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Quantification and micron-scale imaging of spatial distribution of trace beryllium in shrapnel fragments and metallurgic samples with correlative fluorescence detection method and secondary ion mass spectrometry (SIMS)

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Abstract

Recently, a report raised the possibility of shrapnel-induced chronic beryllium disease (CBD) from long-term exposure to the surface of retained aluminum shrapnel fragments in the body. Since the shrapnel fragments contained trace beryllium, methodological developments were needed for beryllium quantification and to study its spatial distribution in relation to other matrix elements, such as aluminum and iron, in metallurgic samples. In this work, we developed methodology for quantification of trace beryllium in samples of shrapnel fragments and other metallurgic sample-types with main matrix of aluminum (aluminum cans from soda, beer, carbonated water, and aluminum foil). Sample preparation procedures were developed for dissolving beryllium for its quantification with the fluorescence detection method for homogenized measurements. The spatial distribution of trace beryllium on the sample surface and in 3D was imaged with a dynamic secondary ion mass spectrometry (SIMS) instrument, CAMECA IMS 3f SIMS ion microscope. The beryllium content of shrapnel (~100 ppb) was the same as the trace quantities of beryllium found in aluminum cans. The beryllium content of aluminum foil (~25 ppb) was significantly lower than cans. SIMS imaging analysis revealed beryllium to be distributed in the form of low micron-sized particles and clusters distributed randomly in X-Y-and Z dimensions, and often in association with iron, in the main aluminum matrix of cans. These observations indicate a plausible formation of Be-Fe or Al-Be alloy in the matrix of cans. Further observations were made on fluids (carbonated water) for understanding if trace beryllium in cans leached out and contaminated the food product. A direct comparison of carbonated water in aluminum cans and plastic bottles revealed that beryllium was below the detection limits of the fluorescence detection method (~0.01 ppb). These observations indicate that beryllium present in aluminum matrix was either present in an immobile form or its mobilization into the food product was prevented by a polymer coating on the inside of cans, a practice used in food industry to prevent contamination of food products. The lack of such coating in retained shrapnel fragments renders their surface a

possible source of contamination for long-term exposure of tissues and fluids and induction of disease, as characterized in a recent study. Methodological developments reported here can be extended to studies of beryllium in electronics devices and components.

Keywords

Beryllium in electronic products; chronic beryllium disease (CBD); SIMS imaging analysis of beryllium in metallurgic samples; beryllium analysis with fluorescence detection method; beryllium in shrapnel; beryllium in aluminum cans and foil

Introduction

Beryllium is a lightweight metal that possesses unique mechanical, electronic and thermal properties which make it ideal for fabrication of devices used in many industries including aerospace, automobiles, defense, nuclear power, and sporting goods (WHO Report, 2001). Beryllium increases hardness and resistance to corrosion when alloyed with aluminum, cobalt, copper, iron, and nickel (Kaczynski, 2002). Beryllium is also a natural contaminant present in military hardware and explosives in association with aluminum, as the bauxite ore from which aluminum is extracted is known to contain beryllium which has not been removed completely by smelting and other processes to produce end-use aluminum products. Consequently, beryllium-induced diseases have been reported in workers in beryllium industry and aluminum smelter industries (Steenland & Ward, 1991; Stange et al., 1996; Sanderson et al., 2001; Taiwo et al., 2010). Acute beryllium pneumonitis, which is a marker for high exposure of beryllium, is associated with higher lung cancer rates (Leonard & Lauwers, 1987; Steenland & Ward, 1991) and chronic beryllium disease (CBD) is associated with long-term exposure of low concentrations of beryllium (Stange et al., 1996; Taiwo et al., 2010).

