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Beryllium

9110

by Field-Portable Fluorescence Measurement

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

METHOD: 9110, Issue 1

EVALUATION: PARTIAL

Issue 1: DRAFT

PROPERTIES: solid; d 1.85 g/ml; MP 1278°C;

OSHA : No PEL

VP 0 kPa (0 mm Hg) @ 25 °C

NIOSH: No REL

ACGIH: No TLV

SYNONYMS: Beryllium metal

SAMPLING

MEASUREMENT

SAMPLER: WIPE (cellulosic)

TECHNIQUE: Field-portable fluorescence measurement

FLOW RATE: N/A

ANALYTE: Complex of Hydroxy benzoquinoline sulfonate
(HBQS) with beryllium

VOL-MIN: N/A

-MAX:

SAMPLE DISSOLUTION: 1% ammonium bifluoride (aqueous)

SHIPMENT: Routine

DETECTION SOLUTION: 63.4 µM HBQS / 2.5 mM EDTA / 50.8
mM lysine monohydrochloride (pH
adjusted to 12.85 with 10 M NaOH)

SAMPLE

STABILITY: Stable

EXCITATION λ: 380 nm

BLANKS: 2 to 10 field blanks

Detection λ range; λ_{max}: 400 – 700 nm; 475 nm

	CALIBRATION: Elemental beryllium in detection solution
ACCURACY	
	RANGE: 0.06 to 6 µg/wipe
RANGE STUDIED: 0.02 to 12.0 µg/wipe	ESTIMATED LOD: 0.02 µg/wipe
BIAS: none identified	PRECISION (,): 0.021 @ ~0.2 µg/wipe (n = 15); 0.076 @ ~1.5 µg/wipe (n = 6); 0.052 @ ~3µg/filter (n = 6)
OVERALL	
PRECISION (\hat{S}_{rr}): 0.057	
ACCURACY: 11.6 (6.4 – 16.8, 95% C.I.)	

APPLICABILITY: The working range of the method is 0.02 to 6.0 µg/100 cm² for surface wipe samples. The analysis is for total beryllium and is not compound specific.

INTERFERENCES: Minor interference (<10%) from Fe 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 or microwave digestion and inductively coupled plasma atomic emission spectrometry) is an alternative (reference) procedure for the determination of elemental beryllium. ASTM method D7202-05 is a similar procedure to detect elemental beryllium by fluorescence.

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REAGENTS:

1. Dissolution solution: 1% Ammonium bifluoride
(prepared from dissolving 1g ammonium bifluoride in 100ml of deionized water).
2. Detection solution: 63.4 μ M hydroxyl benzoquinoline sulfonate (HBQS) [1] / 2.5 mM ethylene diamine tetraacetic acid (EDTA) / 50.8 mM lysine monohydrochloride (pH adjusted to 12.85 with 10 M NaOH).
3. Water, deionized.
4. Beryllium spectroscopic standard solution, ~1,000 μ g/ml (commercially available).
5. Spiked beryllium media (commercially available)

* See SPECIAL PRECAUTIONS

EQUIPMENT:

1. Wipe material, cellulosic, 47-mm minimum diameter, wetted
NOTE: Polyvinyl alcohol (PVA) media are unsuitable for this method.
2. Templates, disposable reusable, 100 cm² minimum area
3. Tape, masking
4. Portable ultraviolet/visible (UV/Vis) fluorometer, with irradiance excitation lamp ($\lambda = 380$ nm) and time-integrating visible detector (400 – 700 nm, $\lambda_{max} \approx 475$ nm)
5. Mechanical agitator, shaker or rotator
6. Fluorescence cuvettes, disposable, 10-mm diameter, transparent to UV/Vis radiation
7. Centrifuge tubes, plastic, 15-ml
8. Syringe filters, 0.45- μ m nylon, 13- or 25-mm diameter, in plastic housings.
NOTE: Polytetrafluoroethylene (PTFE) filters are unsuitable for this method.
9. Pipettors, mechanical, of assorted sizes as needed
10. Pipet tips, plastic, disposable, of assorted sizes as needed
11. Labware, plastic (e.g., beakers, flasks,

graduated cylinders, etc.), of assorted sizes as needed

12. Tweezers, plastic or plastic-coated

13. Laboratory wipes

14. Personal protective wear, e.g., respirators, masks, gloves, lab coats, safety eyewear, etc. as needed

SPECIAL PRECAUTIONS: Wear appropriate personal protection during sampling activities and analysis. Perform sample preparation and analysis in a clean well ventilated area that is well removed from any possible beryllium contamination. It is ESSENTIAL that suitable personal protective equipment, including suitable gloves, eye protection, laboratory coat, etc. is used when working with the chemicals. Any area affected by the detection or dissolution solution must be immediately washed with plenty of water. Ammonium bifluoride will etch glass, so it is essential that all NH_4HF_2 solutions are contained in plastic labware. Avoid exposure by contact with the skin or eyes, or by inhalation of the vapor.

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10 **SAMPLING:**

11 1. Don a clean pair of gloves.

12 2. Demarcate the sampling area (100 cm² minimum) using a clean template or tape. If a template is
13 used, tape the outside edges of the template to the surface to prevent its moving during sampling.

- 14 3. Using a clean wipe, sample the demarcated area using the procedure described in ASTM D6966
15 [2].
16 4. Place each wipe sample into labeled 15-ml plastic centrifuge tubes.
17

18 **SAMPLE PREPARATION:**

- 19 5. Add 5 ml of the dissolution solution (1% ammonium bifluoride) to each 15-ml centrifuge tube
20 containing surface swipe sample, and cap each tube.
21 6. Place each tube into a mechanical rotator, and rotate for at least 30 min.

