Overview of Beryllium Analytical Chemistry – History, State of the Art, and Future Needs

Michael J. Brisson
Savannah River Nuclear Solutions LLC
Aiken, SC 29808

Third International Symposium on Beryllium Particulates and Their Detection
Albuquerque, NM
November 18, 2008
Mention of commercial products in this presentation does not imply endorsement by the author, SRNS, SRS, or the U.S. Department of Energy (DOE).

The findings and conclusions in this presentation are those of the author and do not necessarily represent the views of SRNS, SRS, or DOE.

The speaker is an employee of a Department of Energy (DOE) contractor, and is not a spokesperson for DOE.
Goals

- Review history of trace-level beryllium analysis, particularly since DOE implementation of 10 CFR 850
- Review developments this decade in sample preparation and analysis
- Review issues to be addressed
- Discuss future analytical needs

Note that:
- For many of you, this will be more “review” than “new information”
- Objective is to get everyone on the same page as to where we are and where we need to go

I won’t answer all your questions, but maybe I’ll whet your appetite for what’s to come later in the symposium
Outline

- **Background**
  - Beryllium sources, uses, risks
  - Occupational Exposure Limits (OELs) up to the present
  - Impact of 10 CFR 850 (“Beryllium Rule”)

- **Sample Preparation**
  - Experiences and challenges
  - Keys to success

- **Sample Analysis**
  - Current instrumentation options
  - Data reporting
  - Keys to success

- **Accreditation and Proficiency Testing**

- **Trends and Analytical Impacts**
  - Declining OELs
  - Dermal sampling

- **What Else Do We Need?**
  - Speciation
  - (Near) Real-Time Monitoring
Beryllium is Found in ...

- **Foodstuffs** ($\mu$g per kg fresh weight – ATSDR 2002)
  - Milk (0.2)
  - Potatoes (59)
  - Crisp bread (112)
  - Kidney beans (2200)
- **Soils** (up to 15,000 $\mu$g/kg – USGS)
- **Coal** (0.2% - ATSDR 2002)
- **Orchard Leaves** (26 $\mu$g/kg – ATSDR 2002)
- **Cigarettes** (up to 0.74 $\mu$g/cigarette – ATSDR 2002)
- **Minerals such as bertrandite, beryl, aquamarine, emerald**
Beryllium Properties

• Lightweight
• High melting point (1287°C)
• Thermal conductivity
• Moderator
• Neutron reflector
• Relatively transparent to X-Rays
  – Used in windows for nondestructive analytical equipment
  – Techniques like point-and-shoot XRF not viable for Be detection
Uses for Be Products (20%-100%)

- Satellites and spacecraft
- Guidance systems (military and commercial)
- Brake parts (automotive, aircraft)
- Nuclear weapons (neutron reflector)
- X-Ray windows
- Optical instruments
- High-end audio
- Sports equipment

Beryllium Alloys

- **Copper-beryllium (CuBe)**
  - Resistant to metal fatigue failure
  - Resistant to corrosion
  - Rotary-dial telephone springs
  - Non-sparking tools
- **Aluminum-beryllium (AlBeMet® - Brush-Wellman)**
  - Resistant to corrosion
- **Nickel-beryllium**
- **Uses for alloys:**
  - Fire control sprinkler heads
  - Aircraft landing gear bushings
  - Current-carrying springs
  - Electromagnetic shielding
Beryllium Oxide

- Semiconductor parts
- Integrated circuits
- Good thermal conductivity
- Good electrical insulator
- Nuclear reactors
  - Moderator
  - Neutron reflector

Used with permission)
• Originally based on AEC studies in late 1940’s
• Initial proposal: 25 $\mu$g/m$^3$
  – For protection against acute disease
• Ambient air limit: 0.01 $\mu$g/m$^3$
  – The first ambient air limit in the U.S.
  – Still in effect today
• Ultimately settled on 2 $\mu$g/m$^3$ (8-hr time weighted average)
  – Protect against chronic beryllium disease (CBD)
  – Based on extrapolating prevailing OELs for heavy metals
  – Said to have been proposed in a taxi

