Beryllium colorimetric detection for high speed monitoring of laboratory environments

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Abstract

The health consequences of beryllium (Be^{2+}) exposure can be severe. Beryllium is responsible for a debilitating and potentially fatal lung disease, chronic beryllium disease (CBD) resulting from inhalation of beryllium particles. The US Code of Federal Register (CFR), 10 CFR 850, has established a limit of $0.2\,\mu g$ beryllium/100 cm^2 as the maximum amount of beryllium allowable on surfaces to be released from beryllium work areas in Department of Energy (DOE) facilities. The analytical technique described herein reduces the time and cost of detecting beryllium on laboratory working surfaces substantially. The technique provides a positive colorimetric response to the presence of beryllium on a $30.5\,cm \times 30.5\,cm$ (1 ft^2) surface at a minimum detection of $0.2\,\mu g/100\,cm^2$. The method has been validated to provide positive results for beryllium in the presence of excess iron, calcium, magnesium, copper, nickel, chromium and lead at concentrations 100 times that of beryllium and aluminum and uranium ($UO_2{}^{2+}$) at lesser concentrations. The colorimetric detection technique has also been validated to effectively detect solid forms of beryllium including $Be(OH)_2$, $BeCl_2$, $BeSO_4$, beryllium metal and BeO.
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1. Introduction

Beryllium is a unique metal with exceptional material properties. It is three times lighter than aluminum, six times stiffer than steel, has a high melting point and high heat absorption capacity. Due to it's highly desirable material properties beryllium has become an essential element used in the aerospace, computer, electronics and nuclear industries [1]. Beryllium is used in the manufacture of instruments and structural components such as aircraft and

space shuttle brakes, satellite mirrors, X-ray windows, electrical circuits and computer components and it serves as a neutron moderator in nuclear reactors and in nuclear weapons.

Beryllium is also a toxic metal that poses extreme risks to human health. Inhalation of particulate beryllium is responsible for the often-fatal lung disease, chronic beryllium disease (CBD) [2,3]. New scientific evidence indicates that beryllium sensitization can occur as a result of skin contact with fine particulate beryllium [4]. The United States Environmental Protection Agency (USEPA) has recently added beryllium to the class A carcinogen list. Additionally the toxicity of beryllium is associated with disturbing normal ossification processes of bone [5].

CBD is a lung disease characterized by granulomas that develop from a cell-mediated response to inhaled beryllium. CBD occurs in approximately 1–6% of exposed individuals depending on individual hypersensitivity to the metal [6]. Sympomatic response can be delayed from 10 to 40 years after exposure making it difficult to relate exposure to susceptibility [3,6–9]. There is currently no cure for CBD. Ongoing research is focused on understanding the relationship between CBD occurrence and risk factors such as the form of beryllium and genetic susceptibility [6,7,10,11].

Since beryllium poses such extreme risks to human health, release to workplace environments is heavily regulated. Beryllium air concentration limits have been mandated by Occupational Safety and Health Association (OSHA) regulations, 29 CFR 1910 (1999) [12]. Department of Energy (DOE) rules, 10 CFR 850 (2001), address beryllium air and surface concentration limits [13]. The maximum concentration of beryllium allowable on surfaces in designated DOE beryllium work areas during non-operational periods is $3\,\mu g/100\,cm^2$ [13]. In non-beryllium work areas or in order for equipment to be released from a beryllium area, the surface concentration may not exceed $0.2\,\mu g$ beryllium/100 cm^2 [13]. OSHA's current limits for beryllium are $2\,\mu g/m^3$ as an 8 h time-weighted average (TWA), $5\,\mu g/m^3$ as a 30 min exposure concentration and $25\,\mu g/m^3$ as a ceiling concentration [12]. The National Institute for Occupational Safety and Health (NIOSH) recommends a non-enforceable ceiling limit of $0.5\,\mu g/m^3$ [14].

