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The Beryllium Quandary

Will Lower Exposure Limits Spur New Developments in Sampling and Analysis?

By Michael Brisson

Sampling and analysis of beryllium in the workplace can be more challenging than for many other metals. For starters, the occupational exposure limits for beryllium tend to be in the microgram or sub-microgram per cubic meter range, rather than in the milligram range. Some forms of beryllium, especially beryllium oxide, are not fully dissolved in many commonly used sample preparation methods. And, in many cases, interpreting results for beryllium samples is difficult as well, particularly if most results come back below the laboratory's reporting limit and you don't have the luxury of collecting enough samples for a nonparametric statistical treatment.

At the time this article was written, new rulemakings were under consideration at OSHA and the U.S. Department of Energy (DOE) that would propose changes to occupational exposure limits for beryllium. Given these developments, it's a good time to review the tools and methods available to IHs for assessing beryllium air and surface contamination in the workplace—what's new and different, and what's tried and true.

Limit Values

Limit values and action levels for beryllium vary around the world. Table 1 details the current limit values in various jurisdictions. While many countries use the same value as OSHA's current permissible exposure limit (PEL) of 0.002 mg/m^3 TWA, some jurisdictions have lower limit values for airborne beryllium particulate matter. However, the DOE regulation (10 CFR 850) also has action levels for surface contamination: 0.2 micrograms per 100 cm^2 for free release from beryllium work areas, and a higher action level, 0.003 mg/100 cm^2 for housekeeping within beryllium work areas. Although most practitioners think only in terms of air sampling, tens of thousands of surface samples for beryllium are collected each year, mostly, but not entirely, at DOE sites.

Air and Surface Sampling

This article does not attempt to review the body of guidance on the development of air sampling plans and strategies, but two problematic aspects of beryllium air sampling are important to note. First, the ACGIH® Threshold Limit Value (TLV®) adopted in 2009 is based on the inhalable fraction as defined in ISO 7708, *Air quality – Particle size fraction definitions for health-related sampling*. While inhalable samplers are widely available, they are not disposable and can be a challenge to clean between uses to the stringent levels necessary to ensure no cross-contamination at the sub-microgram level. This is a larger challenge at DOE and other nuclear sites where samples may be radiologically contaminated. Hygienists should review the cleaning protocol to ensure its effectiveness. Researchers at several universities are currently working to develop a disposable inhalable sampler, which would be beneficial for sampling for beryllium and for other particulates with an inhalable exposure limit, such as nickel, vanadium pentoxide, and wood dusts .

Second, it's important to consider the possibility that particulate may adhere to the interior walls of sampling cassettes. NIOSH has issued a recommendation to account for sampler wall deposits when sampling and analyzing airborne particulate matter. This recommendation is available on NIOSH's website at http://bit.ly/samplerwalldeposits. Several ways to account for sampler wall deposits are summarized in a column in the March 2013 issue of the *Journal of*

Occupational and Environmental Hygiene. NIOSH intends to revise affected methods in its *Manual of Analytical Methods* to specifically account for wall deposits.

For those who need to perform surface sampling for beryllium, ASTM International recently published two standards that may be useful. Standard D7707, *Standard Specification for Wipe Sampling Materials for Beryllium in Surface Dust*, was developed to provide a specification for a smaller beryllium surface wipe, reducing the amount of material the laboratory has to dissolve and potentially improving laboratory detection capabilities. ASTM D7659 is a guide for surface sampling strategies for metal and metalloid particulate, and includes references to other documents in the literature.

Sample Preparation

Samples to be analyzed for beryllium and its compounds are typically prepared by hot acid digestion, much like samples for other metal particulate. For beryllium metal and alloys, typical digestion techniques, such as those described in NIOSH Method 7300, are sufficient. However, beryllium oxide (BeO) requires special consideration. A study published by Oatts et al. (see Suggested Readings) notes that the digestion solution needs to contain sulfuric acid, hydrofluoric acid, or ammonium bifluoride. Since hydrofluoric acid has unique hazards that require additional precautions and treatment in the event of skin contact, sulfuric acid is often preferred. However, a nitric acid pre-treatment may be necessary with some sampling media.

