BERYLLIUM in Surface Wipes by Fluorometry

9110

Be MW: 9.0121 CAS: 7440-41-7 RTECS: DS1750000

METHOD: 9110, Issue 2 **EVALUATION:** FULL **Issue 1:** 6 April 2007 **Issue 2:** 12 December 2015

OSHA: none for surfaces
MSHA: none for surfaces
DOE: 3 µg per 100 cm^2 (housekeeping), 0.2 µg per 100 cm^2 (equipment release) [1]
OTHER OELs: [2]

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

SYNONYMS: beryllium metal, beryllia (BeO)

SAMPLING

SAMPLER: WIPE (cellulosic or polyvinyl alcohol)

WIPE AREA: 100 cm^2 minimum

SHIPMENT: routine

SAMPLE STABILITY: stable

BLANKS: 3 field blanks min.

ACCURACY

RANGE STUDIED: 0.0001 to 6 µg per wipe [3,4]

BIAS: negligible [3,4]

OVERALL PRECISION ($\hat{S}_{rT}$): 0.094

ACCURACY: 18.9%

MEASUREMENT

TECHNIQUE: 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 (optional); pH adjusted to 12.85 with 10 mol/L NaOH, as necessary

DETECTOR: excitation, 360 nm to 390 nm; emission, integrated between 470 and 480 nm ($\lambda_{max} \approx 475$ nm)

CALIBRATION: beryllium standard solutions

RANGE: (0.005 to 6) µg per wipe [3,4]

ESTIMATED LOD: 0.0001 µg per wipe

PRECISION ($\bar{S}_r$): 0.021 at ≈0.2 µg per wipe, 0.076 at ≈1.5 µg per wipe, 0.052 at ≈3 µg per wipe

APPLICABILITY: The working range of the method is 0.0005 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 two hours, during which time the solution clears, and then filtering the sample extract before use. An alternative method is to filter the solution (after 30 minutes of standing) through a hydrophilic filter of pore size of 0.2 µm or smaller.

OTHER METHODS: Method 7300 (hot plate digestion and inductively coupled plasma atomic emission spectrometry) is an alternative procedure for the determination of elemental beryllium [5], but with higher detection limits. ASTM method D7202 is a similar procedure to detect elemental beryllium by fluorescence [6].

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). An alternative preparation of dye solution without lysine (lysine-free) may be made by adding 1.104 g of EDTA and 64 µmoles of the 10-HBQS dye in 900 ml of water. After a clear solution is obtained, 114.5 ml of 2.5 N NaOH is added and mixed to obtain the final dye solution. The pH of the dye solution is 13.2. The lysine-free dye solution (commercially available) may be used for all analytical purposes and also provides superior detection limits.
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: Polyvinylalcohol (PVA) media are also suitable for this method [7]
2. Template, disposable/reusable, 100 cm^2 minimum area.
3. Tape, masking
4. 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 ±5 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, hydrophilic polypropylene, 0.2 µm pore size, 25-mm diameter, in plastic housings.
   NOTE: Polytetrafluoroethylene (PTFE) filters are unsuitable for this method
10. Pipettors, mechanical, of assorted sizes. 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 of skin 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 [8,9]:

