BERYLLIUM in Air
by Field-Portable Fluorometry

Be  MW: 9.0121  CAS: 7440-41-7  RTECS: DS175000


U.S. regulatory OELs
OSHA: 2 µg/m³, ceiling 5 µg/m³, peak 25 µg/m³
MSHA: 2 µg/m³
DOE: 2 µg/m³ (action level 0.2 µg/m³)
Other published OELs and guidelines
OTHER: see Table 3

PROPERTIES: solid, d 1.85 g/mL, MP 1,278 °C, VP 0 kPa
          (0 mm Hg) @ 25 °C

SYNONYMS: beryllium metal

SAMPLING

SAMPLER: FILTER
          (mixed cellulose ester or nylon membrane,
           0.8 µm pore size, 25- or 37-mm diameter)
FLOW RATE: (1 to 4) L/min
VOL-MIN: 240 L
         -MAX: 2,000 L
SHIPMENT: routine
SAMPLE
STABILITY: stable
BLANKS: 2 to 10 field blanks

MEASUREMENT

TECHNIQUE: FIELD-PORTABLE UV/VIS FLUOROMETRY
ANALYTE: complex of hydroxybenzoquinoline
         sulfonate (HBQS) with beryllium
DISSOLUTION: ammonium bifluoride (aqueous), 10 g/L
DETECTION
SOLUTION: contains 63.4 µmol/L HBQS, 2.5
           mmol/L EDTA, and 50.8 mmol/L lysine
           monohydrochloride; pH adjusted to
           12.85 with 10 mol/L NaOH
DETECTOR: excitation, 360 nm to 390 nm; emission,
         400 nm to 700 nm (λmax = 475 nm)
CALIBRATION: beryllium standard solutions
RANDGE: (0.005 to 6) µg per filter [1]
ESTIMATED LOD: 0.00075 µg per filter [2]
PRECISION (S): 0.021 at =0.2 µg per filter, 0.076 at =1.5 µg
              per filter, 0.052 at =3 µg per filter

APPLICABILITY: The working range of the method is 0.005 µg/m³ to 6 µg/m³ for an air sample of 1,000 L. The analysis is for
              total beryllium and is not compound specific.

INTERFERENCES: Minor interference from iron can result if iron concentrations are high. Samples high in iron demonstrate
                a yellow or gold coloration. This interference can be minimized by allowing the solution to sit for at least four hours, during
                which time the solution clears, and then filtering the sample extract before use.

OTHER METHODS: Method 7300 (hot plate digestion and inductively coupled plasma atomic emission spectrometry) is an
                alternative (reference) procedure for the determination of elemental beryllium [3]. ASTM method D7202 is a similar proce-
                dure to detect elemental beryllium by fluorescence [4].
REAGENTS:
1. Ammonium bifluoride.*
2. Ethylenediaminetetraacetic acid (EDTA), disodium salt, dihydrate.
3. 10-Hydroxybenzo[h]quinoline-7-sulfonate (HBQS) [5].
4. L-Lysine monohydrochloride.
5. Sodium hydroxide.*
7. Dissolution solution:* aqueous ammonium bifluoride, 10 g/L (prepared by dissolving ammonium bifluoride in deionized water).
8. Detection solution:* 63.4 μmol/L HBQS, 2.5 mmol/L EDTA, and 50.8 mmol/L L-lysine monohydrochloride; pH adjusted to 12.85 with 10 mol/L NaOH.
9. Beryllium standard solution,* 1,000 mg/L (commercially available).

*See SPECIAL PRECAUTIONS.

EQUIPMENT:
1. Sampler: membrane filter, mixed cellulose ester (MCE) or nylon, 0.8 μm pore size, 25- or 37-mm diameter.
2. Personal sampling pump, 1 L/min to 4 L/min, with clamps and flexible connecting tubing.
3. Portable ultraviolet/visible (UV/Vis) fluorometer, with excitation lamp (λ = 380 nm) and time-integrating visible detector (400 nm to 700 nm, λmax = 475 nm) or optical filters for appropriate wavelengths (excitation of 360 nm to 390 nm; emission of 475 nm, with full width at half maximum of less than ±10 nm).
4. Mechanical agitator, shaker, or rotator.
5. Hot block (for beryllium oxide extraction).
6. Fluorescence cuvettes, disposable, 10 mm diameter, transparent to UV/Vis radiation.
7. Centrifuge tubes, plastic, 15 mL.
8. Syringe filters, nylon, 0.45 μm pore size, 13- or 25-mm diameter, in plastic housings.
NOTE: Polytetrafluoroethylene (PTFE) filters are unsuitable for this method.
9. Pipettors, mechanical, of assorted sizes.
10. Pipet tips, plastic, disposable, of assorted sizes.
11. Labware, plastic (e.g., beakers, flasks, graduated cylinders), of assorted sizes.
12. Tweezers, plastic or plastic-coated.
13. Laboratory wipes.
14. Personal protective wear (e.g., respirators, gloves, lab coats, safety eyewear) as needed.