Another important aspect of sample preparation is the final dilution volume. Laboratories need to use enough hot acid to get the sample, including the substrate (filter, surface wipe, etc.), into solution. However, for beryllium and other contaminants requiring measurement at the microgram level, it is desirable to minimize the dilution volume to achieve the best possible detection capability.

Communication between field hygienists and the laboratories they use is important: the laboratory needs to understand the sample it receives and any special requirements for analysis so that the field hygienist gets the best possible results.

Analysis

Most metals analyses for occupational exposure samples are performed using inductively coupled plasma atomic emission spectroscopy (ICP-AES). It's a proven method that can process large numbers of samples with part-per-million (or better in many cases) sensitivity. Standard methods using ICP-AES are available from many sources, including NIOSH, ASTM International, EPA, ISO, and others. For beryllium, the sensitivity of ICP-AES is not always sufficient, especially for personal air samples collected at two liters per minute over a short period of time.

If a more sensitive method is needed, two others are commercially available: inductively coupled plasma mass spectrometry (ICP-MS) and molecular fluorescence. ICP-MS is the most readily available alternative to ICP-AES. For beryllium, a comparison of ASTM International standard D7035 (for ICP-AES) and EPA Method 200.8 (for ICP-MS) suggests a method detection limit of 0.009 micrograms per sample for ICP-AES, and 0.001 micrograms per sample for ICP-MS. In addition, ICP-MS is not as prone to interferences from other metals as ICP-AES. It should be noted that ICP-MS is not as widely available in accredited laboratories as ICP-AES, and it may be more costly per sample. Here, again, communication with the laboratory is important to get the needed results without overspending or going over budget.

Molecular fluorescence is a less widely used method, though both NIOSH and ASTM International have standard methods using fluorescence. Its footprint is small enough to be easily deployed in field settings or mobile laboratories. It has similar sensitivity to ICP-MS, but is specific for beryllium, and the field-deployable method is not automated. For these reasons, it is not used by many commercial laboratories, but is used at several DOE sites.

ICP-AES, ICP-MS, and molecular fluorescence are not the only methods used to measure beryllium. At least one lab outside the U.S. is using microwave-induced plasma spectroscopy (MIPS), and some DOE national laboratories have done work with laser-induced breakdown spectroscopy (LIBS), a method that has the advantage of not requiring sample preparation. However, more research and development is needed for LIBS to be truly viable for workplace samples.

Another area requiring additional research is the differentiation of the various forms of beryllium (for example, metal, alloy, oxide, silicates/borosilicates). Improving this capability would be beneficial because while natural sources of beryllium in soil are not believed to put workers at risk of beryllium disease, anthropogenic forms do carry such risk, and some forms may carry more risk than others. Currently, such differentiation requires research-grade instruments not found in the typical industrial hygiene lab. A more practical approach is greatly needed.

Regardless of the analysis technique, it is important to be sure that the laboratory is proficient in measuring beryllium. Over 40 laboratories participate in the Beryllium Proficiency Analytical Testing (BePAT) program conducted by the AIHA Proficiency Analytical Testing Programs. The BePAT requires demonstration of proficiency for beryllium oxide, which is more difficult to solubilize than beryllium metal or alloy.

Data Evaluation

General overviews of data evaluation are available in ASTM D7659, the *Standard Guide for Strategies for Surface Sampling of Metals and Metalloids for Worker Protection;* in AIHA publications such as *A Strategy for Assessing and Managing Occupational Exposures*; and in other sources. While these sources provide overall guidance, it is worth emphasizing here that upfront development of an appropriate sampling plan and data quality objectives that consider how the data need to be used in the end will facilitate evaluation of the data from the sampling event. If the data set is small, conventional statistical treatments may not be valid, and alternatives such as Bayesian methods may be considered. The assistance of a statistician can be valuable, and appropriate professional judgment is vital, especially for smaller data sets.