(Source: www.ultimatetaxi.com)
Current Occupational Exposure Limits

- **ACGIH® Threshold Limit Value (TLV®) and OSHA Permissible Exposure Limit (PEL)**
  - ACGIH® TLV® and OSHA PEL: 2 μg/m³ (8-hour time-weighted average or TWA)
  - Same limit in Austria, Spain, France, Sweden, U.K., and Ontario
    - Denmark: 1 μg/m³
  - ACGIH® adopted TLV® in 1959 for beryllium; applied to “beryllium and compounds” in 1986

- **Short-term exposure limits (STEL)**
  - Maximum exposure for any 15-minute period
  - U.S.: 5 μg/m³
  - Austria: 8 μg/m³
  - Denmark, Hungary: 2 μg/m³

- **Visit GESTIS database (BGIA) for more limit values**
  - [www.dguv.de/bgia/gestis-limit-values](http://www.dguv.de/bgia/gestis-limit-values)

(Source: Lawrence Livermore National Lab)
Recently Lowered Occupational Exposure Limits

  - See next slide
  - Exposure limit of 0.2 \( \mu g/m^3 \) (air), equal to DOE action level
- Quebec Province (2006)
  - Exposure limit of 0.15 \( \mu g/m^3 \)
- Pending proposals to be discussed later
- Response to studies showing that 2 \( \mu g/m^3 \) is not adequately protective
- Downward trend has an impact on how much analytical sensitivity is needed

It's like the game of limbo ... How low can you go???
(picture from nyiboosterclub.org)
DOE “Beryllium Rule” (10 CFR 850)

- Officially the Chronic Beryllium Disease Prevention Program
- Effective January 7, 2000
- Response to exposure concerns in DOE nuclear facilities
- Action level of 0.2 $\mu$g/m$^3$ (air, 8-hr TWA)
- Housekeeping within Be areas: 3 $\mu$g/100cm$^2$ (surface)
- Release to non-Be area: 0.2 $\mu$g/100cm$^2$ (surface)
  - Based on lab capabilities at that time – not health-based
  - OSHA, ACGIH® do not have surface wipe action levels like DOE; however, Quebec (IRSST) and AWE also do surface wipe measurements
- Measurement uncertainty within $\pm$25% at action level
Impacts of DOE Beryllium Rule

- **Substantial increase in sampling and analysis**
  - 2004 data from nine DOE sites:
    - 11,746 air samples
    - 77,509 surface wipe samples

- **Introduction of surface wiping requirement**
  - No other surface wipe action level currently exists
  - However, IRSST (Quebec), AWE perform surface sampling

- **Potential influence on others**
  - OSHA says surface PEL a possible option
  - NAS study for Air Force suggests possibility of surface sampling

- **Lowered action level by one order of magnitude**
  - Impacts required analytical sensitivity

---

**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)
Sample Preparation - Methods

• **Dissolve or extract**
  - Typically requires acid solutions with heating
    - $\text{HNO}_3$, $\text{HCl}$, $\text{H}_2\text{SO}_4$, $\text{H}_2\text{O}_2$, $\text{HF}$, $\text{HClO}_4$ in various combinations
      (one DOE lab uses all six!)
    - Alternative: $\text{NH}_4\text{HF}_2$ (fluorescence method)
    - Energy sources: hot plate, hot block, microwave, ultrasound
  - Lack of consistency
    - Many DOE labs have modified a “standard” method from ASTM, EPA, NIOSH, or OSHA
    - Additional standard methods: ISO, U.K. Health and Safety Executive, INRS (France)
    - Many use one method for air samples and another for surface wipes
    - Result: difficult to compare results among labs
### Sample Preparation – 2004 Survey Data

