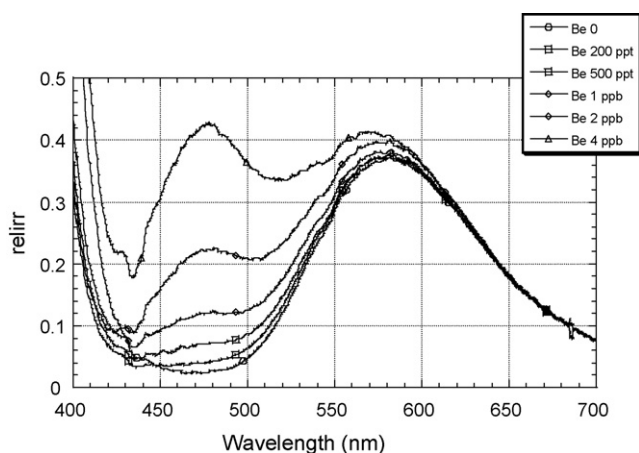

Fig. 1. Fluorescence spectra of trace concentrations of beryllium in the presence of hydroxybenzoquinoline sulfonate (HBQS).
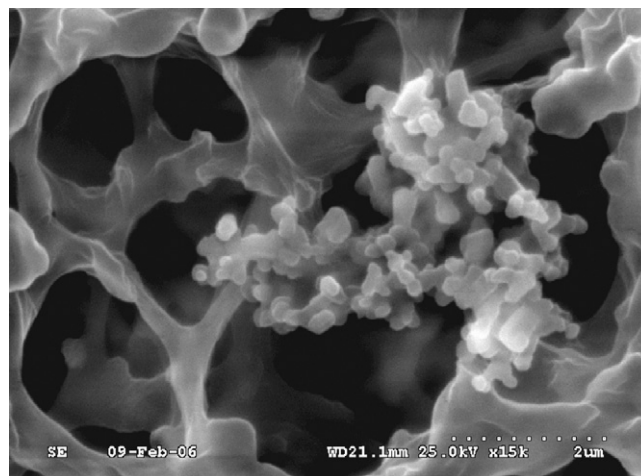

Fig. 2. Scanning electron micrograph of BeO particle on MCE filter (BeO-spiked filters courtesy of High-Purity Standards).

Table 2
Beryllium masses measured from MCE filters spiked with traces of BeO (prepared from slurries [13])

Beryllium loading level	Mass extracted by rotation at $\approx 23\,^{\circ}\mathrm{C}$ ($n=4$)	Mass extracted by heating at $\approx 85\,^{\circ}\mathrm{C}$ ($n=6$)
Media blank	N.D.[a]	N.D.
0.20 µg	0.135 µg ($\pm$0.0034)[b]	0.201 µg ($\pm$0.0074)
0.50 µg	0.365 µg ($\pm$0.040)	0.506 µg ($\pm$0.0068)

[a] None detected (<MDL).
[b] $\pm$Values are standard deviations.

The method detection limit was estimated by measuring a minimum of ten clean (unspiked) filters, and reporting the MDL as three times the standard deviation of repeat media blank measurements, in accordance with a consensus standard procedure [23]. This method of MDL estimation is intended to take into account the potential nonuniformity in blank sampling media. Results from these trials are presented in Table 3 for the three fluorometric instruments investigated in this work. Estimated MDLs for beryllium ranged from <0.8 ng per filter for the Turner instrument to ≈ 2 ng per filter for the Spex device, corresponding to solution beryllium concentrations of ≈ 0.03 to $\approx 0.08\,\mu\mathrm{g\,L^{-1}}$. For purposes of comparison, it is noted that estimated MDLs for beryllium by ICP-MS of $\approx 0.03\,\mu\mathrm{g\,L^{-1}}$ been reported for environmental samples [6,24].