The primary route of human exposure to beryllium is through inhalation of dusts and fumes but skin may also be a source of sensitization. Beryllium may also be ingested in drinking water or food (W.H.O. Report, 2001). Lung disease is prevalent in military personnel exposed to combustion products from burning of waste, hydrogen sulfide, blast exposures, and metal fragments (Rose, 2012). In war veterans, retained metal fragments containing aluminum, arsenic, cobalt, and nickel may induce immunogenic respiratory health effects (Rose, 2012). Recently, a case report by Fireman et al. (2012) that was co-authored by two of us (JLA, SC) described CBD in an Israeli soldier who suffered a mortar shell injury with retained shrapnel in the chest-wall. The presence of trace amounts of beryllium in the aluminum matrix of shrapnel was qualitatively confirmed by SIMS imaging. Consequently, it is important to compare the beryllium content of shrapnel to aluminum containers to observe if it was intentionally added as a poison in the shrapnel or it was present as a natural contaminant in aluminum containers. If beryllium is present as a contaminant in aluminum containers, it would be highly desirable to study its micro-distribution in containers especially used for food products and also to observe if the beryllium in the aluminum matrix is leaching out into the product itself.

In this study we employed a modified fluorescence detection method previously used for soil analysis (Agrawal et al., 2008) for measurements of trace beryllium in metallurgic samples of shrapnel fragments and aluminum cans and foil. Furthermore, the technique of SIMS ion microscopy was used for studying beryllium micro-distribution in the sample matrix and its segregation with other metal species like iron. SIMS ion microscopy is capable of imaging gradients of any elements from H to U, via isotopic detection, with 500 nm spatial resolution and 3D multi-elemental image profiles of the sample surface (Chandra, 2010). Our observations indicate that trace quantities of beryllium was naturally present as a contaminant in the matrix of shrapnel and aluminum cans and that the food products under study were not observed to be contaminated by its migration into the food product.

Materials & Methods

Materials

Small pieces of shrapnel collected from the chest-wall of the Israeli soldier, as described previously (Fireman et al., 2012) were used for beryllium analysis with fluorescence detection method described below. Samples of aluminum cans of soda, beer, carbonated water and aluminum foil-wrap were commercially available (brand names not discussed).

Sample preparation and methodological development for the detection of beryllium in metallurgic and fluid samples with fluorescence detection

method—Typical methods to prepare samples using fluorescence detection method, e.g. standard test method A.S.T.M. D7202 (2006) and A.S.T.M. D7458 (2008), involves treating beryllium containing samples with dilute ammonium bifluoride (ABF), typically 1 to 3% by weight in water so as to extract beryllium into the solution. This solution is then mixed with a buffered dye solution containing hydroxybenzoquinoline sulfonate (HBQS) fluorophore (dye) which binds specifically to beryllium under high pH conditions. The binding of beryllium and HBQS under these conditions (Matsumiya et al. 2002) results in a strong fluorescence at 478 nm when excited by ultraviolet radiation in the wavelength of about 360 to 380 nm. The buffered HBQS dye solution was obtained from Berylliant Inc, Tucson, Arizona, U.S.A. The buffered dye solution contained 1.1 mM HBQS, 1 mM EDTA (disodium dehydrate salt of Ethylenediaminetetraacetic acid) and 100 mM L-lysine monohydrochloride; of which the pH was adjusted to 12.8 (± 0.1) with sodium hydroxide.

Initially we subjected aluminum sample to 1% ABF solution. We noticed that although there was an initial reaction causing dissolution, but soon this reaction stalled. The same happened as we gradually increased the concentration of ABF to 10%. It has been reported that although aluminum reacts with and is extracted in hydrofluoric acid (HF), however, addition of ammonium salts result in formation of a surface coating which resist further action by the acid (Straumanis & Wang, 1995). Since binding of beryllium is sensitive to pH and reaches a maximum at above pH12, we decided to use dilute hydrofluoric acid (HF) to breakdown the aluminum matrix and solubilize the constituents. Once the solubility was completed, this was diluted by ABF solution before mixing with the dye solution so as the resulting measurement mixture could still be at a pH close to or in excess of 12 to make the fluorescence measurements.