<table>
<thead>
<tr>
<th>Site ID*</th>
<th>Energy System</th>
<th>Digestion Reagents</th>
<th>Final Sample Volume (mL)</th>
<th>Storage time (typical/maximum)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Can-1</td>
<td>Hotplate</td>
<td>HNO₃, HClO₄</td>
<td>10</td>
<td>2-3 days/ ...</td>
</tr>
<tr>
<td>DOD-1</td>
<td>Hot block</td>
<td>HNO₃, H₂O₂</td>
<td>50</td>
<td>1-2 weeks/ ...</td>
</tr>
<tr>
<td>DOD-2</td>
<td>Open vessel (OV) microwave</td>
<td>HNO₃, H₂O₂, HCl</td>
<td>25</td>
<td>4 hours/1 week</td>
</tr>
<tr>
<td>DOD-3</td>
<td>Hot block or OV microwave</td>
<td>HNO₃, H₂O₂</td>
<td>15-25</td>
<td>4-16 hours/3 days</td>
</tr>
<tr>
<td>DOE-1</td>
<td>Hotplate</td>
<td>HNO₃, HCl</td>
<td>10</td>
<td>1-7 days/2 weeks</td>
</tr>
<tr>
<td>DOE-2</td>
<td>Closed vessel (CV) microwave</td>
<td>HNO₃</td>
<td>...</td>
<td>&lt;1 day/ ...</td>
</tr>
<tr>
<td>DOE-3</td>
<td>Hotplate</td>
<td>H₂SO₄, HNO₃, H₂O₂, HCl</td>
<td>10</td>
<td>&lt;1 day/2 weeks</td>
</tr>
<tr>
<td>DOE-4</td>
<td>OV microwave</td>
<td>H₂SO₄</td>
<td>25</td>
<td>1-2 days/ ...</td>
</tr>
<tr>
<td>DOE-6</td>
<td>Hot block</td>
<td>H₂SO₄, HNO₃, H₂O₂, HCl, HF, HClO₄</td>
<td>25</td>
<td>1 hour/&lt;1 day</td>
</tr>
<tr>
<td>DOE-7</td>
<td>CV microwave</td>
<td>HNO₃</td>
<td>25</td>
<td>24 hours/30 days</td>
</tr>
<tr>
<td>DOE-8</td>
<td>Hot block</td>
<td>HNO₃, H₂O₂, HCl, HF</td>
<td>25</td>
<td>24 hours/&gt; 2 weeks</td>
</tr>
<tr>
<td>DOE-9</td>
<td>OV microwave</td>
<td>H₂SO₄, HNO₃</td>
<td>10</td>
<td>&lt;1 day/14 days</td>
</tr>
<tr>
<td>NIOSH-1</td>
<td>Hotplate</td>
<td>HNO₃, HClO₄</td>
<td>10</td>
<td>1 day/ ...</td>
</tr>
<tr>
<td>OSHA-1</td>
<td>Hotplate</td>
<td>H₂SO₄, HNO₃, H₂O₂, HCl</td>
<td>50</td>
<td>1 day/15 days</td>
</tr>
<tr>
<td>UK-1</td>
<td>Hotplate</td>
<td>HNO₃, HClO₄</td>
<td>5</td>
<td>&lt;1 week/&lt;2 weeks</td>
</tr>
</tbody>
</table>

Sample Preparation – Robustness

• Robustness an issue, especially for BeO
  – $H_2SO_4$ effective on BeO but problematic for some media
  – Some acids (HF, $HClO_4$) may not be desirable
  – Physical characteristics of BeO can make a difference
    ■ Firing temperature
    ■ Particle size and surface area
  – Concerns about efficacy of $HClO_4$ (NIOSH 7300) on high-fired BeO
  – Ammonium bifluoride extraction method (*Presentations Wednesday*)
    ■ Effective in air, surface wipe and soil samples
  – *It is possible that some labs may not realize their preparation method is not fully effective in dissolving BeO*