SPECIAL PRECAUTIONS: Wear appropriate personal protection during sampling activities and analysis. It is essential that suitable gloves, eye protection, laboratory coat, etc., be used when working with the chemicals. Perform sample preparation and analysis in a clean, well-ventilated area that is well removed from any possible beryllium contamination. Any area affected by the dissolution or detection solutions must be immediately washed with plenty of water. Ammonium bifluoride will etch glass, so it is essential that all ammonium bifluoride solutions be contained in plastic labware. Avoid exposure by contact with skin or eyes, or by inhalation of vapor.

SAMPLING:
1. Calibrate each personal sampling pump with a representative sampler in line.
2. Sample at an accurately known flow rate between 1 L/min and 4 L/min for a total sample size of 240 L to 2,000 L for TWA measurements. Do not exceed a filter loading of ≈2 mg total dust.
3. After sampling, remove the filters from the cassettes using clean tweezers, and place into labeled 15 mL plastic centrifuge tubes.

SAMPLE PREPARATION:
4. Add 5 mL of the dissolution solution (ammonium bifluoride, 10 g/L) to each 15 mL centrifuge tube containing an air filter sample, and cap each tube.

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NIOSH Manual of Analytical Methods (NMAM), 5th Edition (Electronic)
5. Place each tube into a mechanical rotator, and rotate for at least 30 min.

NOTE: Rotator may also be substituted by a shaker or an agitator as long as the dissolution solution wets the filter well. Sonication has also been shown to be effective. For dissolution of refractory materials such as high-fired beryllium oxide, agitation of the dissolution solution with the media must be replaced by heating to 80°C for 30 minutes. Any standard dissolution process is particle-size dependent. The two sources of BeO used to validate the method are described in the backup data report [6].

6. Filter each solution with a nylon syringe filter into a clean tube.

NOTE: This tube should be able to accept a cap so that the solution may be saved and used later for reanalysis if required.

7. Pipet 0.1 mL of each sample filtrate into cuvettes containing 1.9 mL of the detection solution. Cap and mix briefly.

NOTE: The above procedure is typically used to analyze a range of 0.05 μg to 4 μg of beryllium on the sampling media. Alternative ratios of dissolution solution and detection solution may be used for analyzing alternative ranges of beryllium concentration. To test a range of 0.005 μg to 0.4 μg of beryllium on the sampling media, 0.4 mL of the sample filtrate is added to 1.6 mL of the detection solution in the cuvettes.

NOTE: If high iron or titanium concentration is suspected or is evident (owing to the appearance of suspended precipitate), allow the solution to settle and filter the solution using a nylon syringe filter.

NOTE: The stability of the detection and the dissolution solution is more than one year and of the mixed measurement solution comprising both is greater than 30 days. The solutions must be kept in sealed containers, and the detection and mixed solutions must be stored away from light.

CALIBRATION AND QUALITY CONTROL:

8. Calibrate the fluorometer with beryllium stock standard solutions. Prepare a calibration graph of fluorescence intensity vs. beryllium concentration (ng/mL) in the stock standard.

NOTE: To test a range of 0.05 μg to 4 μg of beryllium on the sampling media, beryllium stock standard solutions are made up using beryllium spectrometric standards diluted with the ammonium bifluoride dissolution solution. A recommended series of stock standard solutions is (80, 200, 40, 10, and 0) ng/mL. As with the samples, the stock standards are prepared for analysis by adding 0.1 mL of beryllium stock standard into 1.9 mL of detection solution (20-fold dilution). Please see Table 1.