Potential interferences from a number of other metals have been investigated in previous work and have been found to be negligible, with the exception of iron and titanium dioxide [11]. In subsequent work, interference studies with iron and titanium dioxide were carried out at beryllium levels of 2–5 ng per filter, and with TiO_2 or Fe at 10-fold and 100-fold excess, respectively. Negative interference from TiO_2 observed initially after extraction was alleviated via additional filtering through nylon microsyringe filters: initial recovery of 83% ($\pm$4%) improved to 100% ($\pm$3%) after filtering. Negative interference from Fe seen at first was diminished after allowing the extract solution to sit for several hours to allow for precipitation of suspended hydrates: initial recovery of 75% ($\pm$6%) improved to 98% ($\pm$2%) after settling.

Analytical results from MCE and Whatman 541 filters spiked with beryllium at levels of 0–0.05 µg per sample are summarized in Table 4. Data were reported from four different laboratories using three different fluorescence instruments, and it is reiterated that spike levels were unknown to each analyst. The results of Table 4 show mean reported values that are close to the spike levels, and precision estimates (as measured by relative standard deviations [R.S.D.s]) range from ≈ 2–3% for levels of 0.02–0.05 µg Be, to ≈ 13–19% for MCE and Whatman 541 fil-

Table 3
Estimated method detection limits for beryllium in MCE and Whatman 541 filters from three different fluorometers

Fluorometer	MDL, MCE filters	MDL, Whatman 541 filters
Turner Quantech	0.00075 µg	0.00078 µg
Ocean Optics S2000-FL	0.0015 µg	0.0016 µg
Spex Fluorolog2	0.0019 µg	0.0021 µg

Table 4
Analysis results from MCE and Whatman 541 filters spiked with ultra-low levels of beryllium

Spike level (µg Be) ($n=6$)	Mean ($\pm$S.D.)[a] (µg Be)	R.S.D.[b] (%)
MCE filters		
Blank	N.D.[c]	–
0.002	0.0023 ($\pm$0.00030)	13
0.005	0.0052 ($\pm$0.00012)	2.3
0.020	0.0210 ($\pm$0.00055)	2.6
0.050	0.0504 ($\pm$0.0014)	2.8
Whatman 541 filters		
Blank	N.D.	–
0.002	0.0025 ($\pm$0.00048)	19
0.005	0.0056 ($\pm$0.00035)	6.3
0.020	0.0209 ($\pm$0.00049)	2.3
0.050	0.0507 ($\pm$0.00013)	2.6

Data are pooled from three different laboratories using three different fluorometers.

[a] Standard deviation.
[b] Relative standard deviation.
[c] None detected (<MDL).

ters spiked at 0.002 µg. Results from blanks were all below the MDL for each fluorometer. In consideration of the data shown in Tables 1–4, the fluorescence method demonstrates a dynamic range of over four orders of magnitude.

4. Discussion

GFAAS and ICP-AES techniques offer estimated MDLs of 0.005 and 0.009 µg Be per sample, respectively [25]. These MDLs are adequately low for beyllium measurements with reference to OELs that have been established by regulatory bodies such as the US Occupational Health and Safety Administration (OSHA) [26]. The OSHA beryllium permissible exposure limit (PELs) for 8 h time-weighted average (TWA) sampling is $2.0\,\mu\mathrm{g\,m^{-3}}$, which translates to approximately 2 µg of beryllium per sample (assuming an 8 h sampling time and a sampling flow rate of about $2\,\mathrm{L\,min^{-1}}$). This is a mass that is well greater than $10\times$ the MDLs for GFAAS and ICP-AES, and can therefore be measured quantitatively by these techniques. Also, beryllium measurements pertaining to the OSHA permissible short-term exposure limit (STEL) of $5.0\,\mu\mathrm{g\,m^{-3}}$ do not require lower MDLs than those offered by GFAAS or ICP-AES. Assuming a 15 min minimum sampling time at $2\,\mathrm{L\,min^{-1}}$ typical sampling rate, the OSHA PEL (STEL) is about 0.15 µg of beryllium per sample, a mass that can still be quantified by GFAAS and/or ICP-AES.