• Addressing issue of robustness has been hindered, until now, by lack of BeO Standard Reference Material
  – But now we have it: NIST SRM 1877 (*Winchester presentation Wed.*)
Sample Preparation – Wall Deposits

- Some particulate deposits on inner walls of air filter cassettes; amount varies with different metals
- OSHA procedure for hexavalent chromium (ID-215, Version 2) includes wiping inner sampler wall
  - Being prepared for analysis separately from filter
  - OSHA web site says this should be done for all metals
  - Roughly doubles analytical labor and cost
- Impetus to require accounting for wall deposits for other aerosols and particulates, including Be
- Other sample preparation options:
  - Digest sample within the cassette (French standard)
  - Rinse wall deposits into digestion vessel with filter sample
- *Three presentations Wednesday on this topic*
Sample Preparation – Standards

• Currently available:
  – Air filters, acid digestion: NIOSH 7102, 7300, 7303; OSHA ID-125G, ID-206; HSE 29/2 (UK); IRNS Fiche 003 (France); ASTM D7035, D7439; ISO 15202-2
  – Surface wipes, acid digestion: OSHA ID-125G, ID-206; NIOSH 9102
  – Bulk samples, acid digestion: OSHA ID-125G, ID-206
  – Extraction (air filters, surface wipes): ASTM D7202

• Newly available for soils: ASTM D7458 (Ashley presentation Wednesday)

[Source: Brisson et al., J Environ Monit, Vol. 8, pp. 605-611 (2006), updated]
Sample Preparation – Keys to Success

• For IH field and programs personnel:
  – Make sure your lab’s sample preparation method is fit for purpose
    ■ Can handle the types of samples you will collect
    ■ Can dissolve or extract BeO effectively unless you know for a fact you do not have BeO to worry about
  – Avoid bulky sampling media (can affect dilution factor required and thus affect sensitivity)
  – Avoid sending the lab “surprises” without first discussing with them

• For the lab:
  – Ensure your protocol is robust
    ■ Able to dissolve/extract forms of Be in your samples
    ■ Able to handle sampling media
  – Ensure you have data to demonstrate adequate performance

(Source: www.wikimedia.org)
Sample Analysis – What to Measure?

- OELs are based on beryllium by mass
  - “Total dust” using closed-face cassettes
- Some studies suggest particle number may be a better measure of potential for BeS
- ACGIH has proposed basing its TLV on inhalable sampling convention
  - Reduces size of air sample we are working with
  - Could require greater analytical sensitivity
- *All this matters analytically because with beryllium we are on the ragged edge of what we can detect and quantify*
Sample Analysis and Size-Selective Sampling

- International push to inhalable fraction
  - Particles between 10-100 mm not efficiently sampled by CFC
  - ACGIH NIC for beryllium proposes inhalable fraction
ACGIH® NIC

- TLV of 0.05 $\mu$g/m$^3$ (8-hr time weighted average)
- STEL of 0.2 $\mu$g/m$^3$
  - Typically 15 min/sample of air at 2 L/min
  - That’s 30 L/sample or 0.03 m$^3$/sample
  - Equivalent action level would be 0.2 $\mu$g/m$^3$ times 0.03 m$^3$/sample or 6 ng/sample
  - 10% of that (see above) is 0.6 ng/sample

It’s easy for folk to say “the lab needs to lower its reporting limits” but with beryllium the OELs are far lower than they are for other metals (and, unfortunately, our sensitive rad counting techniques don’t work here)
## Sample Analysis – TLV Comparison

<table>
<thead>
<tr>
<th>Element</th>
<th>TLV (mg/m(^3))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arsenic</td>
<td>0.01</td>
</tr>
<tr>
<td>Barium</td>
<td>0.5</td>
</tr>
<tr>
<td>Beryllium</td>
<td>0.002 (current); 0.00005 (NIC)</td>
</tr>
<tr>
<td>Cadmium</td>
<td>0.01</td>
</tr>
<tr>
<td>Chromium (VI), insoluble</td>
<td>0.01</td>
</tr>
<tr>
<td>Cobalt</td>
<td>0.02</td>
</tr>
<tr>
<td>Lead</td>
<td>0.05</td>
</tr>
<tr>
<td>Selenium</td>
<td>0.2</td>
</tr>
<tr>
<td>Silver (soluble compounds)</td>
<td>0.01</td>
</tr>
</tbody>
</table>

