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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).

Keywords: Air monitoring; Beryllium; Extraction; Fluorescence; Trace analysis; Workplace

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 to12.8 ± 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 laboratory (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