For measurement of beryllium, the amount of censored data frequently poses a challenge. Accredited laboratories are required to not report data below their established reporting limits, or to appropriately caveat such data if they do. There’s a good reason for this: below the laboratory reporting limit, the uncertainty of the data is greater than what is typically acceptable, and laboratories want to preserve both their reputation and their accreditation. However, for beryllium, most or all of a data set may be below the reporting limit. This can be problematic if you wish to construct an upper tolerance limit for such a data set. You cannot necessarily assume a log-normal (or other parametric) distribution for this kind of data set, and since non-parametric statistical treatments require a minimum of 59 data points, there will often not be enough data points for a strictly non-parametric approach.

To study this and related issues, the Beryllium Health and Safety Committee (BHSC), an *ad hoc* group of practitioners from several federal agencies, laboratories, and industry, formed a Data Reporting Task Force (DRTF) in late 2006. One possible, albeit unconventional, approach is to use uncensored data if such data are available and an agreement can be reached between the laboratory and the end user on how the data will be provided and used. Uncensored data should only be provided in a supplemental report with appropriate caveats, and users need to be knowledgeable of the limitations of uncensored data.

Apart from the higher uncertainty associated with uncensored data points, such data sets frequently contain some negative values. Of course, while the beryllium concentration cannot be below zero, negative values can and do occur in a data set as a legitimate instrument response. While methods exist to address such values in a data set, there are limitations, and the use of a knowledgeable statistician is nearly indispensable in such cases. Additional discussion on the use of uncensored data can be found in two DRTF white papers available on the BHSC website (https://bhsc.llnl.gov/resource.html) and in Chapter 8 of *Beryllium: Environmental Analysis and Monitoring* (see Suggested Readings).

Room for Improvement

The collection, analysis, and data evaluation of workplace beryllium samples are more challenging than for many other particulates. This is mostly because the occupational exposure limits are low enough to challenge the sampling and analytical state-of-the-art. ACGIH lowered its TLV in recent years, and it seems likely that OSHA will also lower its PEL within the next few years. These continued changes in limit values and action levels will magnify the existing challenges in beryllium sampling and analysis. Hopefully, several research and development activities now under way will help laboratories meet these challenges.

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[table]

Table 1. Beryllium Limit Values and Action Levels
All values are eight-hour limit values except for DOE surface action levels. Information for non-U.S. jurisdictions was obtained from the GESTIS database maintained by the *Institut für Arbeitsschutz der Deutschen Gesetzlichen Unfallversicherung* (IFA), available at www.dguv.de/ifa/en/gestis. Consult GESTIS for short-term limit values.

Jurisdiction	**Limit Value (mg/m^3)**
ACGIH TLV	0.00005 inhalable
U.S. (OSHA), Australia, Austria, Belgium, Ontario, France, Japan, New Zealand, Singapore, South Korea, Sweden, U.K.	0.002
Cal/ OSHA	0.0002
Denmark, Latvia	0.001
Poland	0.0002
Quebec	0.00015
Spain	0.0002 inhalable
Switzerland	0.002 inhalable
U.S. Department of Energy	Air – 0.0002 mg/m^3; surface –

(10 CFR 850 action levels)*	0.003 mg/100 cm^2 housekeeping, 0.0002 mg/100 cm^2 for release of items or equipment
U.S. NIOSH REL	0.0005 (not to exceed)

* The DOE regulation uses the OSHA PEL as the regulatory limit; the cited values are action levels.

[end table]

Suggested Readings

- *Beryllium: Environmental Analysis and Monitoring*, Royal Society of Chemistry (2009).
- *Beryllium: Sampling and Analysis* (ASTM Special Technical Publication 1473), ASTM International (2006).
- "The Real Issue with Wall Deposits in Closed Filter Cassettes – What's the Sample?", *Journal of Occupational and Environmental Hygiene* (December 2009).
- "Analytical Performance Issues – Closed-Face Filter Cassette (CFC) Sampling – Guidance on Procedures for Inclusion of Material Adhering to Internal Sampler Surfaces," *Journal of Occupational and Environmental Hygiene* (March 2013).
- "Preparation, Certification, and Interlaboratory Analysis of Workplace Air Filters Spiked with High-Fired Beryllium Oxide," *Journal of Environmental Monitoring* (2012).