BERYLLIUM in Air by Field-Portable Fluorometry

7704

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

METHOD: 7704, Issue 1 **EVALUATION: PARTIAL** **Issue 1: 6 April 2007**

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		MEASUREMENT	
SAMPLER:	FILTER (mixed cellulose ester or nylon membrane, 0.8 µm pore size, 25- or 37-mm diameter)	**TECHNIQUE:**	FIELD-PORTABLE UV/VIS FLUOROMETRY
FLOW RATE:	(1 to 4) L/min	**ANALYTE:**	complex of hydroxybenzoquinoline sulfonate (HBQS) with beryllium
VOL-MIN:	240 L	**DISSOLUTION:**	ammonium bifluoride (aqueous), 10 g/L
-MAX:	2,000 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
SHIPMENT:	routine	**DETECTOR:**	excitation, 360 nm to 390 nm; emission, 400 nm to 700 nm ($\lambda_{max} \approx 475$ nm)
SAMPLE STABILITY:	stable	**CALIBRATION:**	beryllium standard solutions
BLANKS:	2 to 10 field blanks	**RANGE:**	(0.005 to 6) µg per filter [1]
ACCURACY		**ESTIMATED LOD:**	0.00075 µg per filter [2]
RANGE STUDIED:	not studied	**PRECISION ($\hat{S}_r$):**	0.021 at ≈0.2 µg per filter, 0.076 at ≈1.5 µg per filter, 0.052 at ≈3 µg per filter
BIAS:	not studied		
OVERALL PRECISION ($\hat{S}_{rt}$):	not studied		
ACCURACY:	not studied		

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 procedure 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.*
6. Water, deionized.
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 lysine monohydrochloride; pH adjusted to 12.85 with 10 mol/L NaOH).
9. Beryllium standard solution,* 1,000 mg/L (commercially available).
10. Beryllium-spiked media* (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, $\lambda_{max} \approx$ 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.

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 (800, 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 λ_{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/m³), of Be in the air volume sampled, V (L), while accounting for the dilution factor (D).

$$C = D \times \frac{[C_s V_s - C_b V_b]}{V}, \text{ ng/L or } \mu g/m^3.$$

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).

Be concentration in stock standard (ng/mL)	Be concentration as analyzed (ng/mL)	Amount of Be in the media* (ng)
0	0	0
10	0.5	50
40	2	200
200	10	1000
800	40	4000

*Equals stock standard Be concentration (ng/mL) × 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).

Be concentration in stock standard (ng/mL)	Be concentration as analyzed (ng/mL)	Amount of Be in the media* (ng)
0	0	0
1	0.2	5
4	1	20
20	4	100
80	16	400

*Equals stock standard Be concentration (ng/mL) × 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 1.0 µmol/L Be in the presence of 0.4 mmol/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:

[1] Agrawal A, Cronin J, Tonazzi J, McCleskey TM, Ehler DS, Minogue EM, Whitney G, Brink C, Burrell AK, Warner B, Goldcamp MJ, Schlecht PC, Sonthalia P, Ashley K [2006]. Validation of a standardized portable fluoresence method for determining trace beryllium in workplace air and wipe samples. J Environ Monit 2006 (8): 619- 624.

[2] Ashley K, Agrawal A, Cronin J, Tonazzi J, McCleskey TM, Burrell AK, Ehler DS [2007]. Ultra-trace determination pf beryllium in occupational hygiene samples by ammonium bifluoride extraction and fluorescence detection using hydroxybenzoquinoline sulfonate. Analytica Chimica Acta *584* (2007): 281-286.

[3] NIOSH [1994]. Elements by ICP (nitric/perchloric acid ashing): Method 7300 (supplement issued 3/15/03). In: NIOSH manual of analytical methods. 4th ed. Cincinnati, OH: U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control and Prevention, National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 94–113.

[4] ASTM [2006]. D7202 – Standard test method for determination of beryllium in the workplace using field-based extraction and fluorescence detection. West Conshohocken, PA: ASTM International.

[5] Matsumiya H, Hoshino H, Yotsuyanagi T [2001]. A novel fluorescence reagent, 10-hydroxybenzo[*h*]quinoline-7-sulfonate, for selective determination of beryllium(II) ion at pg cm^{-3} levels. Analyst *126*:2082–2086.

[6] McCleskey TM, Agrawal A, Ashley K [2007]. Backup data—method nos. 7704 and 9110 / beryllium, Issue 1. NIOSH Docket Office, mailstop C-34, 4676 Columbia Parkway, Cincinnati, Ohio 45226, e-mail: NIOSHDocket@cdc.gov.

[7] Kennedy ER, Fischbach TJ, Song R, Eller PM, Shulman SA [1995]. Guidelines for air sampling and analytical method development and evaluation. Cincinnati, OH: U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control and Prevention, National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 95–117..

[8] Ashley K, McCleskey TM, Brisson MJ, Goodyear G, Cronin J, Agrawal A [2005]. Interlaboratory evaluation of a portable fluorescence method for the measurement of trace beryllium in the workplace. J ASTM Int *2*(9), 8 pp., Paper ID JAI13156.

.BIBLIOGRAPHY:

Minogue EM, Ehler DS, Burrell AK, McCleskey TM, Taylor TP [2005]. Development of a new fluorescence method for the detection of beryllium on surfaces. J ASTM Int *2*(9), 10 pp., Paper ID JAI13168..

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

U.S. Regulatory OELs

Agency	8 Hour inhalation exposure limit ($\mu g/m^3$)	Short-term inhalation exposure limit ($\mu g/m^3$)
MSHA	2	not established
OSHA	2	5 (ceiling) 25 (30 min maximum)
DOE, 10 CFR 850	2 (0.2 action level)	not established

Other published OELs and guidelines†

Country or organization	8 Hour inhalation exposure limit ($\mu g/m^3$)
Germany	5
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	2
Czech Republic, Denmark, Hungary, Norway, Poland, Russia	1
NIOSH REL	0.5‡
China	0.1
AIHA WEEL®	not established

*Abbreviations: ACGIH = American Conference of Governmental Industrial Hygienists, AIHA = American Industrial Hygiene Association, CFR = *Code of Federal Regulations*, DOE = U.S. Department of Energy, TLV® = Threshhold Limit Value, WEEL® = Workplace Environmental Exposure Level.

†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 1990.103). 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/npg/nengapdx.html#a. 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.