Handling of beryllium-containing solids and solutions can result in surface contamination of benchtops, walls, hoods, floors and other workplace surfaces. It is imperative to monitor work environments to prevent worker exposure and to understand or diagnose operations that could result in beryllium contamination. Rapid detection of beryllium contamination is essential to worker protection and contamination control. Presently, a technique to rapidly monitor surfaces for beryllium contamination to levels of $0.2\,\mu g/100\,cm^2$ has not been established. Generally, the technique prescribed by health and safety personnel that monitor beryllium work areas is a surface swipe technique described by OSHA modified method ID-125G. This technique uses hydrogen peroxide and sulfuric acid to digest cellulose ester membranes used to swipe potentially beryllium-contaminated surface areas and HCl to dissolve elements retrieved on the filters. An inductively coupled argon plasma-atomic emission spectrometer (ICP-AES) is used to quantify beryllium in the samples. Analytical costs are high and it takes a minimum of 24 h to obtain analytical results. For example, at Los Alamos National Laboratory, the cost associated with analyzing a single swipe according to OSHA ID-125G is approximately US$ 250. The backlog of beryllium analytical samples at many facilities can lead to delays of up to 1 week to obtain sampling results from routine housekeeping.
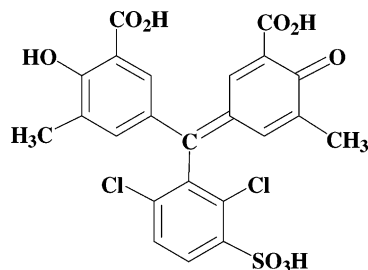
Fig. 1. Structure of chrome azurol S.

A beryllium monitoring technique is required that can be implemented on a routine basis to ensure regulatory requirements are met and to assist workers in characterizing levels of contamination in their personal lab space between quality control assured lab inspections conducted by monitoring specialists. The technique must be technologically simple, inexpensive and able to detect to the legislatively mandated minimum workplace beryllium concentrations. Colorimetry has been successfully used to detect many metals including lead, copper and uranium. Numerous colorimetric techniques exist in the literature for the detection of beryllium. Most of these techniques are for detecting beryllium in drinking water. Table 1 summarizes various beryllium colorimetric techniques. Of the techniques summarized, only Mordberg and Fil'kova developed a spot test to measure beryllium on surfaces [30].

The technique developed by Mordberg and Fil'kova utilized chrome azurol S (CAS; 2″,6″-dichloro-3,3′-dimethyl-4′-hydroxy-3″-sulfofuchson-5,5′-dicarboxylic acid, Fig. 1) as the colorimetric reagent for beryllium detection and ethylenediaminetetraacetic acid (EDTA) to bind interfering elements. The technique required that the surface evaluated be flat because 1 ml of 2% HCl was deposited on the surface being tested. A wax pencil was used to delineate a 4 cm diameter circular area ($12.5 \, cm^2$) to be sampled. The acid was allowed to contact the surface for 5 min before it was removed from the surface with a bulb pipette and placed in a dry test tube. For the colorimetric analysis, ash-free filters were prepared by pressing a paraffin sheet against the filter with a hot (60–80 °C) 13 mm metallic tube to delimit sectors of the filters for the drop analysis. Within each 13 mm ring, 0.01 ml of 1% CAS was applied, the ring was allowed to dry, 0.01 ml of 5% EDTA was applied, the ring was allowed to dry again, 0.01 ml of solution collected from a sampled surface was applied, the ring was allowed to dry, and finally 0.01 ml of a buffer solution (1 M ammonia +1 M ammonium chloride, pH 9.8–10) was applied and allowed to dry. Blue coloration indicated the presence of beryllium on the surface, and the sensitivity of the technique was 16 μg beryllium/100 cm^2.

The objective of this research was to develop a colorimetric test that could be used to sample any surface in a beryllium work area, regardless of the orientation of the surface, to a detection limit of 0.2 μg beryllium/100 cm^2. The resulting beryllium surface swipe technique described herein is a sensitive, qualitative test that can be used to rapidly check for the presence of beryllium on laboratory surfaces with low cost and modest technological requirements. The technique is based on the method employed by Mordberg and Fil'kova