(Source: ACGIH TLV Book)
Sample Analysis – ICP-AES

- Inductively coupled plasma atomic emission spectroscopy
  - Sometimes ICP-OES (O=optical) in literature
- The “workhorse” for metals at most IH labs in the U.S.
  - High throughput, multiple elements
- Measures emission spectrum of atoms excited by high-temp plasma
  - Typical Be lines: 313.042 nm, 313.106 nm, 234.861 nm
- Typical lower reporting limits: 0.01 – 0.05 μg per sample
  - Can be lower if all beryllium is soluble (i.e., no dilution factors)
  - How that translates to μg/m³ or μg/100 cm² depends on how much air was pulled through filter or how much surface was wiped
  - Not low enough for air filters under ACGIH NIC
- Key issue: interferences from other metals (spectral overlap)
  - Instances of different results on split samples due to differences in interference correction
    - Robbins presentation Wednesday
  - Interfering metals may be removed prior to analysis (Bernard presentation Wednesday)
Sample Analysis – GFAA

• Graphite furnace atomic absorption
• Measures absorption by ground-state atoms
• Used in U.K.
• Typical method detection limit: 0.005 μg/sample (based on NIOSH 7102)
  – Versus 0.006 mg for a 30-L air sample measured for STEL of 0.2 μg/m³
• Throughput not as high as ICP-AES or ICP-MS
Sample Analysis – ICP-MS

- Inductively coupled mass spectrometry
- Measures mass/charge ratio of ionized particles
- High throughput but more expensive than ICP-AES or GFAA
- Typical method detection limit: 0.001 μg/sample (based on EPA 200.8)
  - Most newer ICP-MS systems can do better
- Interferences exist but (for Be) are not as severe as for ICP-AES

(ICP-MS installed at Savannah River Site radiological lab)
Sample Analysis – Fluorescence

- Extraction into dilute ammonium bifluoride solution, followed by addition of detection solution and fluorimeter measurement
- Typical lower reporting limit: 0.0002 μg/sample
  - Well able to meet ACGIH NIC requirements
- Currently available version is inexpensive (~$10K) but somewhat labor-intensive
- Specific to beryllium
- Automated version is under development (DOE SBIR Phase II grant) (*Wednesday presentations*)
## Sample Analysis – Standards

<table>
<thead>
<tr>
<th>Method ID</th>
<th>Instrumentation</th>
<th>Air Filters</th>
<th>Surface Wipes</th>
<th>Bulk Samples</th>
</tr>
</thead>
<tbody>
<tr>
<td>ASTM D7035</td>
<td>ICP-AES</td>
<td>X</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ASTM D7439</td>
<td>ICP-MS</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ASTM D7202</td>
<td>Fluorescence</td>
<td>X</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>EPA 200.7</td>
<td>ICP-AES</td>
<td>X</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>EPA 200.8</td>
<td>ICP-MS</td>
<td>X</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>EPA 6010B</td>
<td>ICP-AES</td>
<td>X</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>EPA 6020</td>
<td>ICP-MS</td>
<td>X</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>HSE 29/2 (UK)</td>
<td>GFAA</td>
<td></td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>ISO 15202-3</td>
<td>ICP-AES</td>
<td></td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>NIOSH 7102</td>
<td>GFAA</td>
<td></td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>NIOSH 7300</td>
<td>ICP-AES</td>
<td></td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>NIOSH 7303</td>
<td>ICP-AES</td>
<td></td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>NIOSH 9102</td>
<td>ICP-AES</td>
<td></td>
<td></td>
<td>X</td>
</tr>
<tr>
<td>OSHA ID-125G</td>
<td>ICP-AES</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>OSHA ID-206</td>
<td>ICP-AES</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
</tbody>
</table>
Sample Analysis – Data Reporting

