



Beryllium Analytical Improvements Being Pursued by the Beryllium Health and Safety Committee



Michael J. Brisson
Senior Technical Advisor
Washington Savannah River Company
Aiken, SC 29808

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Overview

- The Beryllium Issue
- About the BHSC and the Sampling and Analysis Subcommittee (SAS)
- Exposure Limits
- Current State of the Analytical Art
- Why do we need better analytical performance?
- Symposia (2002 and 2005)
- BeO Reference Material
- Standard Methods
- Sampling Techniques and Guidance
- Be accreditation
- Validation of methods/equipment
- (Near) Real-time monitors



(Source: ATSDR web site,
www.atsdr.cdc.gov)

The Beryllium Issue

- Industries where beryllium is a concern
 - Aerospace
 - Nuclear weapons
 - Automotive
 - Sports equipment
 - Aluminum (bauxite with high Be levels)
- Health Risks
 - Exposure pathways: inhalation, dermal
 - Beryllium Sensitization (BeS), 2%-19% of those exposed
 - Immunological response
 - Issues with blood tests for BeS
 - Chronic Beryllium Disease (CBD)
 - Occurs in fraction of those sensitized
 - Symptoms may not appear for >10 years
 - Treatable but not curable



(Source: Fermilab
Web site,
www-esh.fnal.gov)

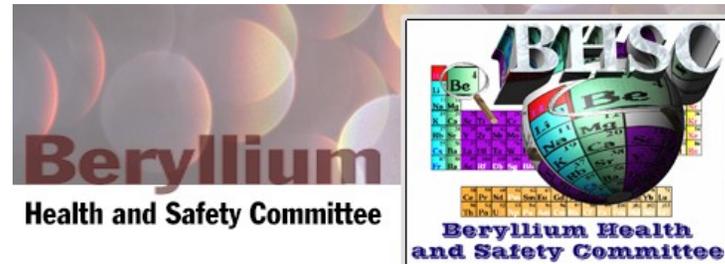
The Beryllium Issue (2)



(Source: U.S.
House of Representatives,
Committee on Resources,
www.resourcescommittee.house.gov)

- U.S. Department of Energy Sites
 - Cleanup of legacy sites
 - Ongoing operations involving Be
 - Fossil energy
- U.S. Defense Industry
 - First confirmed CBD case earlier this year
- Commercial
 - Ongoing operations (Brush-Wellman)
 - Legacy: former Loral plant near Sarasota-Bradenton airport (Florida)
- NASA (telescopes)
- European aluminum plants
- Kazakhstan Be plant

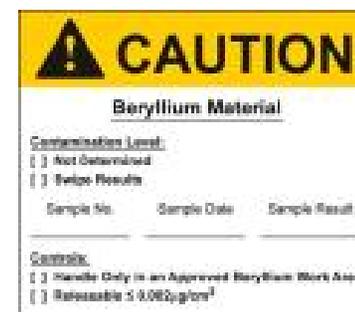
About the BHSC



- Ad hoc group with representatives from DOE sites, other federal agencies and groups
- Successor to Beryllium Monitoring Subcommittee (1990)
 - BMS charter included an “analytical round-robin”
 - Under auspices of Beryllium Coordinating Committee, disbanded in 1994
 - Re-constituted as ad hoc BHSC in 1995
- Mission (www.sandia.gov/BHSC): “To promote the safe use of beryllium and prevent chronic beryllium disease and other adverse health effects in the workplace.”
- Current chair: Kathryn Creek, LANL
- Subcommittees: CBD Prevention, Research Needs, Technical Practices, Medical/Epidemiological, Sampling and Analysis (SAS)
- SAS established November 2003

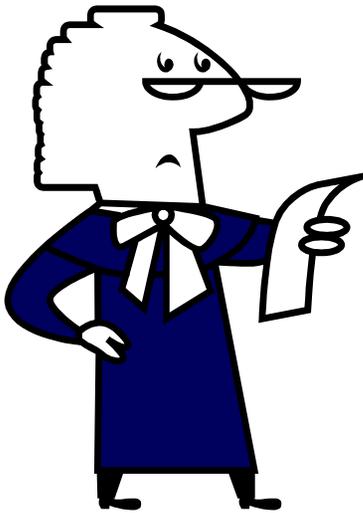
Exposure Limits (OSHA and ACGIH)