Table 1
Summary of beryllium colorimetric tests documented in literature

Medium evaluated	Colorimetric compound	Reference
Ag(I) and Hg(II) in solution; potential for other inorganic salts	LI-complex (reaction product of 2-trichloro-methylbenz-imidazole (TCMB) + pyridine)	[15]
Beryllium in drinking water	Aluminon	[16]
Beryllium determination on human skin	Skin treated with H_2SO_4, chrom azurol S and NH_3 buffered solution; color compared to standard	[17]
Beryllium determination in water and biological samples	Precipitate of beryllium ammonium phosphate with ammonium molybdate then treated with succinyldihydroxamic acid	[18]
Beryllium in coal fly ash	Chrome azurol S in the presence of Zephiramine (ZCl)	[19]
Beryllium(II) determination in water and BeO in atmosphere	Anion-exchange resin Amberlite IRA-400 and chrome azurol S in aqueous solution	[20]
Beryllium determination in water and wastewater	Chromazurine S and hexadecylpyridine chloride (pH 5–5.3)	[21]
Absorption spectra of complexes with alkali and alkaline earth metal ions, including beryllium	4-(2,4-Dinitrophenylazo)-phenol(I), (II), and (III)	[22]
Beryllium determination in water	Ion-exchange colorimetry with eriochrome R	[23]
Beryllium determination in ore samples	Beryllon(III)	[24]
Beryllium determination in water	8-Hydroxynaphthalene-3,6-disulfonic acid (1-azo-1)-2,4-resorcinol	[25]
Analysis of various metals (Cu(II), Mo(VI), Al, Ti(IV), Fe(II, III), V(V), Th(IV), Ga(III), Co(II), Ni(II), Bi(III), Hg(II), Be(II)) in solution	Isticin-9-imine, alizarin-9-imine, 3-sulfoalizarin-9-imine	[26]
Spectophotometric determination of fluoride	Beryllium–carboxylate dye complex	[27]
Beryllium determination in air	Chrome azurol S	[28]
Be(II), Sn(II), Hg(II), VO(III) and Mo(VI) determination in solution	$K_3Cr(CN)_6$	[29]
Beryllium surface spot test	Chrome azurol S	[30]
Beryllium chloride in solution	Ammonium aurintricarb-oxylate (aluminon)	[31]
Beryllium determination in water	Sample extracted three times with CCl_4 (pH adjusted to 5–9), $Na_2H_2 [(O_2CCH_2)_2CH_2]_2$(I) and Ac_2CH_2 and beryllon added	[32]
Beryllium determination in waste-waters	Beryllon(II)	[33]
Beryllium determination in bronze sample	Eriochrome cyanine	[34]
Beryllium determination in coal ash	Beryllon(II)	[35]
Beryllium determination in solution	Chrome azurol S	[36]
Beryllium determination in solution	Beryllon(II), thoron, and arsenazo(I) compared	[37]
Beryllium determination in bronze sample	Chrome azurol S	[38]

[30]. A 4.7 cm filter is pretreated with the colorimetric reagent (CAS) and the chelator for competing metal ions (EDTA). The filter is wetted and used to swipe a surface. Diluted acid (HCl, HNO_3 or H_2SO_4) is applied to the filter to solubilize any recalcitrant species of beryllium. CAS forms a vivid blue complex with beryllium at pH 10. The technique is sensitive

to concentrations at or above $2 \mu g$ beryllium per filter. If a surface $30.5 \, cm \times 30.5 \, cm$ is sampled, the detection limit is $0.2 \, \mu g$ beryllium/100 cm^2. Competing elements that could interfere with beryllium analysis including calcium, magnesium, copper, nickel, chromium, iron and lead are complexed by EDTA up to individual concentrations of at least $200 \, \mu g$ per filter. Uranium and aluminum can also be present, however, special considerations must be applied when preparing samples if uranium and aluminum are known or suspected to be present in the work environment. This technique can provide beryllium workers the ability to avert accidental exposures in their workplace environment between periodic inspections by health and safety professionals and cut down on the number of costly OSHA ID-125G samples that are routinely performed.

2. Experimental materials and methods

2.1. Materials

Beryllium standard solutions were made from $1000 \, mg/l$ ICP standard in 2% HNO_3 (SPEX Centriprep, Acros, Metuchen, NJ, USA) or 2% HCl (ACS Plus, FisherChemicals, Fair Lawn, NJ, USA). All aqueous solutions were prepared with water that was purified using a MilliQ$^®$ analytical deionization water treatment system. Solid forms of beryllium used in experimental procedures were beryllium oxide (BeO 99%, Acros), beryllium sulfate (BeSO$_4$, Acros), beryllium chloride (BeCl$_2$ sublimed 99%, Aldrich, Milwaukee, WI, USA), beryllium metal (Be^0 99%, 325 mesh, Aldrich) and beryllium hydroxide (Be(OH)$_2$, precipitated at pH 11 from $1000 \, mg/l$ beryllium, 2% HNO_3 ICP standard). A 1 wt.% solution of CAS (Acros) served as the colorimetric reagent. EDTA dipotassium salt dihydrate (J.T. Baker, Inc., Phillipsburg, NJ, USA) (5 wt.% solution unless otherwise specified) was instrumental in complexing representative elements that would otherwise compete with beryllium for CAS binding sites resulting in false positive colorimetry. Table 2 summarizes the binding constants from the literature for EDTA (25 °C) with the various metals investigated in this study. A limited number of references were available documenting CAS binding constants

