

BERYLLIUM in Surface Wipes by Field-Portable Fluorometry

9110

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

METHOD: 9110, Issue 1

EVALUATION: PARTIAL

Issue 1: 6 April 2007

U.S. regulatory OELs

OSHA: none for surfaces
MSHA: none for surfaces
DOE: 3 µg per 100 cm² (housekeeping, 10 CFR 850.30[a]), 0.2 µg per 100 cm² (equipment release, 10 CFR 850.31)

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

Other published OELs and guidelines

OTHER: none for surfaces

SYNONYMS: beryllium metal

SAMPLING	MEASUREMENT
<p>SAMPLER: WIPE (cellulosic)</p> <p>WIPE AREA: 100 cm² minimum</p> <p>SHIPMENT: routine</p> <p>SAMPLE STABILITY: stable</p> <p>BLANKS: 2 to 10 field blanks</p>	<p>TECHNIQUE: FIELD-PORTABLE UV/VIS FLUOROMETRY</p> <p>ANALYTE: complex of hydroxybenzoquinoline sulfonate (HBQS) with beryllium</p> <p>DISSOLUTION: ammonium bifluoride (aqueous), 10 g/L</p> <p>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</p> <p>DETECTOR: excitation, 360 nm to 390 nm; emission, 400 nm to 700 nm ($\lambda_{\max} \approx 475$ nm)</p> <p>CALIBRATION: beryllium standard solutions</p> <p>RANGE: (0.005 to 6) µg per wipe [1]</p> <p>ESTIMATED LOD: 0.00075 µg per wipe [2]</p> <p>PRECISION (\bar{S}): 0.021 at ≈ 0.2 µg per wipe, 0.076 at ≈ 1.5 µg per wipe, 0.052 at ≈ 3 µg per wipe</p>
ACCURACY	
<p>RANGE STUDIED: not studied</p> <p>BIAS: not studied</p> <p>OVERALL PRECISION (\bar{S}_n): not studied</p> <p>ACCURACY: not studied</p>	

APPLICABILITY: The working range of the method is 0.005 µg to 6 µg for surface wipe samples. 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 $\mu\text{mol/L}$ 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: wipe, cellulosic, 47 mm diameter minimum.
Note: Polyvinyl alcohol (PVA) media are unsuitable for this method.
2. Template, disposable/reusable, 100 cm² minimum area.
3. Tape, masking.
4. Portable ultraviolet/visible (UV/Vis) fluorometer, with excitation lamp ($\lambda = 380$ nm) and time-integrating visible detector (400 nm to 700 nm, $\lambda_{\text{max}} \approx 475$ 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).
5. Mechanical agitator, shaker, or rotator.
6. Hot block (for beryllium oxide extraction).
7. Fluorescence cuvettes, disposable, 10 mm diameter, transparent to UV/Vis radiation.
8. Centrifuge tubes, plastic, 15 mL.
9. 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.
10. Pipettors, mechanical, of assorted sizes.
11. Pipet tips, plastic, disposable, of assorted sizes.
12. Labware, plastic (e.g., beakers, flasks, graduated cylinders), of assorted sizes as needed.
13. Tweezers, plastic or plastic-coated.
14. Laboratory wipes.
15. 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 [6]:

1. Don a clean pair of gloves.
2. Demarcate the sampling area (100 cm² minimum) using a clean template or tape. If a template is used, tape the outside edges of the template to the surface to prevent its moving during sampling.
3. Wet a clean wipe with 0.2 mL of deionized water and wipe the surface to be sampled with firm pressure, using 3 to 4 vertical S-strokes. Fold the exposed side of the wipe in and wipe the area with 3 to 4 horizontal S-strokes. Fold the wipe once more and wipe the perimeter of the area.
4. Fold the wipe sample, exposed side in, and place into a labeled 15 mL plastic centrifuge tube.

SAMPLE PREPARATION:

5. Add 5 mL of the dissolution solution (ammonium bifluoride, 10 g/L) to each 15 mL centrifuge tube containing a surface wipe sample, and cap each tube.

6. 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 wipe 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].

7. 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.

8. 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:

9. 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.

10. 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.

11. 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).

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 per 100 cm^2), of Be in the surface area sampled, A (cm^2), while accounting for the dilution factor (D).

$$C = D \times \frac{[C_s V_s - C_b V_b]}{10 \times A}, \mu\text{g per } 100 \text{ cm}^2.$$

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) \times 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) \times volume (5 mL) of dissolution solution used to extract media.

EVALUATION OF METHOD:

The method was evaluated [7] in accordance with published guidelines [8]. 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 Whatman #541 cellulose and nylon 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).

The method was also field-tested using real-world samples (collected using Whatman #541 cellulose and nylon filters) obtained at U.S. Department of Energy sites suspected to be contaminated with beryllium. Field samples measured by portable fluorometry were also analyzed using hot-plate digestion and ICP-AES analysis. The latter served as a reference analytical method. Observed sample loadings ranged from below the detection limit ($<0.02 \mu\text{g}$ per sample) to $\approx 12 \mu\text{g}$ per sample.

Long-term stability of samples was verified from spikes (number $[n] = 30$) of $0.1 \mu\text{g}$ Be on Whatman #541 cellulose and nylon 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 $1.0 \mu\text{mol/L}$ 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 [9].

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 fluorescence 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 of 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] ASTM [2003]. D6966 - Standard practice for wipe sampling of surfaces for subsequent determination of metals. West Conshohocken, PA: ASTM International.

- [7] McCleskey TM, Agrawal A, Ashley K [2005]. 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
- [8] 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.
- [9] 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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