Beryllium Laboratory Analysis

The Regulations May Drive the Science

By Seuri Taruru

Beryllium has many industry-specific applications, such as medical X-ray windows for diagnostic equipment, nuclear reactors, aerospace applications, precision instrumentation, and other consumer products for which lightness and rigidity is essential. According to the National Toxicology Program, beryllium oxide (BeO) is one of the most significant beryllium compounds in production. Although beryllium and its compounds have a wide array of beneficial uses, due to its unique properties it is not an ideal metal to be used in all situations. Exposure to beryllium is linked to beryllium sensitization and Chronic Beryllium Disease (CBD), which is incurable, debilitating, and potentially fatal. The International Agency for Research on Cancer classifies beryllium and beryllium compounds as “carcinogenic to humans” (Group I), and EPA classifies beryllium as a likely human carcinogen, the lung being the primary target organ.

Laboratory analysis for beryllium samples has always presented a challenge to the analytical community. While most metals of interest to industrial hygienists have occupational exposure limits (OELs) in milligrams per cubic meter (mg/m^3), the beryllium OELs are in micrograms per cubic meter (µg/m^3). Some regulatory agencies have recently published beryllium OELs so low that in some cases a laboratory limit of detection (LOD) in nanograms (ng) is required. For most substances, science drives the regulations, but for beryllium, regulations appear to be driving science to develop laboratory analytical methods that can adequately support the proposed OELs. (EPA has issued guidelines regarding ambient and community airborne beryllium exposure, but this article focuses on beryllium from an occupational exposure perspective.)

CURRENT AND PROPOSED OELS

In 2009, ACGIH revised the beryllium threshold limit value (TLV) to 0.05 µg/m^3 based on an inhalable fraction. ACGIH TLVs are not consensus standards; therefore, they do not represent all issues raised by all interested parties (for example, issues of technical or economic feasibility).

OSHA proposed a beryllium rule in 2015 that lowers the permissible exposure limit (PEL) to 0.2 µg/m^3 in air with an action level of 0.1 µg/m^3 for an 8-hour time-weighted average (TWA). The OSHA rule also establishes a new short-term exposure limit (STEL) of 2.0 µg/m^3 over a 15-minute sampling period. Neither the PEL nor the STEL invokes the inhalable fraction. OSHA’s final rule took effect on May 20, 2017, but compliance with most provisions is not required until March 12, 2018, or later.

In 2016, the Department of Energy (DOE) issued a Notice of Proposed Rulemaking (NOPR) for 10 CFR 850, Chronic Beryllium Disease Prevention Program. The NOPR proposes a beryllium air action level (AL) of 0.05 µg/m^3 for an 8-hour TWA. The proposed AL does not include an inhalable fraction. Currently, the DOE surface contamination limit is 0.2 µg/100 cm^2 for free release and 3.0 µg/100 cm^2 removable contamination for housekeeping in beryllium operational areas during non-operational periods.

Within the European Union, the Scientific Community on Occupational Exposure Limits (SCOEL) proposed an OEL based on an 8-hour TWA of 0.02 µg/m^3, a STEL of 0.2 µg/m^3 using the inhalable fraction of airborne beryllium concentrations, and a Biological Guidance Value (BGV) of 0.04 micrograms per liter of urine. The SCOEL proposal was reviewed by the EU’s

Working Party of Chemicals, which has agreed to propose an 8-hour TWA of 0.6 µg/m^3 for a five-year transitional period followed by a permanent value of 0.2 µg/m^3. The Working Party also agreed to the STEL and BGV as proposed by SCOEL.

METHODS OF LABORATORY ANALYSIS

With these lowered beryllium OELs, industrial hygienists must determine the sampling and analytical methods that comply with regulatory requirements, meet their scientific goals, and are appropriate for the type of beryllium, as well as the sampling duration and methods sensitivity. It is important to note that some methods have trouble digesting the different forms of beryllium. For example, digestion of BeO using NIOSH method 7300 may be challenging. A study published in 2012 by the *Journal of Environmental Monitoring* notes that the use of aggressive digestion reagents such as ammonium biflouride, hydrogen fluoride, or sulfuric acid may be necessary.