NOTE: To test a range of 0.005 μg to 0.4 μg of beryllium on the sampling media, a recommended series of stock standard solutions is (80, 20, 4, 1, and 0) ng/mL. These standards with lower beryllium concentration can be prepared by 10-fold dilution of the stock standards mentioned in the note above. As with the samples, these stock standards are prepared for analysis by adding 0.4 mL of beryllium stock standard into 1.6 mL of detection solution (5-fold dilution). Please see Table 2.

NOTE: If alternative ratios of dissolution solution and detection solution are used for sample preparation, then a similar ratio for calibration is required.

9. Analyze a stock standard, a reagent blank, and a media blank at least once every 20 samples. Ensure that the concentration range of the stock standards spans the beryllium levels found in the samples.

10. Analyze one media spike and one quality control blind spike per 20 samples (minimum of three each per sample set) to insure that percent recovery is in control (e.g., 100 ± 15). Correct sample results for the average recovery if it differs significantly from 100 %.

NOTE: If it is suspected that beryllium oxide may be present, then it is recommended to use beryllium oxide for media and blind spikes.
MEASUREMENT:

11. For each sample, obtain the fluorescence intensity at $\lambda_{\text{max}}$ or with optical filter for appropriate wavelength.

12. If the fluorescence response for any of the samples is above the range of responses for the stock standards, dilute the sample filtrate with dissolution solution, reanalyze, and apply the appropriate dilution factor ($D$) in subsequent calculations.

CALCULATIONS:

13. Obtain the solution concentration for each sample filtrate, $C_s$ (ng/mL), and the average media blank, $C_b$ (ng/mL) from the calibration graph.

14. Using the dissolution volumes (normally 5 mL) of sample, $V_s$ (mL), and media blank, $V_b$ (mL), calculate the concentration, $C$ (µg/m$^3$), of Be in the air volume sampled, $V$ (L), while accounting for the dilution factor ($D$).

$$C = D \times \frac{[C_sV_s - C_bV_b]}{V}, \text{ ng/L or µg/m}^3.$$

NOTE: Tables 1 and 2 can be used for correlating the amount of beryllium in the sampling media with the concentrations of beryllium in solution. Table 1 is for testing media with 0.2 µg to 4 µg of beryllium at 20-fold dilution and Table 2 is for testing media with 0.02 µg to 0.4 µg of beryllium at 5-fold dilution.

Table 1. Correlation of amount of Be in sampling media with Be concentration in stock standard and Be concentration as analyzed, assuming 0.1 mL of sample or stock standard is added to 1.9 mL of detection solution (20-fold dilution).

<table>
<thead>
<tr>
<th>Be concentration in stock standard (ng/mL)</th>
<th>Be concentration as analyzed (ng/mL)</th>
<th>Amount of Be in the media* (ng)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>10</td>
<td>0.5</td>
<td>50</td>
</tr>
<tr>
<td>40</td>
<td>2</td>
<td>200</td>
</tr>
<tr>
<td>200</td>
<td>10</td>
<td>1000</td>
</tr>
<tr>
<td>800</td>
<td>40</td>
<td>4000</td>
</tr>
</tbody>
</table>

*Equals stock standard Be concentration (ng/mL) x volume (5 mL) of dissolution solution used to extract media.

Table 2. Correlation of amount of Be in sampling media with Be concentration in stock standard and Be concentration as analyzed, assuming 0.4 mL of sample or stock standard is added to 1.6 mL of detection solution (5-fold dilution).

<table>
<thead>
<tr>
<th>Be concentration in stock standard (ng/mL)</th>
<th>Be concentration as analyzed (ng/mL)</th>
<th>Amount of Be in the media* (ng)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>1</td>
<td>0.2</td>
<td>5</td>
</tr>
<tr>
<td>4</td>
<td>1</td>
<td>20</td>
</tr>
<tr>
<td>20</td>
<td>4</td>
<td>100</td>
</tr>
<tr>
<td>80</td>
<td>16</td>
<td>400</td>
</tr>
</tbody>
</table>

*Equals stock standard Be concentration (ng/mL) x volume (5 mL) of dissolution solution used to extract media.
EVALUATION OF METHOD:

The method was evaluated [6] in accordance with published guidelines [7]. Experiments were conducted using an Ocean Optics® portable fluorescence device with the following components:

- USB 200 spectrometer with spectral grating #2 (UV/Vis 600),
- LS-1 lamp (380 nm) in LS-450 housing,
- UV-2 casting,
- OFLV linear filter 200-850,
- L2 collection lens and slit-200.