Table 2
Binding constants for beryllium and interference metals with EDTA

Metal cation	EDTA log K (25 °C and ionic strength $(I) = 0.1$ unless otherwise noted)	References
Be^{2+}	9.7 (± 1), 8.9 (± 1, $I = 0.5$)	[39,40]
Al^{3+}	16.4 (± 1), 14.56 (22 °C, $I = 0$)	[39,41]
Fe^{3+}	25.1	[39]
Ca^{2+}	10.65 (± 8), 10.25	[39,42]
Mg^{2+}	8.79 (± 6)	[39]
Cu^{2+}	18.78 (± 8)	[39]
Ni^{2+}	18.4 (± 1)	[39]
Cr^{2+}	13.6 (20 °C)	[39]
Pb^{2+}	18.0 (± 1)	[39]
UO$_2{}^{2+}$	7.4 (-4), 10.72 (± 0.3)	[39,43]
Cd^{2+}	16.5 (± 1), 13.79 (22 °C, $I = 0$)	[39,41]

with the elements evaluated in this study. The $\log K$ values available in the literature for CAS are as follows: Al^{3+} $\log K = 5.2$ (± 0.02) ($25\,°C$, [44]), Fe^{3+} $\log K = 3.9$ ($20\,°C$, [39]), Cu^{2+} $\log K = -0.7$ ($20\,°C$, [39]) and UO_2^{2+} $\log K = 0.45$ ($20\,°C$, [39]). A buffer solution was required to raise solution pH to 10, where the color of the beryllium–CAS complex was blue. For the buffer solution, ammonia (7 N in methanol, Acros) was diluted to 1 M along with 1 M ammonium chloride (FisherChemicals), and the pH was adjusted to 10 with KOH (FisherChemicals). Interference metals (Al^{3+}, Ca^{2+}, Cr^{3+}, Cu^{2+}, Fe^{3+}, Mg^{2+}, Ni^{2+}, Pb^{2+} and UO_2^{2+}) were prepared from 1000 mg/l ICP standards in 2% HNO_3 (SPEX Industries, Inc.).

Representative fluids were obtained to characterize potential interferences that may result when sampling machine shops. Aluminicut® (Mistic Metal Mover, Inc., Princeton, NJ), Trim Tap Light® (Master Chemical Co., Perrysburg, OH) #1 Gold Cutting Fluid® (PS Labs, Inc., Chicago, IL), Tap Magic® Cutting Fluid (Original Formula and Aluminum Formula, Steco Corp., Little Rock, AR), Kool Mist® spray coolant (Kool Mist, Santa Fe Springs, CA), mineral oil and dark cutting oil were mixed together in equal amounts and smeared on surfaces that were subsequently sampled. Professional Formula Fantastik® spray cleaner (National Brands, Inc., Fountain Inn, SC) was also evaluated as a potential interference.

The surface swipes are performed with 4.7 cm Whatman 541 filters (Fisher Scientific, Pittsburgh, PA, USA). Whatman 541 filters are hardened for sampling surfaces that are slightly rough. Other materials used include 15 cm Whatman 42 filters, 4.7 cm petri dishes, forceps coated with Teflon® PTFE and a two reusable polypropylene aerosol spray bottles that can be pressurized manually to produce a fine mist (Fisher Scientific).

2.2. Methods

The analytical 4.7 cm Whatman 541 filters were prepared by holding them individually in the forceps, immersing them in 1% CAS solution until saturated and immediately transferring them to be manually pressed between two 15 cm Whatman 42 filters to remove excess solution (Fig. 2). Teflon-coated or plastic forceps are required because the chelating solutions can solubilize elements from metallic forceps that interfere with the colorimetric procedure. The filters were then allowed to dry at room temperature on a clean surface. Drying times will vary depending on temperature and humidity, but generally did not exceed 30 min. If filters were placed in a hood drying times were reduced to approximately 15 min. The procedure was repeated using 5% EDTA solution for the second immersion. Filters were stored in a dark, dry environment at room temperature and were stable for analysis for up to 2 weeks.