Method sensitivity is a crucial aspect in beryllium sample analysis. Sensitivity in this context refers to the lowest beryllium concentration level in the sample submitted to the laboratory for analysis that can be accurately detected and reported. Laboratory sensitivity is normally explained using the Limit of Detection (LOD), Limit of Quantification (LOQ), and the Reporting Limit (RL):

- LOD, also known as Method Detection Limit (MDL) or Lower Limit of Detection, represents the lowest analyte concentration that produces a response that can be distinguished above the background level of the measurement system.
- LOQ, also known as Lower Limit of Quantification or Method Quantitation Limit (MQL), represents the lowest analyte concentration that can be successfully quantified with a given level of reliability (for example, 95 percent confidence). It is commonly considered to be 3.3 times the LOD/MDL.
- Reporting Limit (RL) represents the lowest analyte concentration that the laboratory will actually report. The RL could be equal to the LOQ/MQL or could be set at a value above the LOQ/MQL to account for fluctuations that may occur from instrument to instrument or year to year.

Traditional beryllium analysis using instrumental methods such as inductively coupled plasma atomic emission spectroscopy (ICP-AES) and atomic absorption spectroscopy (ICP-AAS) have been common in analytical laboratories for many years. However, with the proposal of lowered OELs by DOE, OSHA, and SCOEL, methods such as ICP-AES and ICP-AAS may not be sufficient.

The most frequently used beryllium analytical techniques in the U.S. are ICP-AES, inductively coupled plasma mass spectroscopy (ICP-MS), ICP-AAS, graphite furnace atomic absorption spectroscopy, and fluorescence. Some of the commonly used beryllium-specific analytical methods are OSHA IDG125G/ID206, NIOSH 7704, NIOSH 9110, and NIOSH 9102.

Typical laboratory sample detection is based on the mass on the collection media such as the MCE filter in a sample cassette, wipe, and so on. For air samples, mass on the collection media is based on the amount of air drawn through the filter. The higher the air volume, the higher the probability of “capturing” more mass of interest on the filter; therefore, the easier it is for the laboratory analysis to “see” it. Lowering the OEL for beryllium means that the analytical detection limits for shorter-duration tasks like the OELs would be challenging. The lower the air volume, the higher the analytical sensitivity needed to achieve the desired limits of detection. Tables 1 and 2 show the relationships between beryllium air sampling rates, amount of volume collected, and the resulting lab detection limit. ISO 20581 and best practices set the detection limit for the analytical laboratory at 10 percent of the OEL. This means that if the target OEL is the ACGIH TLV of 0.05 µg, the lab should have an LOD of 0.005 µg (5 ng). According to the NIOSH Manual of Analytical Methods, fluorometry can achieve an LOD of 0.1 ng.

Table 1. Sampling Rate, Resulting Air Volume, and Sample Duration

	Sampling Duration (hr.) and the resulting volume of air drawn (in cubic meters, m^3)					
Sampling Rate (L/min)	0.25 hr. (15-minute STEL)	0.5 hr. (30 min., Excursion Limit)	1.0 hr.	2.0 hrs.	4.0 hrs.	8.0 hrs. (TWA)
2.0	0.03 m^3	0.06 m^3	0.12 m^3	0.24 m^3	0.48 m^3	0.96 m^3
3.5	0.05 m^3	0.10 m^3	0.21 m^3	0.42 m^3	0.84 m^3	1.68 m^3
4.0	0.06 m^3	0.12 m^3	0.24 m^3	0.48 m^3	0.96 m^3	1.92 m^3

Table 2. Mass Collected on an Air Filter at Different Concentrations in Relation to the Air Volume Collected