Tests were carried out in relative irradiance mode using 2- or 5-second integration times.

The method was evaluated using beryllium oxide spiked onto mixed cellulose ester (MCE) filters at levels of (0, 0.02, 0.1, 0.2, 0.3, 0.4, 1.5, 3.0, and 6.0) μg (five samples at each level).

Long-term stability of samples was verified from spikes (number \( n = 30 \)) of 0.1 μg Be on MCE filters. Samples were analyzed at day one \( (n = 12) \) and then one week \( (n = 6) \), ten days \( (n = 3) \), two weeks \( (n = 3) \), three weeks \( (n = 3) \), and one month \( (n = 3) \) after spiking. No diminution of fluorescence signal was observed from samples prepared and analyzed after having been stored for up to thirty days.

Interference tests were carried out using solutions of 0 nmol/L, 100 nmol/L, and 10 μmol/L Be in the presence of 0.4 nmol/L Al, Ca, Co, Cu, Fe, Ti, Li, Ni, Pb, Sn, U, V, W, or Zn (separate experiments were carried out for each potential interferant). An interlaboratory evaluation of the method was also performed [8].

REFERENCES:


.BIBLIOGRAPHY:

METHOD WRITTEN BY:
T. Mark McCleskey, Los Alamos National Laboratory, Los Alamos, NM; Kevin Ashley, CDC/NIOSH, Division of Applied Research and Technology; Anoop Agrawal, Berylliant Inc., Tucson, AZ.

Table 3. U.S. regulatory occupational exposure limits (OELs) and other published occupational exposure limits and guidelines for beryllium*

<table>
<thead>
<tr>
<th>Agency</th>
<th>8 Hour Inhalation Exposure Limit (µg/m³)</th>
<th>Short-term Inhalation Exposure Limit (µg/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MSHA</td>
<td>2</td>
<td>not established</td>
</tr>
<tr>
<td>OSHA</td>
<td>2</td>
<td>5 (ceiling) 25 (30 min maximum)</td>
</tr>
<tr>
<td>DOE, 10 CFR 850</td>
<td>2 (0.2 action level)</td>
<td>not established</td>
</tr>
</tbody>
</table>

*Other published OELs and guidelines†*

<table>
<thead>
<tr>
<th>Country or organization</th>
<th>8 Hour Inhalation Exposure Limit (µg/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Germany</td>
<td>5</td>
</tr>
<tr>
<td>ACGIH TLV®, Argentina, Belgium, Bulgaria, Canada (Alberta, British Columbia, Ontario, Quebec), China (Hong Kong), Columbia, Egypt, Finland, France, Ireland, India, Japan, Jordan, Korea (Republic of), Malaysia, Mexico, Netherlands, New Zealand, Philippines, Singapore, South Africa, Spain, Sweden, Switzerland, Thailand, Turkey, United Kingdom, Vietnam</td>
<td>2</td>
</tr>
<tr>
<td>Czech Republic, Denmark, Hungary, Norway, Poland, Russia</td>
<td>1</td>
</tr>
<tr>
<td>NIOSH REL</td>
<td>0.5†</td>
</tr>
<tr>
<td>China</td>
<td>0.1</td>
</tr>
<tr>
<td>AIHA WEEL®</td>
<td>not established</td>
</tr>
</tbody>
</table>


†Occupational exposure limits and guidelines other than NIOSH’s recommended exposure limit (REL) have not been reviewed by NIOSH. Professional society and other country exposure limits and guidelines are provided as an aid to NMAM users seeking additional information. Inclusion of these standards and guidelines does not constitute endorsement by NIOSH.

‡This NIOSH REL was developed using a previous NIOSH policy for carcinogens (29 CFR 1990103). The current NIOSH policy for carcinogens was adopted in September 1995. The previous and current NIOSH carcinogen policies are available at http://www.cdc.gov/niosh/ngp/engapdx.html#. Under the previous policy, NIOSH usually recommended that exposures to carcinogens be limited to the “lowest feasible concentration,” which was a nonquantitative value. Under the previous policy, most quantitative RELs for carcinogens were set at the limit of detection (LOD) achievable when the REL was originally established.