Analytical Methods for Beryllium

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Introduction

Background:
- Applicable limit values
- Current state of the art / trace analysis
- Validated methods ensure defensibility of data

Sample Preparation & Analysis:
- Governmental & Consensus standard methods
- Available reference materials
- Standards & methods development activities

Summary:
- What is available now? Data gaps?
- What methods & standards are still needed?
Beryllium limit values

- DOE (10 CFR 850):
  - 0.2 µg/m³ Air contamination
  - 0.2 µg/100 cm² Surface contamination for equipment release
  - 3 µg/100 cm² Surface contamination for housekeeping

- OSHA Permissible Exposure Limit (PEL):
  - 2 µg/m³ Air contamination

- NIOSH Recommended Exposure Limit (REL):
  - 0.5 µg/m³ Air contamination

- ACGIH Threshold Limit Value® (TLV®) NIC:
  - 0.05 µg/m³ Air contamination (8-hr TWA)
  - 0.2 µg/m³ Air contamination (STEL)
Media for beryllium analysis:

Air samples (membrane filters)
Surface samples (e.g., wipes; vacuum):
  Hard / Smooth
  Soft / Rough
Dermal samples (e.g., wipes; patch)
Bulks (e.g., soils; thick dust deposits)
Salient standardized methods for beryllium sampling in workplace air

<table>
<thead>
<tr>
<th>Method(s)</th>
<th>Aerosol fraction(s)</th>
<th>Filter type(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>USA (NIOSH &amp; OSHA)</td>
<td>“Total”</td>
<td>Membrane</td>
</tr>
<tr>
<td>UK (HSE); Germany (BGIA)</td>
<td>Inhalable</td>
<td>Membrane</td>
</tr>
<tr>
<td>France (INRS)</td>
<td>Inhalable</td>
<td>Quartz filter</td>
</tr>
<tr>
<td>ISO 15202-1</td>
<td>Inhalable or Respirable</td>
<td>Membrane or Fibrous</td>
</tr>
<tr>
<td>ASTM Int’l: D7035; D7202</td>
<td>“Total”, Inhalable or Respirable</td>
<td>Membrane or Fibrous</td>
</tr>
</tbody>
</table>
# Standardized Surface Sampling Methods

<table>
<thead>
<tr>
<th>Method(s)</th>
<th>Media / Device</th>
<th>Surface(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>OSHA (several)</td>
<td>Wet or dry filter or wipe</td>
<td>Smooth / Hard; Dermal</td>
</tr>
<tr>
<td>NIOSH (several)</td>
<td>Wet wipe</td>
<td>Smooth; Dermal</td>
</tr>
<tr>
<td>ASTM D6966</td>
<td>Wet wipe</td>
<td>Smooth surfaces</td>
</tr>
<tr>
<td>ASTM E1216</td>
<td>Adhesive tape</td>
<td>Smooth surfaces</td>
</tr>
<tr>
<td>NIOSH &amp; OSHA</td>
<td>Patch or Rinse</td>
<td>Dermal samples</td>
</tr>
<tr>
<td>ASTM D7296</td>
<td>Dry wipe (Be only)</td>
<td>Special substrates</td>
</tr>
<tr>
<td>ASTM D5438</td>
<td>Vacuum sampler</td>
<td>Carpets</td>
</tr>
<tr>
<td>ASTM D7144</td>
<td>Micro-vacuum</td>
<td>Rough, porous or fragile surfaces</td>
</tr>
</tbody>
</table>
# Standardized sample preparation methods for beryllium

<table>
<thead>
<tr>
<th>Method</th>
<th>Matrix</th>
<th>Acids</th>
<th>Δ, ≈, )))</th>
</tr>
</thead>
<tbody>
<tr>
<td>NIOSH 7102</td>
<td>Air filter</td>
<td>HNO$_3$ / H$_2$SO$_4$</td>
<td>Δ</td>
</tr>
<tr>
<td>NIOSH 7300 / 7302</td>
<td>Air filter / Wipe</td>
<td>HNO$_3$ / HClO$_4$</td>
<td>Δ or ≈</td>
</tr>
<tr>
<td>OSHA ID-125G</td>
<td>Air filter, Wipe or Bulk</td>
<td>HNO$_3$ / H$_2$SO$_4$ / HCl</td>
<td>Δ</td>
</tr>
<tr>
<td>OSHA ID-206</td>
<td>Air filter, Wipe or Bulk</td>
<td>HCl / HNO$_3$</td>
<td>Δ</td>
</tr>
<tr>
<td>HSE 29/2 (UK)</td>
<td>Air filter</td>
<td>HNO$_3$ / H$_2$SO$_4$</td>
<td>Δ</td>
</tr>
<tr>
<td>INRS 003 (France)</td>
<td>Air filter</td>
<td>HNO$_3$ / HF</td>
<td>Δ or ≈</td>
</tr>
<tr>
<td>ASTM D7035</td>
<td>Air filter</td>
<td>Various options</td>
<td>Δ or ≈</td>
</tr>
<tr>
<td>ISO 15202-2</td>
<td>Air filter</td>
<td>Various options</td>
<td>Δ, ≈ or )))</td>
</tr>
</tbody>
</table>
Beryllium spectrometric analysis

Atomic spectrometry by:
- GFAAS (single element)
- ICP-AES (multielement)
- ICP-MS (ultratrace analysis)
Standardized methods for beryllium by spectrometric analysis