The mass of beryllium on a 4.7 cm filter that triggers a positive (blue) colorimetric response to beryllium at pH 10 is 2 μg. To achieve a detection limit of 0.2 μg beryllium/100 cm^2 the surface area sampled must be 30.5 cm × 30.5 cm (1 ft^2). To achieve a detection limit of 3 μg of beryllium/100 cm^2, an 8 cm × 8 cm area must be sampled.

The CAS, EDTA pretreated filter should be wetted with approximately 200 ml of distilled water or acid (2 vol.% HNO_3 or 2% HCl for most beryllium compounds; 10% H_2SO_4 for BeO). Water is the preferred wetting agent for most industrial hygienists, especially if sampling will be performed in the vicinity of highly sensitive equipment such as beryllium machining instruments. The prepared 4.7 cm filter should be handled with a gloved hand and

Fig. 2. Preparation of beryllium colorimetric analytical Whatman 541 filters.

other personal protection equipment as deemed appropriate from this point on. The surface should be swiped with the filter contacting the entire surface area specified. The surface area swiped should be accurately recorded. The filter should be placed in a 4.7 cm petri dish. The petri dish top can be secured if transferring swipes to a central location for analysis. At the analysis location, the petri dish top should be removed and the filter allowed to air dry in the dish. Selecting an analysis location with a hood substantially reduces drying times. If the surface was swiped with distilled water the filter should be re-wetted with approxi-
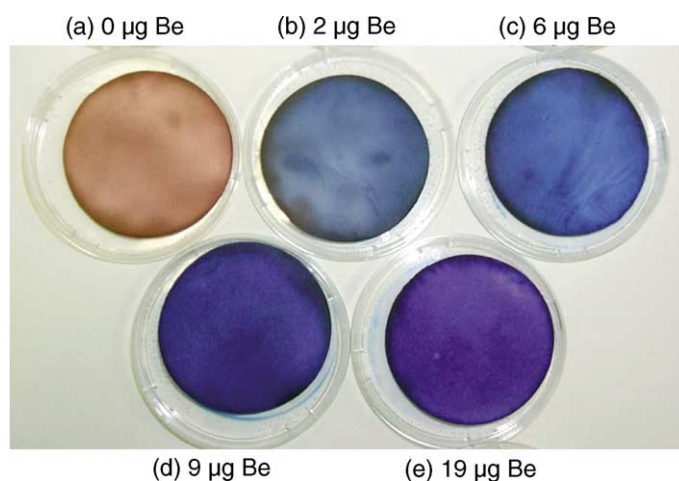
Fig. 3. Beryllium colorimetric standard curve. If a 30.5 cm × 30.5 cm surface area were sampled, the concentrations on the filters would correspond to the following: (a) 0, (b) 0.2, (c) 0.5, (d) 1 and (e) 2 μg beryllium 100^{-1}cm^{-2}.

mately 200 μl of acid. If beryllium oxide is suspected to be present the acid used should be 10% H_2SO_4, otherwise 2% HNO_3 or 2% HCl will be adequate. After drying, the filter should be sprayed with 1 M ammonia + 1 M ammonium chloride buffer solution adjusted to pH 10 just until saturated (approximately 200 μl). The filter should be dry before visual inspection.

Interference elements were mixed in 2% HNO_3 with and without beryllium in solution to evaluate the prevalence and character of interfering metals up to concentrations 100 times that of the beryllium low limit of detection (2 μg per filter). Interference element experiments were conducted in 2% HNO_3 because all the metals were readily available as ICP standards in 2% HNO_3. Two hundred microliters of each element was applied to individual filters at concentrations more than 100 times (1000 mg/l solution concentration or 200 μg per filter) that of the beryllium low limit of detection (2 μg per filter). A minimum of five samples were prepared per element evaluated.

Solid forms of beryllium were handled in a plastic glovebox placed inside a hood by a respirator trained beryllium worker. Beryllium solids, approximately 20 mg normalized to beryllium, were weighed into 15 ml centrifuge tubes and 10 ml of 2% HNO_3, 2% HCl, or 5% HCl were added to the vials. The solids were placed on a batch rotator and monitored over the course of 24 h. A Liberty 220 ICP-AES (Varian, Inc.) was used quantify beryllium concentrations 24 h after acid addition to evaluate the equilibrium capacity of HNO_3 (2%) and HCl (2 and 5%) to dissolve solid forms of beryllium. Additionally, a kinetic batch experiment was performed to measure beryllium solubility in 2% HCl, 10% HCl, 5% H_2SO_4 and 10% H_2SO_4 as a function of time (2, 5, 15, 30, 45, 60, 120, 240, 480, 720 min). A minimum of triplicate swipes and samples were evaluated for each beryllium solid tested.