BHSC task force addressing these issues:
• Drive for lower detection and reporting limits
• Desire for labs to report values below their reporting limits (i.e., provide non-censored data)
  – Many data sets are mostly below reporting limits, requiring more samples for needed statistics (i.e., 59 samples for non-parametric)
  – EPA: flag data below reporting limit
  – AIHA LQAP Policy Module 2A: do NOT report data below reporting limit
  – Do NOT ask labs to violate requirements for their accreditation
  – Thus, reporting of any non-censored data would need to be clearly identified as NOT covered under AIHA accreditation
• Potential changes to EPA method of determining MDL and potential impacts to IH labs
• Need for guidance documentation
• C. Davis presentation Wednesday
Sample Analysis – Keys to Success

• For field IH and programs personnel:
  – Clearly define your data quality objectives
  – Work with lab to select sampling media that optimizes lab’s detection capabilities
  – Ensure proper interpretation of data received from lab (may require statistician assistance or statistical software)

• For laboratory personnel:
  – Select methods/instruments that meet data quality objectives
  – Address interferences (especially important for ICP-AES)
    ■ Ion exchange removal and/or software-based correction
  – Ensure proper data reporting

(Source: www.wikimedia.org)
Accreditation

- Provides assurance of quality of laboratory results
- NOT a guarantee
  - In 2002, SRS changed its sample preparation method after getting different results from two accredited laboratories (issue with interference correction)
- Governing standard: ISO 17025, General requirements for the competence of testing and calibration laboratories
- Two sanctioned ISO 17025 accrediting bodies in U.S.:
  - A2LA
  - AIHA
  - Representatives from both scheduled to speak Wednesday
Accreditation Issues

• Fluorescence method is field-deployable
  – At least five DOE sites are considering field measurement of Be

• Current AIHA accreditation program can be used *in theory* by field-portable or mobile labs, but there are issues with:
  – Number of personnel at field location
  – Data review and reporting

• EPA also needs a viable field-portable/mobile lab program

• Concept under development by AIHA (*Morton presentation Wednesday*)
Proficiency Testing

- **AIHA beryllium PAT samples use soluble beryllium acetate**
  - Easy to dissolve
  - Not indicative of how robust the sample preparation method is with respect to refractory forms such as BeO

- **DOE working with AIHA toward a BeO PAT program**
  - Details being worked out
  - Would be better indicator of sample preparation robustness
  - *Morton presentation Wednesday*
Trends - OELs

• When will OELs stop trending lower?
  – We do not have an exposure-response relationship
  – We have studies with empirical data suggesting lack of BeS and/or CBD at various levels
  – Further discussion in Tuesday Med/Epi presentations and Wednesday presentation on research needs

• Labs should expect continued pressure to push the envelope on detection capabilities
Trends – Dermal Sampling

- Recent studies suggest a possible dermal exposure route for BeS
- Possible dermal exposure methodologies
  - Removal techniques (such as wiping)
  - Interception techniques (such as wearing gloves)
  - In-situ detection on skin surface (not tried for Be to my knowledge)
- Some sampling techniques may present challenges for laboratory analysis due to matrix effects
Other Needs: Speciation

- Ability to differentiate between various anthropogenic forms of beryllium (metal, alloy, oxide) and natural forms
- Some forms may be more toxic than others
  - Cases of BeS/CBD from natural forms (silicates, borosilicates) generally unknown
  - BeO may be “worse” than Be metal due to lower solubility
- Research-grade instruments (such as X-Ray diffraction) can differentiate
- Sequential digestion schemes have been reported in literature, but not independently verified
Other Needs: (Near) Real-Time Monitoring