<table>
<thead>
<tr>
<th>Method(s)</th>
<th>Technique</th>
<th>MDL (µg Be)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NIOSH 7102</td>
<td>GFAAS</td>
<td>0.005</td>
</tr>
<tr>
<td>NIOSH 7300</td>
<td>ICP-AES</td>
<td>0.005</td>
</tr>
<tr>
<td>OSHA ID-125G; ID-206</td>
<td>ICP-AES</td>
<td>0.013; 0.0072</td>
</tr>
<tr>
<td>EPA 7091</td>
<td>GFAAS</td>
<td>0.005</td>
</tr>
<tr>
<td>EPA 200.7; 6010B</td>
<td>ICP-AES</td>
<td>0.008; 0.005</td>
</tr>
<tr>
<td>EPA 200.8; 6020</td>
<td>ICP-MS</td>
<td>0.001; 0.0005</td>
</tr>
<tr>
<td>ASTM D7035</td>
<td>ICP-AES</td>
<td>0.009</td>
</tr>
<tr>
<td>ISO 15202-3</td>
<td>ICP-AES</td>
<td>---</td>
</tr>
</tbody>
</table>
Voluntary consensus standard ICP-MS method for elements in workplace air:

- Under parallel development within ASTM International and ISO

- Interlaboratory study to evaluate ~20 elements (beryllium is one)

- Sample preparation procedures to include:
  - Hot plate digestion
  - Microwave digestion
  - Hot-block extraction
  - [Ultrasonic extraction an option]
Alternative dissolution solution for beryllium

Dilute aqueous ammonium bifluoride, \((NH_4)HF_2\):

- Less hazardous than concentrated acids (e.g., \(H_2SO_4\), HF)
- Effective for dissolving Be metal and BeO
- Does not dissolve matrix (filter or wipe)
- Heat (~85 °C) assists in dissolution of refractory “high-fired” BeO
Beryllium fluorescence method: fluorophore for trace detection

- Beryllium binds phenolate groups strongly
- A six member chelate ring provides ideal Be-O / Be-N stereochemistry

![Chemical structure of Hydroxybenzoquinoline sulfonic acid (HBQS)]
Beryllium fluorescence with HBQS

- Detection is quantitative above 0.036 ppb (<0.001 µg Be/sample)
- Linear response, wide dynamic range
- Verified lack of interference from other metals
Beryllium fluorescence method (1)

- Collect sample on media:
  - Surface wipe
  - Air filter

- Dissolve beryllium:
  - Dilute ammonium bifluoride
  - Heating block for BeO samples
  - Recovery >90% in ~30 min.
Beryllium fluorescence method (2)

- **Filter**
  - Commercial filter syringe

- **Mix**
  - Mix fluorescent dye and sample
    - (1:19 routine; 1:4 trace)

- **Measure**
  - Place cuvette in instrument
  - Measure [Be] to trace levels
Key advantages:
Beryllium-by-fluorescence method

- Field or laboratory deployable
- Detection limit <0.0003 µg Be/sample (0.011 ppb)
- Good recoveries from Be & BeO with (NH₄)HF₂
- Rapid turnaround (test results within one hour)
- High throughput (can process ~30 samples/90 minutes)
- Beryllium-specific (other metals do not interfere)
- Low capital cost (< $10,000)
- Quantification from <0.002 µg to >4 µg using portable fluorometer (5x / 20x dilution)

→ LOD for Be comparable to ICP-MS
Beryllium fluorescence method
acceptance:

- **ASTM International:**

- **CDC/NIOSH:**
  - NIOSH Manual of Analytical Methods ([www.cdc.gov/niosh/nmam](http://www.cdc.gov/niosh/nmam))
  - Methods 7704 (air) & 9110 (wipes)
## Beryllium NIST SRMs

<table>
<thead>
<tr>
<th>SRM No.</th>
<th>Material</th>
<th>Certified [Be]</th>
</tr>
</thead>
<tbody>
<tr>
<td>458; 459; 460</td>
<td>Be-Cu alloy (chips)</td>
<td>0.360%; 1.82%; 1.86%</td>
</tr>
<tr>
<td>C1122</td>
<td>Be-Cu alloy (block)</td>
<td>1.75%</td>
</tr>
<tr>
<td>1632c</td>
<td>Bituminous coal</td>
<td>1.0 µg/g</td>
</tr>
<tr>
<td>1944</td>
<td>NY/NJ waterway sediment</td>
<td>1.6 µg/g</td>
</tr>
<tr>
<td>3105a</td>
<td>Single element standard solution</td>
<td>10 mg/L</td>
</tr>
<tr>
<td>4325</td>
<td>Be 10/9 MS standard solution</td>
<td>5 mg/L (Be 10/9 = $3 \times 10^{-11}$)</td>
</tr>
</tbody>
</table>
Desired beryllium CRMs

**Compound:**

Beryllium Oxide (esp. high-fired)

- NIST/DOE/NIOSH BeO SRM project

**Media:**

Air filters (aerosols)

Spiked wipes

⇒ BeO-spiked filter CRMs are commercially available.
SEM of BeO on MCE filter*

*BeO-spiked filters courtesy of High-Purity Standards; SEM by J. Fernback, CDC/NIOSH
Analytical methods for Beryllium:

- Use of more sensitive methods than ICP-AES and GFAAS (i.e.: ICP-MS, fluorescence) may be required in near future
- Data gaps remain for Be recoveries from sampling media & sample prep protocols
- Reference materials lacking, but efforts to fill this need are underway

IHs & labs should harmonize sampling & analysis procedures!
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Kenn White, AIHA Fellow

- Beryllium Health & Safety Committee, Sampling & Analytical Subcommittee
- ASTM International Subcommittee D22.04 on Workplace Air Quality
- ISO Workplace Air Quality subcommittee, Inorganic working group (ISO TC 146/SC 2/WG 2)