Criterion	OEL Air Conc. (µg/m^3)	Volume of air collected and the resulting mass collected on filter					
		0.03 m^3	0.06 m^3	0.25 m^3	0.50 m^3	1.0 m^3	2.0 m^3
ACGIH TLV and Proposed DOE AL	0.05	0.0015 µg	0.003 µg	0.013 µg	0.025 µg	0.05 µg	0.10 µg
OSHA Action Level in 2017 Final Rule; 8-hr. TWA	0.1	0.003 µg	0.006 µg	0.025 µg	0.05 µg	0.10 µg	0.20 µg
OSHA PEL in 2017 Final Rule; 8-hr. TWA	0.2	0.006 µg	0.012 µg	0.05 µg	0.10 µg	0.20 µg	0.40 µg
OSHA STEL in 2017 Final Rule (15 minutes)	2.0	0.06 µg	0.12 µg	N/A (requires sampling rate > 4L/min for the target 15-minute STEL)			

Values in red = fluorescence; yellow = fluorescence, GF-AAS, or ICP-MS; and green = fluorescence, GF-AAS, ICP-MS, and ICP-AES. This table does not account for higher reporting limits or samples requiring extra dilution.

Going by these tables, if the target OEL is 0.05 µg/m^3, the sample duration is 30 minutes or less with a flow rate of around 2.0 liters per minute, and the analytical laboratory follows the ISO 20581 guidelines for the detection limit at 10 percent of the OEL, then the target OEL can currently be met only using molecular fluorescence.

If the target OEL is from the new OSHA Beryllium Rule, with a PEL of 0.2 µg/m^3, then at 2.0 L/min with sampling duration of 30 minutes the target OEL can be met using ICP-MS.

The beryllium analytical methods mentioned here are not the only methods used for beryllium analysis. Microwave-induced plasma spectroscopy is another, and some DOE national laboratories are exploring the use of direct-reading instrumentation such as laser-induced breakdown spectroscopy. Beryllium direct-reading instrumentation is currently in the research and development phase.

Typically, industrial hygienists are trained to manage carcinogenic risks to As Low As Reasonably Achievable (ALARA). However, given the laboratory analytical challenges, the implementation of ALARA for beryllium exposure management strategies could be modified to As Low As Accurately Detectible as described in Tables 1 and 2. This approach assumes that the personnel who manage beryllium risks have already considered elimination, substitution, and engineering controls and still must use beryllium for their projects.

LABORATORY ACCREDITATION

Laboratories currently performing industrial hygiene sample analysis follow the accreditation guidelines from ISO/IEC 17025. The AIHA Laboratory Accreditation Programs, LLC is the accrediting body utilized by most IH laboratories. Currently DOE 10 CFR 850 requires laboratory accreditation for beryllium sampling analysis or demonstration of equivalent quality assurance, but OSHA and the EU do not. (However, the new OSHA rule 1910.1024 does state that sample analysis be evaluated by a laboratory that can measure beryllium to an accuracy of plus or minus 25 percent within a statistical confidence level of 95 percent for airborne concentrations at or above the action level.)

Accreditation, even when not required, allows clients to have greater confidence in laboratory data. However, accreditation by itself does not guarantee that the laboratory is experienced in handling beryllium samples. It is prudent for the client to inquire about a lab's experience in dealing with the intricacies of beryllium analysis, data expectations, and the associated sample media. For example, some laboratories are familiar with air sampling filter cassettes but not with beryllium surface wipes or bulk samples. Another reason for communication is that most samples, in my experience, are lower than the RL. The client must then deal with censored data (results that are below the laboratory's RL). Laboratory accreditation guidelines do not discourage the laboratory from reporting results that are below the RL. In these instances, the results are reported as "less than" the RL or "ND" (not detected), and cannot be reported as zero. (As mentioned earlier, no laboratory can currently detect beryllium at the zero level.)