22 NOTE: Rotator may also be substituted by a shaker or an agitator as long as the dissolution
23 solution wets the wipe well. Sonication has also been shown to be effective. Dissolution of
24 refractory material such as beryllium oxide by heating the solution to 80°C for 30 minutes
25 without agitation has been shown to be effective.

- 26 7. Into clean beakers, flasks, or tubes, filter each solution with a nylon syringe filter.
27 8. Into cuvettes containing 1.9 ml of detection solution, pipet 0.1 ml of each sample filtrate. Cap and
28 mix briefly.

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

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

36 NOTE: Alternative ratios of dissolution solution comprising beryllium and detection solution may
37 be used for analyzing alternative range of beryllium concentration.
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39 **CALIBRATION AND QUALITY CONTROL:**

- 40 9. Calibrate the fluorometer according to the manufacturer's recommendations.

41 NOTE: Beryllium stock standard solutions are made up using Beryllium spectrometric standards
42 diluted into 1% ammonium bifluoride. Calibration check standards are then prepared by

43 adding 0.1 ml of beryllium stock standards into 1.9 ml of detection solution (20-fold
44 dilution). A recommended series of standard stock solutions are 800 ppb, 200 ppb, 40
45 ppb, 10 ppb and 0 ppb to measure a range of 0.2 μg to 4 μg of beryllium on the sampling
46 media.

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

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50 10. Analyze a calibration standard, a reagent blank, and a media blank at least once every 20
51 samples. Ensure that the concentration range of the calibration standards spans the measured
52 beryllium levels in the samples.

53 11. Check recoveries with at least two media spikes per ten samples.

54 NOTE: It is recommended to use beryllium oxide (BeO) for media spikes.

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56 **MEASUREMENT:**

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58 12. For each sample, obtain the fluorescence spectrum using a 380-nm excitation lamp and visible
59 (400-700 nm) detector (follow instrument manufacturer's instructions).

60 13. If the fluorescence values for any of the samples are above the range of the calibration
61 standards, dilute the solutions with detection solution, reanalyze, and apply the appropriate
62 dilution factor in subsequent calculations.

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64 **CALCULATIONS:**

65 14. Obtain the solution concentration for each sample, C_s ($\mu\text{g}/\text{l}$), and the average media blank, C_b
66 ($\mu\text{g}/\text{l}$).

67 15. Using the solution volumes of sample, V_s (ml), and media blank, V_b (ml), calculate the
68 concentration, C ($\mu\text{g}/100 \text{ cm}^2$) of Be in the sample of area A , while accounting for the dilution
69 factor DF . The calculations below give the amount of beryllium in the wipe. It is assumed that 100
70 cm^2 area was wiped to collect the sample. If the area wiped is different from this number then the
71 calculations need to be adjusted so that the results are normalized to 100 cm^2 area.

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

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NOTE: The table below can be used for correlating the amount of beryllium in the solution to the beryllium in the sampling media.

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Preparation of Standard Solutions	Final concentration of beryllium (ppb) in calibration standard solutions	Corresponding amount of beryllium in the media*
0.1 ml of 0 ppb standard + 1.9 ml of detection solution	0.0	Corresponds to 0.00 μg Be on media
0.1 ml of 10 ppb standard + 1.9 ml of detection solution	0.5	Corresponds to 0.05 μg Be on media
0.1 ml of 40 ppb standard + 1.9 ml of detection solution	2.0	Corresponds to 0.2 μg Be on media
0.1 ml of 200 ppb standard + 1.9 ml of detection solution	10.0	Corresponds to 1 μg Be on media
0.1 ml of 800 ppb standard + 1.9 ml of detection solution	40.0	Corresponds to 4 μg Be on media

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*Incorporating sample dilution factor for 5 ml of dissolution solution; note that volumes other than 5 ml will require a different appropriate dilution factor.

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81 EVALUATION OF METHOD:

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The method was evaluated in accordance with published guidelines [3]. Experiments were conducted using an Ocean Optics® portable fluorescence device with the following components:

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USB 200 spectrometer with spectral grating #2 (UV/Vis 600)

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LS-1 lamp (380-nm) in LS-450 housing

87 UV-2 casting

88 OFLV linear filter 200-850

89 L2 collection lens and slit-200

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

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93 The method was evaluated using beryllium oxide spiked onto Whatman #541 cellulose and nylon filters at
94 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).

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96 The method was also field-tested using real-world samples (collected using Whatman #541 cellulose and
97 nylon filters) obtained at U.S. Department of Energy sites suspected to be contaminated with beryllium.

98 Field samples measured by portable fluorometry were also analyzed using hot plate digestion and ICP-

99 AES analysis; the latter served as a reference analytical method. Sample loadings observed ranged from
100 below detection limit ($<0.02 \mu\text{g}/\text{sample}$) to $\sim 12 \mu\text{g}/\text{sample}$.

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102 Long-term stability of samples was verified from spikes (n = 30) of 0.1 µg Be on Whatman #541 cellulose
103 and nylon filters. Samples were analyzed at day one (n = 12) and then one week (n = 6), ten days (n = 3),
104 two weeks (n = 3), three weeks (n = 3), and one month (n = 3) after spiking. No diminution of fluorescence
105 signal was observed from samples prepared and analyzed after having been stored for up to thirty days.

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107 Interference tests were carried out using solutions of 0 nM, 100 nM, and 1.0 µM Be in the presence of 0.4
108 mM Al, Ca, Co, Cu, Fe, Ti, Li, Ni, Pb, Sn, U, V, W, and Zn (separate experiments were carried out for each
109 potential interferant).

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