- ACGIH® TLV® and OSHA Permissible Exposure Limit (PEL)
 - TLV® and PEL 2 $\mu\text{g}/\text{m}^3$ (8-hour time-weighted average)
 - Originally proposed in 1949 from Atomic Energy Commission studies
 - ACGIH® adopted TLV® in 1959 for beryllium; applied to “beryllium and compounds” in 1986
- In 1990’s, learned that this level not necessarily protective
 - Incidences of sensitization and CBD at lower exposure levels
 - 1999: ACGIH® proposed a TLV-TWA of 0.2 $\mu\text{g}/\text{m}^3$; not adopted
 - 2005: ACGIH® Notice of Intended Change (NIC) to 0.02 $\mu\text{g}/\text{m}^3$ TLV-TWA; not adopted
 - 2006: ACGIH® NIC for 0.05 $\mu\text{g}/\text{m}^3$ TLV-TWA and short term exposure limit (STEL) of 0.2 $\mu\text{g}/\text{m}^3$
 - Change in OSHA PEL being considered independently of ACGIH® (process began with request for info in 2002)



(Source: Lawrence
Livermore
National Lab)

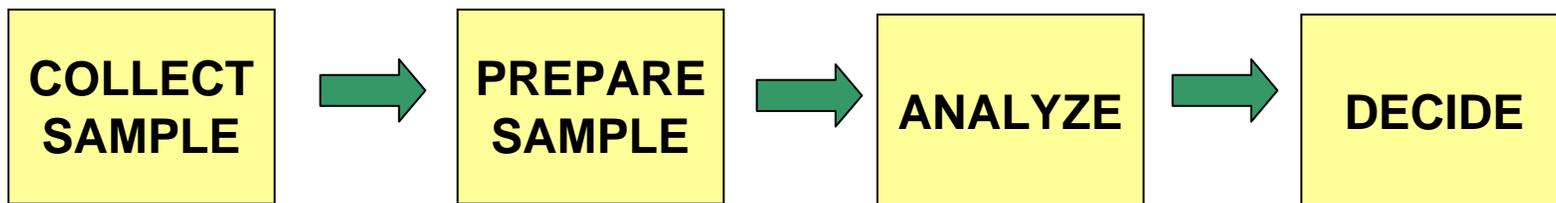
10 CFR 850 and 10 CFR 851



- DOE Beryllium Rule (10 CFR 850)
 - Effective January 7, 2000
 - Response to exposure concerns in DOE nuclear facilities
 - Action levels of $0.2 \mu\text{g}/\text{m}^3$ (air, 8-hr TWA) and $0.2 \mu\text{g}/100\text{cm}^2$ (surface)
 - Based on lab capabilities at that time – not health-based
 - OSHA, ACGIH do not have surface wipe action levels like DOE
 - Measurement uncertainty within $\pm 25\%$ at action level
- DOE Worker Health and Safety Rule (10 CFR 851)
 - Effective 2/9/07
 - Integrated with 10 CFR 850
 - Requires compliance with 2005 ACGIH[®] TLVs[®] (if lower than OSHA PEL's)
 - Changes to OSHA PEL's would be applicable
 - Changes to ACGIH[®] TLV[®] would not be applicable across DOE, but could apply to individual DOE sites or contracts

Current State of the Analytical Art

- Based on results from stationary laboratories
 - Lagging indicator
 - A “rush” sample can be done in a couple of hours, but typical delay factor is 24+ hours at best
 - Thousands of samples per year
 - Y-12, AWE: approximately 30,000 per year (each)
 - At least two other DOE sites >15,000 per year (each)
 - Relatively expensive, especially for rad-contaminated samples (can be \$200+/sample if rad-contaminated)



Current State of the Analytical Art (2)

■ Sample Preparation

- Dissolve or extract
- Typically requires acid solutions with heating
- Robustness an issue, especially for BeO
 - H_2SO_4 effective on BeO but problematic for some media
 - HF, HClO_4 effective but may not be desirable
 - Ammonium bifluoride extraction method
- Typical techniques hard to make field-portable



Current State of the Analytical Art (3)



(ICP-MS installed
at Savannah River Site)

- Sample Analysis
 - Atomic absorption (flame or furnace) – U.K.
 - ICP Emission Spectroscopy
 - Dominant method at U.S. labs
 - ICP Mass Spectroscopy
 - Not widely used for industrial hygiene purposes
 - Atomic Fluorescence
 - Recently developed method
 - Requires lab space, chemist and technician support
 - Lab reporting limits
 - OK for current OSHA PEL
 - DOE action level pushes envelope
 - ACGIH® TLV-TWA of $0.05 \mu\text{g}/\text{m}^3$, if adopted, would push it even more