3. Results and discussion

Beryllium standard solutions were prepared to determine the lower limit of detection for the technique. Standards of 1.1, 3.1, 6.3, 9, 13, 25 and 50 mg/l (in 2% HNO_3 and HCl) were prepared. CAS (1%) + EDTA (5%) pretreated filters were medium burgundy in color before application of 200 μl of 2% HNO_3 or HCl containing beryllium. After application of the buffer solution, a blue tint to the filter paper indicated beryllium was detectable by colorimetry. A blue tint was barely observed on the filter treated with 200 μl of 6.3 mg/l beryllium (1 μg of beryllium per filter). This result was not 100% reproducible. The lower limit of the technique, indicated by 100% reproducibility of blue filters, was observed with application of 200 μl of the 9 mg/l solution (approximately 2 μg per filter). Higher concentrations of beryllium resulted in filters with more vibrant, deep colors of blue. Lower concentrations resulted in filters that were orange–red in color. For beryllium concentrations in excess of 9 μg per filter, the depth of the color blue does not change significantly, thus, making it difficult to make beryllium concentration inferences based on color vibrancy. Fig. 3 provides an example standard curve for beryllium colorimetric detection.

Filters were visually inspected within the first 24 h after sampling. There was no visual difference between 2% HNO_3 and 2% HCl standard solutions. If stored in a dark dry environment, the color of beryllium standard filters remained true for up to 4 weeks. Blue
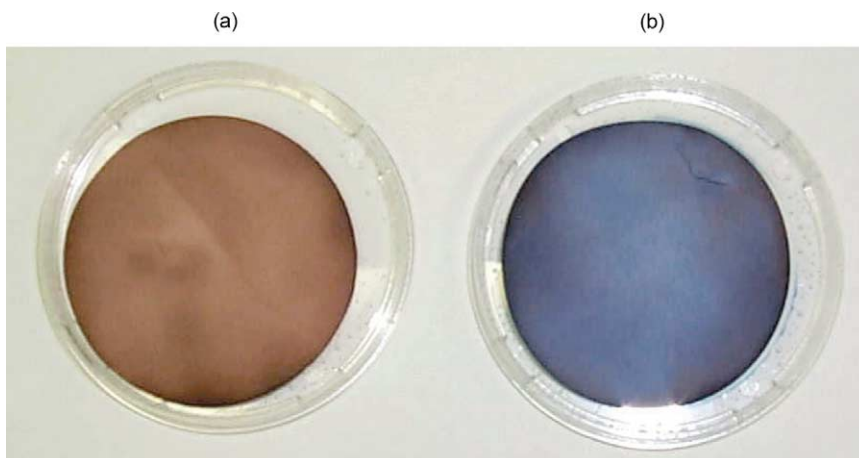
Fig. 4. Interference element colorimetric results for (a) Ni^{2+} (22 μg Ni^{2+}/100 cm^2) and (b) Ni^{2+} and Be^{2+} (22 μg Ni^{2+} mixed with 0.2 μg Be^{2+}/100 cm^2).

color associated with the lower detection limit of 2 μg per filter began to fade when exposed to sunlight after 24 h.

The original work by Mordberg and Fil'kova resulted in a minimum detection limit of 16 μg beryllium/100 cm^2 [30]. This work improved the detection limit by nearly 2 orders of magnitude. The notable changes in the technique that improved the detection limit were that the size of the surface sampled was increase from a 4 cm diameter circle to 30.5 cm $\times$ 30.5 cm, and more importantly the liquid solution applied to the filter was used to swipe the entire surface as opposed to analyzing only 0.01 ml of a total 1 ml solution volume applied to a 4 cm diameter surface.
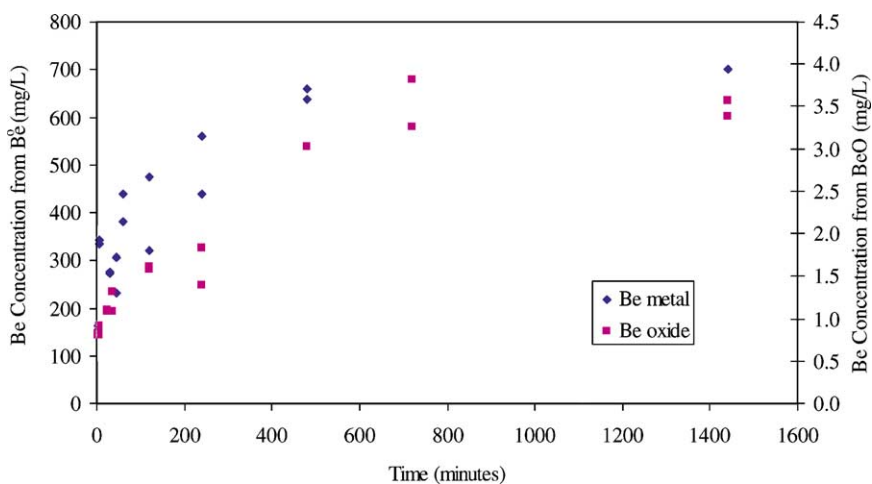

