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# Beryllium - DRAFT

7704

## by Field-Portable Fluorescence Measurement

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

**METHOD: 7704, Issue 1**

**EVALUATION: PARTIAL**

**Issue 1: DRAFT**

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

**OSHA :** 0.002 mg/m<sup>3</sup>; Ceiling 0.005 mg/m<sup>3</sup>

**VP** 0 kPa (0 mm Hg) @ 25 °C

**NIOSH:** 0.0005 mg/m<sup>3</sup>; Carcinogen

**ACGIH:** 0.0002 mg/m<sup>3</sup>; Carcinogen

**SYNONYMS:** Beryllium metal

### SAMPLING

### MEASUREMENT

**SAMPLER:** Filter (0.8-µm, cellulose ester membrane, 25 or 37mm)

**TECHNIQUE:** Field-portable fluorescence measurement

**FLOW RATE:** 1 to 4 L/min

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

**VOL-MIN:** 1250 L

**SAMPLE DISSOLUTION:** 1% ammonium bifluoride

**-MAX:** 2000 L

**DETECTION SOLUTION:** 63.4 µM HBQS / 2.5 mM EDTA / 50.8

**SHIPMENT:** Routine

mM lysine monohydrochloride (pH adjusted to 12.85 with 10 M NaOH)

**SAMPLE**

**EXCITATION λ:** 380 nm

**STABILITY:** stable

**Detection λ range:** λ<sub>max</sub>: 400 – 700 nm; 475 nm

**BLANKS:** 2 to 10 field blanks

**CALIBRATION:** Elemental beryllium in detection solution

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**ACCURACY**

**RANGE:** 0.06 to 6 µg/filter

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**RANGE STUDIED:** 0.02 to 12.0 µg/filter

**ESTIMATED LOD:** 0.02 µg/filter

**BIAS:** none identified

**PRECISION (s):** 0.021 @ ~0.2 µg/filter (n = 15);

0.076 @ ~1.5 µg/filter (n = 6); 0.052 @

~3 µg/filter (n = 6)

**OVERALL**

**PRECISION (S<sub>r</sub>):** 0.057

**ACCURACY:** 11.6 (6.4 – 16.8, 95% C.I.)

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**APPLICABILITY:** The working range of the method is 0.06 to 6 µg/m<sup>3</sup> for a 1,000-L air sample. The analysis is for total beryllium and is not compound specific.

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**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.

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**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  $\mu\text{M}$  hydroxy benzoquinoline sulfonate (HBQS) [1] / 2.5 mM ethylene diamine tetraacetic acid disodium dihydrate (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  $\mu\text{g}/\text{ml}$  (commercially available).
5. Spiked beryllium media (commercially available)

\* See SPECIAL PRECAUTIONS

**EQUIPMENT:**

1. Sampler: Membrane filters, mixed cellulose ester (MCE) or nylon, 0.8- $\mu\text{m}$  pore size, 25- or 37-mm diameter
2. Personal sampling pump, 1 to 4 l/min, with clamps and flexible connecting tubing
3. Portable ultraviolet/visible (UV/Vis) fluorometer, with irradiance excitation lamp ( $\lambda = 380 \text{ nm}$ ) and time-integrating visible detector (400 – 700 nm,  $\lambda_{\text{max}} \approx 475 \text{ nm}$ ) or optical filters for appropriate wavelengths
4. Mechanical agitator, shaker or rotator
5. Fluorescence cuvettes, disposable, 10-mm diameter, transparent to UV/Vis radiation
6. Centrifuge tubes, plastic, 15-ml
7. Syringe filters, 0.45- $\mu\text{m}$  nylon, 13- or 25-mm diameter, in plastic housings  
NOTE: Polytetrafluoroethylene (PTFE) filters are unsuitable for this method.
8. Pipettors, mechanical, of assorted sizes as needed
9. Pipet tips, plastic, disposable, of assorted sizes as needed
10. Labware, plastic (e.g., beakers, flasks, graduated cylinders, etc.), of assorted sizes as needed
11. Tweezers, plastic or plastic-coated

12. Laboratory wipes

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

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**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 dissolution or the detection solution must be immediately washed with plenty of water. Ammonium bifluoride will etch glass, so it is essential that all  $\text{NH}_4\text{HF}_2$  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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13 **SAMPLING:**

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- 15 1. Calibrate each personal sampling pump with a representative sampler in line.
- 16 2. Sample at an accurately known flow rate between 1 and 4 L/min for a total sample size of 500 to
- 17 2000 L for TWA measurements. Do not exceed a filter loading of ~2 mg total dust.
- 18 3. After sampling, remove the filters from the cassettes using clean tweezers, and place into labeled
- 19 15-ml plastic centrifuge tubes.