Recently there has been a trend toward reduced airborne beryllium OELs, resulting in a need for even lower analytical method detection limits for this element. The US Department of Energy (DOE) promulgated an OEL for beryllium (8 h TWA) of $0.2\,\mu\mathrm{g\,m^{-3}}$, and also established a surface beryllium contamination limit of 0.2 µg per $100\,\mathrm{cm^2}$ of sampled surface area [27]. These limit values are nonetheless accessible by GFAAS and ICP-AES. Yet based on research suggesting beryllium sensitization and disease from extremely low exposures to this element [28], OSHA is considering a significant reduction in the beryllium permissible exposure limit (PEL) [29]. In 2005

the American Conference of Governmental Industrial Hygienists (ACGIH) issued a Notice of Intended Change (NIC) to the beryllium Threshold Limit Value (TLV®), which entailed a 100-fold reduction in the TLV, from 2 to $0.02 \, \mu g \, m^{-3}$ of sampled air [30]. Such a reduction in the limit value would necessitate a lower MDL than that offered by GFAAS or ICP-AES. A revised NIC was published by ACGIH a year later, which proposed TLVs for 8 h TWA and STEL sampling of 0.05 and $0.2 \, \mu g \, m^{-3}$, respectively [31]. The use of ICP-MS or another highly sensitive technique such as the HBQS fluorescence method would be needed to achieve MDLs necessary for determination of the ultra-trace levels of beryllium that could be required in view of reduced OELs for this element.

It is of interest to investigate the ability of the HBQS fluorescence method to determine beryllium at the lowest potentially applicable OEL. Consider a hypothetical situation in which a personal air sample is obtained to measure beryllium in the workplace with respect to the proposed ACGIH STEL. If a 15 min sample is collected using a typical sampling flow rate of $2 \, L \, min^{-1}$, the $0.2 \, \mu g \, m^{-3}$ STEL would correspond to approximately $0.006 \, \mu g$ of beryllium. The results of Table 4 show R.S.D.s of about 2% for beryllium levels near this value, thereby demonstrating that beryllium can be measured quantitatively at this low level. In view of short-term exposure measurement, it is especially noteworthy that the NH_4HF_2 extraction/HBQS fluorometry method is field-portable, thereby allowing for on-site monitoring of beryllium with respect to the proposed STEL. The portable extraction/fluorescence method is also applicable to field-based measurement of trace beryllium on surfaces at levels well below the DOE action level of $0.2 \, \mu g$ Be per $100 \, cm^2$ sample area. Although such low levels of beryllium can be measured by ICP-MS, this spectrometric technique is not field-portable.

Apart from issues of analytical sensitivity, it is also noteworthy that the use of 1% NH_4HF_2 and heating affords the ability to quantitatively extract beryllium from BeO (Tables 1 and 2), which is refractory. This obviates the need for the use of strong acid/high heat digestions (using, e.g. HF and H_2SO_4), which are required for BeO dissolution when using reference spectrometric methods. We also note that the BeO-spiked filters are useful as representative performance evaluation materials (PEMs), in that they present a more realistic and challenging matrix to laboratories. The morphology of the BeO particle shown in the SEM image (Fig. 2) is consistent with that of airborne particles of BeO fired at temperatures of >2000 °C [32]. It is planned to prepare BeO-spiked PEMs for proficiency testing programs, to which the NH_4HF_2 extraction/HBQS fluorescence method could be used as a recognized analytical test method by laboratory accreditation organizations such as the American Industrial Hygiene Association (AIHA) [33].

In conclusion, ultra-trace determination of beryllium can be carried out by means a field-portable extraction procedure, using fluorescence for detection. The method performance is comparable to that of ICP-MS, but fluorescence analyses can be carried out at a fraction of the cost of atomic spectrometry. Analytical attributes of the NH_4HF_2 extraction/HBQS fluorescence method are: (1) the estimated MDLs (<0.8 to ≈2 ng per sample) are comparable to those of ICP-MS; (2) high specificity

for beryllium, as evidenced by lack of interferences from other metals; (3) recoveries from refractory BeO are quantitative; and (4) the dynamic range extends over four orders of magnitude. Other key advantages of the technique include field portability, low cost (compared to, e.g. ICP-MS), and high throughput (≈30 samples per 90 min). If necessary in the future, even lower detection limits for beryllium in workplace samples should be attainable through the use of preconcentration techniques such as solid-phase extraction [34].

Acknowledgments

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