- Could save millions per year in analytical costs for DOE alone
- Would improve worker protection by providing faster results
- Within DOE, most needed for surface sampling, but also needed for air monitoring
  - NAS study recommends housekeeping for which a surface direct-reading instrument (DRI) would be beneficial
- For aerosols, DRI could eliminate issue of wall deposits
  - Most labs only analyze filter catch
  - May underestimate Be to which workers are exposed
Attempts at (Near) Real-Time Measurement

- Laser-Induced Breakdown Spectroscopy (LIBS)
- Microwave-Induced Plasma Spectroscopy (MIPS)
- Anodic Stripping Voltammetry (ASV)
- (Aerosol) Time of Flight Mass Spectrometry (TOFMS)
- Surface-Enhanced Raman Spectroscopy (SERS)
- Colorimetric Wipes
- Many of these presented at First International Symposium on Be Particulates and Their Detection (Feb 2002, Santa Fe, NM)

Issues common to all:
- Incomplete validation
- Standard method not established/published (needed for AIHA accreditation purposes)

Other issues:
- Direct-solid methods lack adequate precision at trace levels
- Many of these are large and/or expensive

For field measurements, fluorescence method is only viable method currently available
The Ultimate Real-Time Monitor

- Advantage: Can measure almost anything, almost anywhere.
- Drawback: Will not be available until early 23rd century.

(Courtesy Gary Whitney, Los Alamos National Laboratory)

(Source: www.racprops.com)
(N)RTM: What Will It Take???

- **Technology**
  - We have not really tried to find a DRI technology that would work for Be
  - Technologies like XRF will not work for Be due to its transparency to X-Rays
  - Thus, some technology development required
  - Technology for aerosols and for surfaces may or may not be the same

- **Funding**
  - Single-source approach to obtaining funding no longer viable
  - Multi-year effort needed to develop and deploy viable technology
  - Collaboration needed among multiple groups/sources kicking in for joint projects

- **Benefits for a real-time device (such as DRI) need to be more widely understood**
  - Improved worker protection
  - Significant cost savings
  - Process improvements
Summary

• Beryllium poses unique analytical challenges
  – Adequacy of sample preparation
  – OELs/action levels on the ragged edge of detection capabilities

• We have made a lot of progress
  – BeO reference material
  – Improvements in standard methods
  – Improved information exchange

• There is still much to do
  – Validation of sample preparation methods
  – Improve ultra-trace-level detection capabilities
  – Improve proficiency testing and field lab accreditation
  – Speciation
  – Develop (near) real-time monitoring
It’s In the Book!

To be published in 2009 by Royal Society of Chemistry – Mike Brisson and Amy Ekechukwu, co-editors

• 1-Overview (M. Brisson)
• 2-Air Sampling (M. Harper)
• 3-Surface Sampling (G. Rondeau)
• 4-Sample Dissolution Reagents (K. Ashley, T. Oatts)
• 5-Heating Sources (M. McCleskey)
• 6-Analysis by ICP-AES/MS (M. Archuleta, B. Duran)
• 7-Analysis by Non-Plasma (A. Agrawal, A. Ekechukwu)
• 8-Data Reporting (C. Davis, N. Grams)
• 9-Future Trends (G. Braybrooke, P. Wambach)
Acknowledgements

Apologies in advance for any inadvertent omissions!

• NIOSH: Martin Harper, Mark Hoover, Kevin Ashley, Greg Day, Mike McCawley (retired)
• SRS: Maureen Bernard, Linda Youmans-McDonald, Sherrod Maxwell, Matt Nelson, Steve Jahn, Burney Hook, Amy Ekechukwu, Paula Cable-Dunlap
• Y-12: Tom Oatts, Larissa Welch
• LANL: Gary Whitney
• Former LANL: Kathy Creek (now with Bureau Veritas)
• BGIA (Germany): Dietmar Breuer

• BHSC Members, especially the Sampling and Analysis Subcommittee