Approximately 50 mg of aluminum sample (shrapnel or sample from a can) along with 2.5 ml of the 4.75% HF solution was placed in a 15ml polypropylene bottle with a screw cap. The sample bottle was left at room temperature with the cap loosely placed overnight (about 16 hours) in a fume hood. The cap on the polypropylene bottle was then tightened and placed in the oven at 90C for several hours until the aluminum was completely dissolved. However, it was important to periodically remove the sample bottle (every 15 minutes to 30 minutes) from the oven and vented in the fume hood as needed. Once the aluminum was completely dissolved the sample was removed from the oven and cooled to room temperature. The pH of the solution at the end of the procedure was close to 2. 2.5 ml of 1wt % ABF was added to the above bottle to bring the total volume of liquid to 5 ml. The pH of this solution mixture was in the range of 3 and 4. The bottle after capping was again placed in the oven at 90C for at least one hour. After one hour the sample was cooled to room temperature and was filtered using a 0.2 μ m GHP hydrophilic polypropylene syringe filter. Samples for fluorescence analysis are prepared by mixing the aluminum sample solution (0.1 ml) with buffered dye solution (1.9 ml). These mixtures (measurement solutions) were left to sit at room temperature for several hours in order to precipitate iron or titanium impurities (Agrawal et al., 2006) which may be present in the samples. The measurement solutions were then filtered to remove any precipitation using GHP hydrophilic polypropylene syringe filters (0.2 μ m) and were then measured for fluorescence.

Each sample (measurement solution) was tested in a polystyrene cuvette in triplicate, calibration solutions were made using 0.1 ml of 3% ABF solution spiked with various amounts of beryllium and 1.9 ml of dye solution. Fluorescence measurements were made by measuring on Modulus™ instrument (Turner Biosystems, Sunnyvale, California, U.S.A.) using excitation at 365 nm and measured fluorescence using an emission band-pass filter with transmission between 475 and 485 nm. In these measurement solutions, beryllium could be read at quantitative levels starting from about 0.005 ppb, which would suggest a detection limit of a third of this value, i.e. 0.002 ppb. This would correspond to a beryllium quantity of 0.0005 μ g and 0.002 μ g, respectively. Since this beryllium came from about 50 mg of aluminum, the method quantification and the detection limit of beryllium would be 0.01ppm and 0.004 ppm of beryllium in aluminum.

Water from the cans or bottles was tested by preparing three samples, each containing 0.4 ml of water and 1.6ml of HBQS dye solution to make a measurement solution (5 $\times$ dilution method). Beryllium calibration standards, available in 1wt% ABF from Berylliant Inc., were used. These were first diluted with deionized water using a 20 times dilution to minimize the quantity of ABF so that the effect on the resulting pH when mixed with the buffered dye solution will be minimum and close to such mixed solutions prepared using can-water. The calibration standards were then prepared using 0.4 ml of these deionized water diluted standards and 1.6 ml of dye solution. As discussed above in these measurement solutions (mixture of water and the dye solution), beryllium could be read at quantitative levels of 0.005 ppb, with a detection limit of about 0.002 ppb. This corresponded to respective quantification and the detection limits of the method using 5 $\times$ dilution method as 0.03 ppb and 0.01ppb beryllium in the water being analyzed.

Sample preparation for SIMS imaging analysis—Five to six small pieces (approximately 0.5 cm² surface area) were cut from the unpolished surface of commercially available soda and beer aluminum cans (brand names not specified here). Similarly, small pieces of aluminum foil wrap were cut for SIMS analysis of beryllium. The samples were washed in distilled water and pressed onto the indium foil on the silicon substrate (Chandra, 2010). The pressing of samples onto the soft indium kept them adhered to an electrically conducting substrate for SIMS analysis. An electrically conducting substrate is a necessity for imaging SIMS analysis since the sample is held at 4500 volts in the high vacuum chamber of the Cameca IMS-3f SIMS ion microscope instrument used in the study. The samples were sputter coated with a 10 Å layer of Au/Pd for enhancing their electrical conductivity for SIMS imaging analysis. The Au/Pd coating also minimizes surface charging effects generated from topographic irregularities of the sample surface.