Fig. 5. Results of kinetic batch tests for beryllium metal and BeO contacted with 2% HCl.

Interfering elements were evaluated on filters with and without 2 µg beryllium per filter (200 µl of 9 mg/l beryllium in 2% HNO_3) present in solution. Elements evaluated included: Al^{3+}, Ca^{2+}, Cr^{3+}, Cu^{2+}, Fe^{3+}, Mg^{2+}, Ni^{2+}, Pb^{2+} and UO_2^{2+}. Filters treated with the individual following metals turned orange–red in color: Ca^{2+}, Cr^{3+}, Cu^{2+}, Mg^{2+}, Ni^{2+}, Fe^{3+} and Pb^{2+}. When 9 mg/l beryllium was introduced to individual solutions containing 1000 mg/l of the interference metals and 200 µl of the solutions were applied to new filters they turned blue. Fig. 4 illustrates the results for nickel, which were typical for the metals evaluated.

False positive results were obtained for UO_2^{2+} at 200 µg per filter. Filters with UO_2^{2+} had a light blue tint. False positive results were eliminated when the UO_2^{2+} concentration was reduced to 160 µg UO_2^{2+} per filter (80 times the beryllium lower limit of detection). When 9 mg/l beryllium was introduced to solutions containing 1000 mg/l and 800 mg/l of UO_2^{2+} and 200 µl of the solutions were applied to new filters they turned the color of blue corresponding to 2 µg beryllium per filter as seen in Fig. 3b. If a 10% EDTA solution was used to bind UO_2^{2+}, then no blue color was observed. Beryllium was still detectable at 2 µg per filter when mixed with 200 µg UO_2^{2+} per filter using 10% EDTA.

Aluminum did not result in a positive blue response for beryllium, however, Al^{3+} formed a vibrant purple complex with CAS. Aluminum concentrations were reduced to 200 mg/l (40 µg Al^{3+} per filter) before the purple colorimetric response was eliminated. Although the aluminum caused a purple colorimetric response, it did not obscure the blue color when beryllium was present at the minimum detection limit of 2 µg per filter. The aluminum concentration was successfully increased to 100 µg aluminum per filter without a purple colorimetric response using 10% EDTA with no reduction in beryllium colorimetric detection capability.

The utility of the technique was also evaluated by applying mixtures of competing elements to filters with and without beryllium present. Mixture 1 consisted of 100 µg Pb^{2+}, 40 µg Fe^{3+}, 30 µg Cd^{2+}, 30 µg Zn^{2+} and 20 µg Mn^{2+} per filter. The mixture did not yield positive blue colorimetry until 2 µg Be^{2+} per filter was added. Mixture 2 consisted of 20 µg Fe^{3+}, 20 µg Mg^{2+}, 20 µg Pb^{2+}, 10 µg Tl^{3+} and 5 µg Ni^{2+} per filter. Blue coloration was only observed after Be^{2+} (2 µg per filter) was added to the mixture.

Other potential interferences common in work environments that may be contaminated by beryllium include machine shop fluids, cleaning solutions, oxidized paint, and stainless steel or aluminum working surfaces. Cutting oils and a coolant typically used in machine shop environments were obtained and mixed in equal proportions. Surface areas (100 cm^2) smeared with 20 µl of the mixture did not produce false positive beryllium indication, nor did the mixture prevent positive detection of beryllium (2 µg per filter) when it was added to the solution. Fantastik® spray cleaner, which is often used for decontamination of surfaces, applied to filters (200 µl) did not produce false colorimetry or interfere with beryllium detection. An oxidized paint surface, an unpainted stainless steel hood and an aluminum box were all swiped. No false colorimetry was observed for any of the swipes.