Need for Better Analytical Performance

Impacts of Beryllium Rule

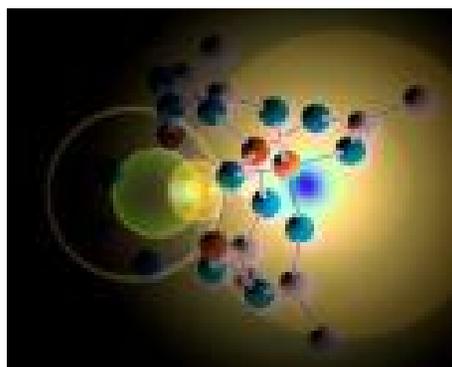
- Operational impacts due to delays in receiving results
- Characterization of legacy areas
- Analytical issues
 - Wide variety of sampling and analysis methods
 - Discrepancies among accredited labs
 - Need for faster results and lower quantification limits

SUMMARY: The Department of Energy (DOE) is today publishing a final rule to establish a chronic beryllium disease prevention program (CBDPP) to reduce the number of workers currently exposed to beryllium in the course of their work at DOE facilities managed by DOE or its contractors, minimize the levels of, and potential for, exposure to beryllium, and establish medical surveillance requirements to ensure early detection of the disease. This program improves and codifies provisions of a temporary CBDPP established by DOE directive in 1997.

EFFECTIVE DATE: This rule is effective January 7, 2000.

(64 FR 68854, 12/8/1999)

Need for Better Analytical Performance (2)



(Source: Los Alamos
National Lab web site,
www.lanl.gov)

- Current DOE action level
 - Need to be able to quantify at 10% of an action level to assure reliable detection at that level
 - Action level of $0.2 \mu\text{g}/\text{sample}$ requires ability to quantify at $0.02 \mu\text{g}/\text{sample}$, or $20 \text{ ng}/\text{sample}$
- ACGIH[®] NIC (STEL of $0.2 \mu\text{g}/\text{m}^3$)
 - Typically 15 min/sample of air at 2 L/min
 - That's 30 L/sample or $0.03 \text{ m}^3/\text{sample}$
 - Equivalent action level would be $0.2 \mu\text{g}/\text{m}^3$ times $0.03 \text{ m}^3/\text{sample}$ or $6 \text{ ng}/\text{sample}$
 - 10% of that (see above) is $0.6 \text{ ng}/\text{sample}$
 - Beyond reach of ICP-AES
 - High-volume samplers would help

Need for Better Analytical Performance (3)

- Medical/epidemiological issues
 - What should the PEL really be? How well can we measure there?
 - Exposure pathways other than air
 - Species of concern
 - Is BeS/CBD risk the same for BeO, Be metal, and alloys, or is it different for each species?
 - Does analytical community need to measure Be by species rather than total Be?



Need for Better Analytical Performance (4)

- Current methods are for beryllium by mass
- Some studies have indicated that particle number may be a better measure of potential for BeS
- Particle number hypothesis (McCawley and others) needs to be validated
- We would then need to collect appropriate sample fractions and measure them separately
 - Might require even lower quantification limits

Symposia (2002 and 2005)

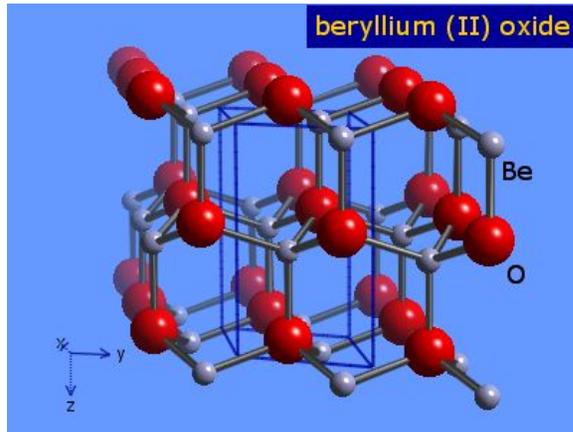
- February 2002, Santa Fe, NM
 - Sponsored by LANL and Network of Senior Scientists and Engineers
 - Focused on instrumentation developments
- April 2005, Reno, NV
 - Sponsored by ASTM International
 - Sampling and analytical topics
- November 2005, Salt Lake City, UT
 - Sponsored by BHSC SAS, DOE, NIOSH, SRNL, and others
 - Sampling and analytical topics
- Another one in 2008?