SIMS imaging analysis of beryllium and associated elements in Aluminum

Cans and Foil samples—A CAMECA IMS-3f SIMS ion microscope (CAMECA, Paris, France) capable of producing isotopic images with a lateral resolution of 500 nm was used in the study (Chandra et al., 2000). Over the course of its usage, the instrument has been heavily upgraded and is equipped with a primary beam mass filter and a 5f Hall Probe control chassis. The control system of the instrument has also been upgraded with a Charles Evans and Associates model PC-1CS Computer Interface system and Windows-based computer. For this study, the instrument was operated in the positive secondary ion imaging mode with samples biased to +4500 V. An O₂⁺ primary ion beam, accelerated to 10 keV, was focused and adjusted to a nominal beam current of ~300 nA with a diameter of ~70 µm when viewed as a stationary spot at the surface of the sample. Primary beam was raster scanned over 500-µm × 500-µm square regions during the analysis. The 400-µm transfer optics in conjunction with a 60-µm contrast aperture was employed for the analysis. The energy window of the mass spectrometer was centered and set to a maximal value of 130 eV. Energy and mass filtered secondary ion images were magnified and projected on a single microchannel plate/phosphor screen detection assembly. The gain of the microchannel plate was set at 60% of the maximum. SIMS ion images were recorded from the image detection assembly using a Photometrics CCD CoolSNAP HQ² FireWire Digital Camera capable of 14 bits/pixel image digitization (Photometrics, Tuscon, Arizona, U.S.A.). The digitized images were transferred from the camera controller to the PC workstation with a Nikon NIS-Elements Imaging Software for storage and digital image processing (Princeton Digital Corp., Irvine, California, U.S.A.). The camera was operated in the 2 × 2 binning mode for enhancing the detection of trace quantities of beryllium in samples. In the positive secondary ion detection mode, images of isotopes with masses 9, 27, 56, and 115 revealed the micron scale distribution of positive secondary ions of ⁹Be, ²⁷Al, ⁵⁶Fe, and ¹¹⁵In, respectively. For the imaging of trace quantities of ⁹Be signals originating from the sample matrix, the mass 9 was accurately calibrated in the SIMS instrument by analyzing a standard electron microscopy beryllium grid (Ted Pella, Inc., Redding, California, U.S.A.). Fig. 1 shows SIMS mass 27 image of ²⁷Al positive secondary ions as a calibration for instrumental optics (Panel A) and mass 9 image from the beryllium grid showing a portion of the grid-bars with bright ⁹Be intensities.

Results

The measurement of trace quantities of beryllium by fluorescence detection method

The homogenized beryllium contents from the fluorescence detection method in fragments of shrapnel, samples of Al-cans of soda, carbonated water, beer and Al-foil are listed in Table 1. The beryllium content of shrapnel (~100 ppb) was the same as samples of aluminum cans, irrespective of their identity as soda, beer, and carbonated water. The Al-foil contained a substantially lower amount of beryllium, approximately 25 ppb (Table 1). These observations establish that beryllium in shrapnel was not intentionally added as a poison, as it is not significantly different from the amount of beryllium present in the matrix of aluminum cans. The beryllium present in the matrix of cans may potentially leach out and contaminate the fluids inside. However, the analysis of carbonated water contained inside the cans revealed that its beryllium content was below the detection limits of the method and that there was no significant difference between the carbonated water contained in aluminum cans or in plastic bottles (Table 1). These observations indicated that beryllium present in the matrix of cans was either present in an immobile bound form plausibly in association with other metal species or its mobilization into fluids was protected by a barrier polymer layer generally used for coating the inside surface of aluminum cans.

SIMS imaging analyses of ^9Be and associated elements in aluminum cans and foil

Recently, the presence of beryllium in shrapnel fragments was confirmed by us (SC, JLA), as co-authors, with the SIMS ion microscope (Fireman et al., 2012). Here, SIMS imaging was used for studying beryllium micro-distribution and its association with other elements in X-Y-Z-planes in aluminum cans and foil samples. A typical SIMS imaging analysis of a sample from an aluminum soda can is shown in an image composite containing designated elemental (isotopic) distributions in the sample matrix (Fig. 2). Figure 2A shows the ^{115}In image revealing the boundary of the sample that was pressed in the indium substrate, as the bright signals for indium are only located in the top left corner of the image and the dark regions are occupied by the Al-can sample. The distribution of ^{27}Al in the matrix of the soda-can-sample reveals bright and saturated signals since Al is the main matrix element of the can (Fig. 2B). The further 3D SIMS analysis of the sample unequivocally reveals the presence of ^9Be signals as low micron size dots shown in green (Fig. 2C). The punctate distribution of these beryllium particulates only in certain locations of the analyzed area was typical for the analyses of soda-can-samples. Further 3D SIMS analysis of this region shows the presence of iron in the sample matrix as illustrated in the ^{56}Fe SIMS image shown in red (Fig. 2D). An overlay of the Be/Fe image reveals that some of the beryllium particulates co-localize with the iron and the others do not. This is indicative of a plausible formation of the Be-Fe-Al alloy in some beryllium particulates and Be-Al alloy in others. The further 3D SIMS analysis of this region shows the second ^{115}In substrate image (Fig. 2F). Since this image resembles the first ^{115}In image shown in panel A and does not reveal any indium signals originating from the regions occupied by the samples, the 3D SIMS analysis shown above for the sample accurately represent elemental micro-distributions within the sample alone. It should also be noted that approximately 50% of the areas analyzed with SIMS imaging revealed the presence of beryllium in the matrix of soda-can samples as