1. Don a clean pair of gloves.
2. Demarcate the sampling area (100 cm^2 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 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 85 °C for 60 minutes or more. Any standard dissolution process is particle-size dependent [10]. The two sources of BeO used to validate the method are described in the backup data report [11].
7. Filter each solution with a hydrophilic polypropylene 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 6 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. The lysine-free dye solution may also be used for obtaining even lower detection limits at a dilution ratio of 3x, where 1.33 mL of the dye solution is mixed with 0.67 mL of the filtered solution extracts (Table 3), and beryllium in the range of 0.0005 µg to 0.4 µg may be determined.
   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 hygroscopic syringe filter (e.g., polyethersulfone, or hydrophilic polypropylene).
   NOTE: The stability of the detection and the dissolution solution is more than six months 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.
   NOTE: If the samples are suspected of having a contaminant that fluoresces and has excitation and emission spectra that overlap with that of the signal produced by the fluorescent dye bound to beryllium, then this contaminant needs to be removed. The presence of such a contaminant can be verified by subjecting the filtered sample to fluorescence excitation after the extraction step (without adding the fluorescent dye). If a fluorescence signal is detected, then that signal is ascribed to the presence of a fluorescent contaminant. To remove the contaminant, high-purity activated charcoal is added to the beryllium extraction solution (~10mg/mL) and the extraction procedure is carried out at elevated temperature (80 to 90 °C for at least 45 minutes). If the beryllium extraction procedure has already been performed, then after the addition of activated charcoal, the extraction process is repeated at the elevated temperature. The solution is filtered to remove the activated charcoal before adding this to the detection solution to make the measurement solution. Details of this process have been published [12,13].

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 6 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. Either of the two detection solutions may be used.

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. Either of the two detection solutions may be used.

NOTE: When using the lysine-free dye solution ONLY, a range can be tested of 0.0005 to 0.4 µg of beryllium on the media using a recommended series of stock solutions is (0, 0.15, 0.3, 0.6 and 2.4) ng/mL. These standards with lower beryllium concentration can be prepared by dilution of the stock standards mentioned in the note above. The standards are prepared for analysis by adding 0.67 mL of beryllium stock standard into 1.33 mL of detection solution (3-fold dilution). This dilution will result in 0, 0.05, 0.1, 0.2 and 0.8 ppb of beryllium in these standards; see Table 3. Cellulosic filters (47 mm in diameter) were spiked with a solution of beryllium acetate and analyzed in triplicate after extracting beryllium in 5 ml of 1% ABF solution at 85°C for 60 minutes and then mixed with lysine-free dye solution in a 3-fold dilution; these results are shown in Table 4. The difference in the average fluorescent signals from blanks and the 0 ppb standard were subtracted from the fluorescent readings of the spiked filters.

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

12. For each sample, obtain the fluorescence intensity at λ_{max} or with optical filter for appropriate wavelength.
13. 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:

14. 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.
15. Using the dissolution volumes (normally 5 mL) of sample, V_s (mL), and media blank, V_b (mL), calculate the concentration, *C* (µg/m^2), of Be in the surface area sampled, *A* (cm^2), while accounting for the dilution factor (*D*).

$$C = D \times (C_s V_s - C_b V_b)/(10 \times A) \ \mu g/100\ cm^2$$

NOTE: Tables 1, 2 and 3 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 0.05 µg to 6 µg of beryllium at 20-fold dilution; Table 2 is for testing media with 0.005 µg to 0.4 µg of beryllium at 5-fold dilution; and Table 3 is for testing media with 0.0005 µg to 0.012 µg of beryllium at 3-fold dilution. Lysine-free dye solution may be used for any of these dilutions, but for 3x dilution, lysine-free dye solution must be used.

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	25
20	4	100
80	16	400

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

Table 3. Correlation of amount of Be in sampling media with Be concentration in stock standard and Be concentration as analyzed, assuming 0.67 mL of sample or stock standard is added to 1.33 mL of lysine-free dye solution (3-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
0.15	0.05	0. 75
0.3	0.1	1.5
0.6	0.2	3
2.4	0.8	12

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

Table 4: Analysis of beryllium spiked cellulosic filters (47mm in diameter) using 3-fold dilution of the extraction solution with lysine-free dye solution. Beryllium concentration of calibration solutions after mixing with the dye solutions were 0, 0.05, 0.1, 0.2 and 0.8 ng/ml. Samples analyzed in triplicate, Averages and standard deviations are shown both in ppb in the solution and as µg on the filter.