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22 **SAMPLE PREPARATION:**

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- 24 4. Add 5 ml of the dissolution solution (1% ammonium bifluoride) to each 15-ml centrifuge tube
- 25 containing an air filter sample, and cap each tube.

26 5. Place each tube into a mechanical rotator, and rotate for at least 30 min.

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

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

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

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

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

42 NOTE: Alternative ratios of dissolution solution comprising beryllium and detection solution may  
43 be used for analyzing alternative range of beryllium concentration.

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46 **CALIBRATION AND QUALITY CONTROL:**

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48 8. Calibrate the fluorometer according to the manufacturer's recommendations

49 NOTE: Beryllium stock standard solutions are made up using Beryllium spectrometric standards  
50 diluted into 1% ammonium bifluoride. Calibration check standards are then prepared by  
51 adding 0.1 ml of beryllium stock standards into 1.9 ml of detection solution (20-fold  
52 dilution). A recommended series of standard stock solutions are 800 ppb, 200 ppb, 40  
53 ppb, 10 ppb and 0 ppb to measure a range of 0.2 µg to 4 µg of beryllium on the sampling  
54 media.

55 NOTE: If alternative ratios of dissolution solution comprising beryllium and detection solution are

56 used for sample preparation, then a similar ratio for calibration is required.

57 9. Analyze a calibration standard, a reagent blank, and a media blank at least once every 20  
58 samples. Ensure that the concentration range of the calibration standards spans the measured  
59 beryllium levels in the samples. Prepare a calibration graph.

60 10. Check recoveries with at least two media spikes per ten samples.

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

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65 **MEASUREMENT:**

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67 11. For each sample, obtain the fluorescence spectrum using a 380-nm excitation lamp and visible  
68 (400-700 nm) detector (follow instrument manufacturer's instructions).

69 12. If the fluorescence values for any of the samples are above the range of the calibration  
70 standards, dilute the sample filtrate with dissolution solution, reanalyze, and apply the  
71 appropriate dilution factor in subsequent calculations.

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74 **CALCULATIONS:**

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

78 14. Using the solution volumes of sample,  $V_s$  (ml), and media blank,  $V_b$  (ml), calculate the  
79 concentration,  $C$  ( $\mu\text{g/m}^3$ ) of Be in the air volume sampled,  $V$  (l), while accounting for the dilution  
80 factor DF:

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

85 NOTE: The table below can be used for correlating the amount of beryllium in the solution to the beryllium  
 86 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

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

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92 **EVALUATION OF METHOD:**

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

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

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

99 UV-2 casting

100 OFLV linear filter 200-850

101 L2 collection lens and slit-200

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103 Tests were carried out in relative irradiance mode using 2- or 5-sec integration times [4].

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105 The method was evaluated using beryllium oxide spiked onto mixed cellulose ester (MCE) filters at levels  
106 of 0, 0.02, 0.1, 0.2, 0.3, 0.4, 1.5, 3.0, and 6.0  $\mu\text{g}$  (five samples at each level).

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

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113 Interference tests were carried out using solutions of 0 nM, 100 nM, and 1.0  $\mu\text{M}$  Be in the presence of 0.4  
114 mM Al, Ca, Co, Cu, Fe, Ti, Li, Ni, Pb, Sn, U, V, W, and Zn (separate experiments were carried out for each  
115 potential interferant). An interlaboratory evaluation of the method was also performed [5].

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#### 118 REFERENCES:

119

120 [1] Matsumiya H, Hoshino H, Yotsuyanagi T [2001]. A novel fluorescence reagent, 10-  
121 hydroxybenzo(h)quinoline-7-sulfonate, for selective determination of beryllium(II) ion at  $\text{pg cm}^{-1}$  levels.  
122 Analyst 126: 2082-2086.

123

124 [2] ASTM D6966 [2003]. Standard Practice for Collection of Surface Wipe Samples for Subsequent  
125 Determination of Metals. American Society for Testing and Materials (ASTM): West Conshohocken,  
126 PA.



127 [3] Kennedy ER, Fischbach TJ, Song R, Eller PM, Shulman SA [1995]. Guidelines for Air Sampling and  
128 Analytical Method Development and Evaluation. CDC/NIOSH: Cincinnati, OH; DHHS (NIOSH) Publ.  
129 No. 95-117.

130

131 [4] Minogue EM, Ehler DS, Burrell AK, McCleskey TM, Taylor TP [2005]: Development of a new  
132 fluorescence method for the detection of beryllium on surfaces. J. ASTM Int., in press.

133

134 [5] Ashley K, McCleskey TM, Brisson MJ, Goodyear G, Cronin J, Agrawal A [2005]: Interlaboratory  
135 evaluation of a portable fluorescence method for the measurement of trace beryllium in the workplace.  
136 J. ASTM Int., in press.

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