demonstrated above. This is indicative of non-homogeneous distribution of trace quantities of beryllium in the sample.

An example of SIMS imaging analysis of a sample from an aluminum beer can is shown in Fig. 3. The ^{27}Al SIMS image shows the Al-matrix (Fig. 3A) and the ^9Be image shown in green indicate the presence of beryllium in a localized region (Fig. 3B). Further SIMS analysis of this sample for iron localization shown in red (Fig. 3C) indicate that beryllium signals are present in selected regions of the Al matrix and that there is a co-localization of beryllium and iron, as demonstrated by the Be/Fe overlay image (Fig. 3D). These observations are consistent with SIMS analysis shown above for Al soda can. Once again, approximately 50% of the areas analyzed with SIMS imaging revealed the presence of beryllium in the matrix of beer-can samples.

SIMS imaging analysis of beryllium in Al-foil showed the presence of very few particulates in the foil matrix (Fig. 4). The first ^{27}Al image of the foil sample (Fig. 4A) demonstrates Al to be distributed throughout the matrix with much less micro-scale heterogeneity than observed for Al-can samples. The presence of beryllium in the Al-foil matrix is indicated by one small particulate observed in the sample (Fig. 4B). The further SIMS analysis of this region in 3D for the second ^{27}Al image (Fig. 4C) and the second ^9Be image confirm the presence of this particle in the matrix of Al-foil. Typically, only 10% of the SIMS areas analyzed for Al-foil revealed the presence of small beryllium particles as demonstrated here. These SIMS observations are consistent with substantially lower concentrations of beryllium observed in Al-foil samples in comparison to the samples of cans (Table 1).

Discussion

Observations discussed in this study provide compelling support that the trace amounts of beryllium found in shrapnel fragments (~100 ppb) were not intentionally added as poison in the shrapnel since aluminum cans from soda, beer, and carbonated water contained similar concentrations of beryllium in their matrix (~100–200 ppb, Table 1). These observations support the notion that the trace amounts of beryllium are present in aluminum products. The bauxite ore from which aluminum is extracted is known to contain beryllium which is not completely removed by smelting and other processes to produce end-use aluminum products. The lower content of trace beryllium in the aluminum foil in comparison to cans cannot be explained with naturally present beryllium in the bauxite ore (Table 1, Fig. 4) and may depend on manufacturing processes used in foil making that further reduce beryllium content of the bauxite ore.

SIMS imaging studies revealed low micron-sized particulates of beryllium distributed randomly in the aluminum matrix of cans (Fig. 2–3). Some of these particulates were associated with iron raising the possibility that beryllium was present in the segregated form with iron in the aluminum matrix. The formation of iron-beryllium alloy has been described in the literature (Aldred, 1966). The process of segregation (complexation) of beryllium with other metal species may reduce its mobilization or leaching out of beryllium into the fluids contained in the aluminum containers.