SAS Membership and Working Groups

- Over 40 members from throughout DOE as well as DOD, AWE, NIOSH, and other groups
- Multi-discipline (analytical, IH, researchers, managers)
- SAS divided into working groups:
 - BeO/Digestion
 - Standard Methods
 - Sampling
 - Accreditation
 - Validation

BeO Reference Material



(Source:
WebElements™,
www.webelements.com
Used with permission)

- Most difficult form typically encountered in workplace samples
- Why needed:
 - Validation of sample preparation methods
 - Proficiency Acceptance Testing (PAT) samples (pedigree required by AIHA)
 - Validation of lab and field analytical equipment
- Status:
 - Funding recently obtained
 - Purchasing well-characterized material from Brush-Wellman
 - Working with NIST to establish pedigree

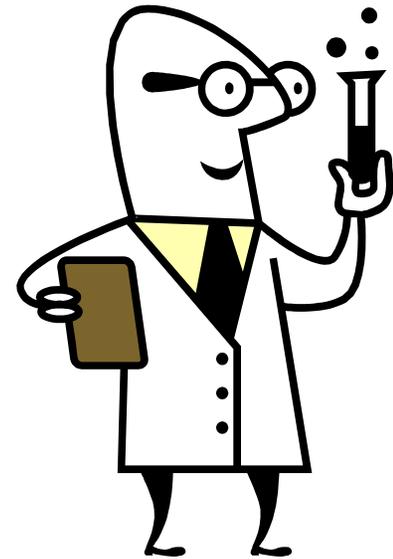
BeO Reference Material (2)

BeO/Digestion Working Group Path Forward:

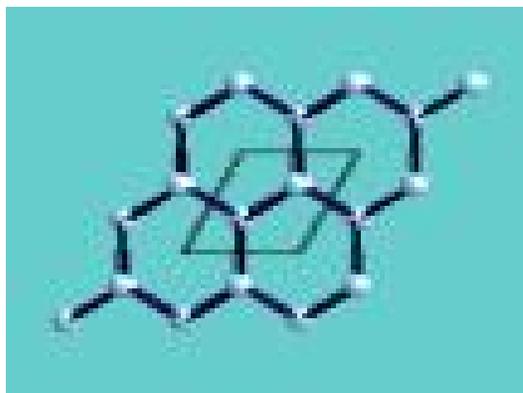
- Establish BeO Reference Material
- Change AIHA proficiency testing samples from Be acetate to BeO
- Identify/validate optimal sample preparation methods
 - Every DOE site using a different method
 - Many are modifications of “standard” methods or are in-house methods
 - Desire a method that does not use HF or HClO₄, if possible

Standard Methods

- Strategy: develop voluntary consensus standards via ASTM
 - Consistent with National Technology Transfer & Advancement Act (1995)
 - Easiest consensus path forward
 - DOE can choose to incorporate or not
 - Non-DOE entities can also use
- Sampling: dry wipe method being balloted in ASTM
- Sample Preparation: awaiting BeO reference material
- Analysis:
 - Atomic fluorescence method has been published (ASTM D7202)
 - ICP-MS method for wipes being drafted



Sampling Techniques and Guidance



(Source: Oxford University web site, www.chem.ox.ac.uk)

- Air Sampling
 - Inhalable versus respirable
 - ACGIH NIC proposes inhalable
- Guidance on bulk versus wipe sampling
- Wipe Collection Efficiency
 - Number of times a surface is wiped
 - Wet versus dry
 - Optimal wiping media

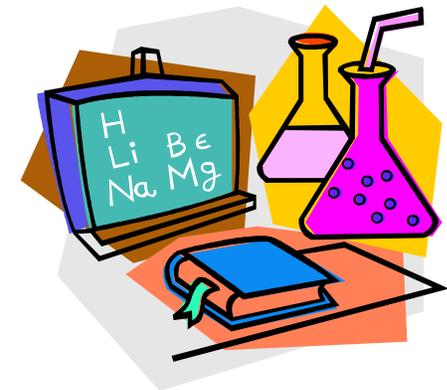
Accreditation Working Group

- Has provided information to AIHA assessors
 - Appropriate sample preparation for forms of Be expected in samples
 - Interference correction (ICP-AES)
 - Appropriate media/matrix matching
 - Lab reporting limit
 - Appropriate quality control
- Accreditation of mobile labs and portable equipment
 - Currently no mobile labs are AIHA accredited
 - Need fields of testing for portable equipment
 - Establishing dialogue with AIHA on these issues
- Terminology
 - Lexicon of terms to cut through confusing terminology (example: IDL, MDL, ML, PQL, EQL)
 - Seeking opportunity to harmonize

Validation of Methods and Equipment

Why Is This So Important?