COMMUNICATION AND EXPECTATIONS

Before commencing a sampling event, it is important to ensure the following:

- the data quality objectives are established and understood by both the laboratory and the client
- the analytical laboratory's capabilities and limitations are based on the client's target OEL

- information is made available to the laboratory regarding the type of samples that are to be analyzed (air, swipe, vacuum, bulk) and the anticipated number of samples
- possible interferences, especially when using ICP-AES, are discussed
- lab QA/QC procedures and acceptance criteria are established

Agree on a turnaround time—how quickly can the results be provided based on when the laboratory receives the samples? This is important because “rush” samples typically cost more. However, most sampling jobs are limited by time and budget. In such cases, communication with the laboratory ensures that they can meet the project’s schedule. In some cases, the laboratory might have other projects that may not match up with the client’s schedule.

SEURI TARURU, CIH, is senior scientist at National Security Technologies in Mercury, Nev. He can be reached at (702) 295-1414 or **tarurusk@nv.doe.gov**.

Author’s note: I gratefully acknowledge Mike Brisson, the vice chairman of the AIHA Sampling and Laboratory Analysis Committee as well as the chairperson of the Beryllium Health and Safety Committee, Sampling and Analysis Subcommittee for providing guidance and support during the writing of this article.

*This manuscript has been authored with support by National Security Technologies, LLC, under Contract No. DE-AC52-06NA25946 with the U.S. Department of Energy, National Nuclear Security Administration, Office of Infrastructure and Environment. The United States Government retains and the publisher, by accepting the article for publication, acknowledges that the United States Government retains a non-exclusive, paid-up, irrevocable, worldwide license to publish or reproduce the published content of this manuscript, or allow others to do so, for United States Government purposes. The U.S. Department of Energy will provide public access to these results of federally sponsored research in accordance with the DOE Public Access Plan (**http://energy.gov/downloads/doe-public-access-plan**). DOE/NV/29546--3234.*

Resources

ACGIH: *TLVs and BEIs: Based on the Documentation of the Threshold Limit Values for Chemical Substances and Physical Agents and Biological Exposure Indices* (2009).

Brisson, M. “Laboratory Analysis Considerations for Beryllium: OSHA Final Rule, DOE Proposed Rule, European Union Proposal,” presented at AIHce EXP 2017 (June 2017).

Brisson, M. and A. Ekechukwu, ed.: *Beryllium: Environmental Analysis and Monitoring*, (August 2009).

DOE: 10 CFR Part 850, Chronic Beryllium Disease Prevention Program, Final Rule (December 1999).

DOE: 10 CFR Part 850, Chronic Beryllium Disease Prevention Program (June 2016).

EPA: Toxicological Review of Beryllium and Compounds, **http://bit.ly/berylliumtoxreview** (PDF, April 1998).

EPA: Toxicological Review of Beryllium and Compounds (May 2008).

ISO: 20581:2016, *Workplace air - General requirements for the performance of procedures for the measurement of chemical agents* (November 2016).

ISO/IEC: 17025:2005, *General requirements for the competence of testing and calibration laboratories* (May 2005).

Journal of Environmental Monitoring: "Preparation, Certification and Interlaboratory Analysis of Workplace Air Filters Spiked with High-Fired Beryllium Oxide" (February 2012).

National Toxicology Program: *11th Report on Carcinogens* (January 2005).

NIOSH: *Manual of Analytical Methods*, fifth edition, Beryllium in Air by Fluorometry, Method 7704, **http://bit.ly/nmam7704** (PDF, December 2015).

OSHA: 29 CFR Parts 1910, 1915, and 1926, Occupational Exposure to Beryllium (January 2017).

SCOEL: SCOEL/REC/175, Beryllium and Inorganic Beryllium Compounds, Recommendation from the Scientific Committee on Occupational Exposure Limits, European Commission (2017).