Observations in this study also demonstrate that the trace amounts of beryllium found in the matrix of aluminum cans did not contaminate the carbonated water contained inside, since beryllium contents of carbonated water contained in aluminum cans as well as plastic bottles were both below the detection limits of about 0.01 ppb of the current fluorescence detection method used in the study. It is plausible that the trace beryllium found in the aluminum matrix of cans is present in a bound form which cannot be mobilized. But our study cannot answer this question as the aluminum cans in food industry contain a protective plastic layer in the interior surface so that food content does not react directly with the metal. In either case, the confirmation of not having the food product contaminated with the trace amounts of beryllium from the aluminum matrix is a valuable contribution of this study. Unfortunately, no such protective polymer layer is present in shrapnel and military explosives to protect the direct surface contact of biological tissues with retained metal fragments in war veterans. So, there will always be a possibility of beryllium sensitization *via* long-term exposures from surfaces of embedded shrapnel fragments, as confirmed in a recent report in the Israeli soldier's case (Fireman et al., 2012). Methodological developments discussed here on the characterization of trace beryllium concentrations and its micron-scale spatial distribution in metallurgic samples can be extended to studies of beryllium in electronics devices and components.

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Fig. 1.

The calibration of SIMS optics for beryllium imaging analysis. SIMS images of positive secondary ions of ^{27}Al from the Standard Cu-Al grid (A) and ^9Be from an electron microscopy Beryllium grid (B) used for SIMS experiments for the calibration of exact mass of beryllium. The image integrations times on the CCD imager were 0.2 sec for ^{27}Al image and 1 sec. for ^9Be image.

Fig. 2.

Three dimensional SIMS imaging analysis of beryllium in an aluminum soda-can. The positive secondary ion SIMS images are shown in the image composite. The ^{115}In SIMS image illustrates the indium substrate signals (A). Note that the bright indium substrate signals are restricted to the top left-side of the image revealing a boundary between the substrate and the aluminum sample embedded on the substrate. The ^{27}Al image shows bright intensity matrix signals of the Al-soda-can (B). Further analysis of this sample in the 3D reveals the presence of beryllium shown in green in the ^9Be SIMS image (C) and iron,

shown in red, in the ^{56}Fe SIMS image (D). An overlay image of $^9\text{Be}/^{56}\text{Fe}$ signals demonstrates that some of the beryllium particulates co-localize with iron particulates and other do not (E). The last image in panel “F” shows the 2nd SIMS image of the indium substrate after the recording of Al, Be, and Fe images. The image integrations times on the CCD imager were 0.4 sec for each ^{115}In image, 0.2 sec for ^{27}Al image, 2 min for ^9Be image, and 2 min for ^{56}Fe image.

Fig. 3. SIMS imaging analysis of beryllium in an aluminum beer-can. The ^{27}Al SIMS image shows bright intensity matrix signals of the Al-beer-can (A). Further analysis of this sample in the 3D reveals the presence of beryllium shown in green in the ^9Be SIMS image (B) and iron, shown in red, in the ^{56}Fe SIMS image (C). An overlay image of $^9\text{Be}/^{56}\text{Fe}$ signals demonstrates that the location of beryllium clusters matches with iron clusters in this region (D). The image integrations times on the CCD imager were 0.2 sec for ^{27}Al image, 2 min for ^9Be image, and 2 min for ^{56}Fe image.

Fig. 4.

SIMS imaging analysis of trace beryllium in a sample from aluminum foil. The first ²⁷Al SIMS image shows bright intensity matrix signals of the Al-foil (A). Further analysis of this sample in the 3D reveals the presence of a beryllium particle in the ⁹Be SIMS image (B). The 2nd ²⁷Al SIMS image (C) was recorded after the recording of the 1st Be image. The 2nd ⁹Be SIMS image recorded after the 2nd ²⁷Al image unequivocally demonstrates the presence of this beryllium particle in the matrix of aluminum foil. The image integration times on the CCD imager were 0.2 sec for each ²⁷Al images, 2 min each for ⁹Be images.

Table 1

Concentration of trace beryllium as measured by fluorescence detection method in shrapnel fragments, aluminum cans and foil, and carbonated water from aluminum and plastic containers. Analyses represent measurements in triplicates.

Sample Type	Beryllium Concentration (ppb, mean $\pm$ SD)
Shrapnel fragments	105.3 $\pm$ 5.6
Al-Soda Can	183.7 $\pm$ 8.8
Al-Beer Can	120.0 $\pm$ 7.6
Al-Carbonated water Can	110.7 $\pm$ 3.4
Al-Foil	25.0 $\pm$ 2.1
Carbonated water from Al-Cans	below detection limits
Carbonated water from Plastic-bottles	below detection limits