- Many attempts have been made at new/improved field analysis methods
- Some have been commercially advertised
- Except for atomic fluorescence method, none known to have undergone interlaboratory evaluation
- Result: questionable field applicability



Validation of Methods and Equipment (2)

- Independent validation (does not endorse any method or equipment)
- Typically involves six labs as required by ASTM
- Has validated atomic fluorescence method (8 labs)
- Preparing to validate a beryllium column separation resin
- Plans to write a generic validation protocol



Real-Time Analysis: A Real Need

- Current lab-based analyses cost DOE about \$4 million/year
- (Near) real-time monitoring could save over \$1 million/year in analytical costs
- Faster field decision-making would improve worker protection and reduce operating costs
- Needed for air monitoring and surface wipe samples
 - Is that one device or two?
- Examples of techniques that have been considered:
 - Laser Induced Breakdown Spectroscopy (LIBS)
 - Microwave Induced Plasma Spectroscopy (MIPS)
 - Time of Flight Mass Spectroscopy (TOF-MS)
 - Anodic Stripping Voltammetry
 - Colorimetric methods
 - Atomic Fluorescence



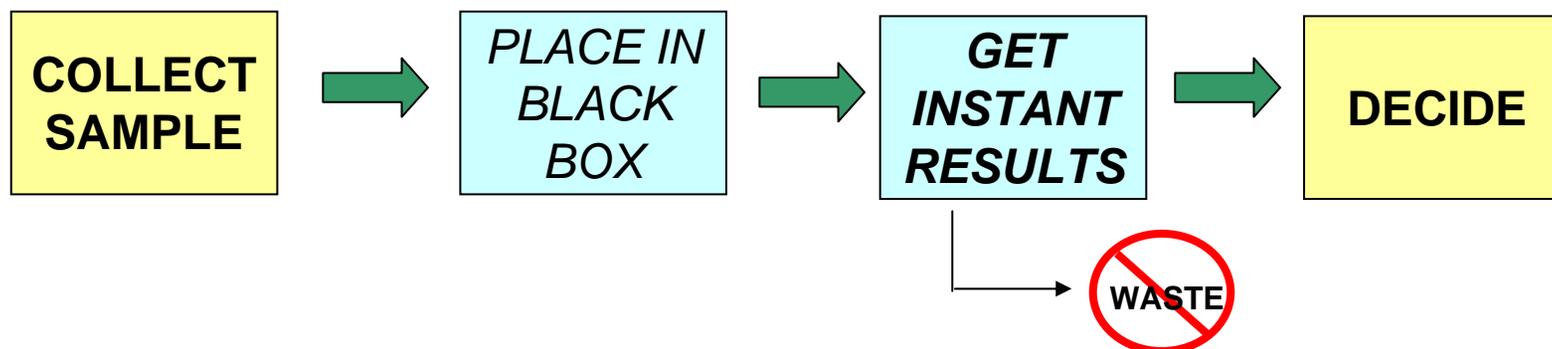
Real-Time Analysis: A Real Need (2)

Issues:

- **Validation**
 - About a dozen known development efforts so far
 - To our knowledge, only one independently validated (just last year) – that one still needs field testing
 - Need qualified test bed for aerosol testing
- **Cost and Portability**
- **Detection Limit (lower TLV may exacerbate issue)**
- **Direct-solid versus liquid-based methods**
 - Direct-solid techniques do not produce liquid waste but are typically less precise
 - Liquid-based methods are more precise but produce liquid waste
- **Most are not beryllium-specific**
 - Some made for other applications and then marketed for Be
 - Result: some needs may not be met

Real-Time Analysis: A Real Need (3)

- The “black box” wish list:
 - Real-time air monitor and surface wipe analyzer (ideally the same device)
 - Reporting limits comparable to lab analysis
 - Avoid/minimize liquid waste
 - Portable (NOT just “transportable”)
 - Easy to use and maintain
 - Cheap
- Funding for a coordinated development effort just now becoming available (NNSA Defense Programs)



If You Would Like to Help ...

BHSC Sampling and Analysis Subcommittee (SAS)

- Monthly conference calls
- Meet twice per year
- Next BHSC and SAS meeting:
April 4-5, Bethesda, MD



Acknowledgements

- BHSC Sampling and Analysis Subcommittee members
- IH Lab Directors throughout DOE
- Kathy Creek, BHSC Chair

Thanks!