It was important to evaluate the applicability of the colorimetric swipe technique for various forms of beryllium that may be present on surfaces as solid phase species. Beryllium solids evaluated included $Be(OH)_2$, $BeCl_2$, $BeSO_4$, beryllium metal (Be^0) and BeO. A series of batch solubility studies were done employing the acids used to solubilize beryllium in the swipe test. The liquid to solid loading rate was 10 ml acid to 20 mg of solid as beryllium.

Initial batch tests were performed for 24 h. The compounds $Be(OH)_2$, $BeCl_2$ and $BeSO_4$ were completely and immediately soluble in 2% HNO_3, 2 and 5% HCl. Metallic beryllium had a higher solubility in 5% HCl (1870 ± 65.8 mg/l) than in 2% HCl (770 ± 115 mg/l) and 2% HNO_3 (161 ± 12.2 mg/l). Metallic beryllium would produce a positive colorimetric detection using any of the acid solutions described earlier if equilibrium conditions were achieved. Beryllium oxide was the compound most resistant to dissolution with solubilities of 9.5 (±1.56), 3.51 (±0.24) and 1.45 (±0.35) mg/l in 5, 2% HCl and 2% HNO_3, respectively. In order to detect 2 μg of BeO on a 30.5 cm $\times$ 30.5 cm to achieve a detection limit of 0.2 μg/100 cm^2, it would be essential to have an acid solubility of at least 9 mg/l. Although 9.5 mg/l of beryllium was present after 24 h of contact with 5% HCl, it was necessary to evaluate kinetic limitations with respect to solid BeO on filters because equilibrium solubilization may not be achieved before filters dry (approximately 15 min if place in a hood).

Kinetic batch results verified that $Be(OH)_2$, $BeCl_2$, $BeSO_4$ were completely soluble in 2% HCl within 2 min of contact under gentle mixing conditions. Kinetic batch results for Be^0 and BeO contacted with 2% HCl are summarized in Fig. 5. It is clear from the results that equilibrium solubilities for both compounds were not achieved until approximately 720 min (12 h) of gentle mixing were attained. After 2 min of contact 0.82 ($\pm7.1 \times 10^{-3}$) and 159 (±7.1) mg/l of BeO and Be^0, respectively, were in solution. Metallic beryllium is soluble enough after 2 min of contact with 2% HCl to be detected at the regulatory limits using the colorimetric technique. Beryllium oxide was extremely difficult to solubilize under these conditions. After 15 min of contact, the solubilities of beryllium from BeO contacted with 2, 10% HCl, 5, 10% H_2SO_4 were 1.09 (±0.014), 2.29 (±0.19), 5.86 (±0.32) and 9.14 (±0.05) mg/l, respectively. Therefore, in order for this technique to be utilized successfully for BeO contaminated surfaces, the acid utilized must be H_2SO_4 at a concentration of 10%.

Numerous field trials of the beryllium colorimetric technique described herein are being executed at present. To demonstrate the utility of the technique it is useful to share the results of one field application. Colorimetric swipes were performed alongside standard swipes analyzed according to OSHA method ID-125G. Additionally, after colorimetric analyses were performed, the filters were digested and analyzed according to OSHA method ID-125G. Nine samples and a blank were collected by an independent industrial hygienist at LANL. The colorimetric technique accurately provided positive results indicating the presence of beryllium for the nine field samples, which ranged in concentration from 16 to 20 μg beryllium/100 cm^2 determined by ICP-AES analysis according to OSHA ID-125G. The test did not detect beryllium on the blank filter. A database of similar field applications is currently being assimilated at LANL.

4. Conclusions

The berylium surface swipe technique developed in this research investigation permits beryllium workers to monitor their work environment thoroughly on a regular basis without expense or delay in obtaining analytical results. The technique can be performed and interpreted easily without training or specialty education. The method can reduce downtime and ensure efficient cleanup after beryllium spills. The technique accounts for the presence of

common interference elements that may co-contaminate surfaces with beryllium. Results from random sampling throughout an entire work area can be ready for visual inspection in less than 1 h. The technique was developed with an eye to simplifying the sampling process, therefore, there are no quantitative restrictions imposed on the sampler in the pretreatment of filters or the preparation of samples, except that the area sampled must be $30.5\,\mathrm{cm} \times 30.5\,\mathrm{cm}$ to obtain the detection limit of $0.2\,\mu\mathrm{g}/100\,\mathrm{cm}^2$.

Acknowledgements

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