Nominal Be concentration on the spiked filter, µg	Be concentration measured in the mixture of dye and sample solution, ppb ± Std Dev	Be concentration measured on the wipes, µg ± Std Dev
0	0.0003±0.0057	0.0000±8.5E-5
0.0005	0.0375±0.0073	0.00056±11.0E-5
0.001	0.0735±0.0058	0.0011±8.7E-4
0.002	0.1262±0.0047	0.0019±7.11E-4
0.005	0.3396±0.0093	0.0051±1.39E-4
0.05	3.275 ±0.051	0.049±7.58E-4
0.48	32.29±0.293	0.484±4.40E-3

EVALUATION OF METHOD:

The method was evaluated [3,4,11,14] in accordance with published guidelines [15]. Experiments were conducted [11] 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) [12]. The procedure was also evaluated on polyvinyl alcohol (PVA) wipes in an interlaboratory trial with media spiked with BeO at 0.030, 0.16, 0.32, 1.8, 2.8 and 5.6 µg [7].

Long-term stability of samples was verified from spikes (number [*n*] = 30) of 0.1 µg Be on MCE filters [9]. 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) [13]. Interlaboratory evaluations of the method were also performed [4,7,14].

The method using the lysine-free detection solution was compared and tested (with the detection solution with lysine for comparison) (Table 4) and this was carried out on a Glomax™ spectrometer (Turner Biosystems, Sunnyvale, CA) with an emission filter of 475 ± 5 nm and the excitation was at 360 nm

REFERENCES:

[1] US Department of Energy [1999]. 10 CFR 850, Chronic Beryllium Disease Prevention Program. Washington: Code of Federal Regulations.

[2] Dion C, Perrault G [2005]. Summary of good cleanup and decontamination practices for workplaces with beryllium-containing dust (Publ. no. R-409). Montreal, Canada: IRSST.

[3] 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 *8*: 619- 624.

[4] 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. Anal Chim Acta *584*: 281-286.

[5] 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: National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 94–113.

[6] ASTM International [2015]. D7202 – Standard test method for determination of beryllium in the workplace using field-based extraction and fluorescence detection. West Conshohocken, PA: ASTM International.

[7] Ashley K, Wise TJ, Marlow D, Agrawal A, Cronin JP, Adams L, Ashley E, Lee PA [2011]. Trace beryllium determination in polyvinyl alcohol wipes by extraction and fluorescence detection – Interlaboratory analysis. Anal Methods *3*: 1906-1901.

[8] ASTM International [2013]. D6966 - Standard practice for wipe sampling of surfaces for subsequent determination of metals. West Conshohocken, PA: ASTM International.

[9] ASTM International [2011]. D7707 - Standard Specification for Wipe Sampling Materials for Beryllium in Surface Dust. West Conshohocken, PA: ASTM International.

[10] Goldcamp MJ, Goldcamp DM, Ashley K, Fernback JE, Agrawal A, Millson M, Marlow D,Harrison K [2009]. Extraction of beryllium from refractory beryllium oxide with dilute ammonium bifluoride and determination by fluorescence – A multi-parameter performance evaluation. J Occup Environ Hyg *6*: 735-744.

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

[12] Youmans-McDonald L, Brisson MJ, Bernard M, Agrawal A, Cronin J, Adams, L [2011]. Determining beryllium by optical fluorescence using pre-wetted wipes. J ASTM Int *8*(3) [JAI 103489].

[13] Agrawal A, Adams LL, Agrawal A, Cronin JP, Tonazzi JCL, Duran BL [2011]. Beryllium measurement by optical fluorescence in samples contaminated by fluorescent impurities, J ASTM Int *8(*8) [JAI 103411].

[14] 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) [JAI13156].

[15] Kennedy ER, Fischbach TJ, Song R, Eller PM, Shulman SA [1995]. Guidelines for air sampling and analytical method development and evaluation. Cincinnati, OH: National Institute for Occupational Safety and Health; DHHS (NIOSH) Publication No. 95–117

METHOD REVISED 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.