

BERYLLIUM and compounds, as Be

7102

Be MW: 9.01 CAS: 7440-41-7 RTECS: DS1750000

METHOD: 7102, Issue 2

EVALUATION: FULL

Issue 1: 15 February 1984
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OSHA : 2 µg/m³; C 5 µg/m³; P 25 µg/m³/30 min
NIOSH: not to exceed 0.5 µg/m³ (suspect carcinogen)
ACGIH: 2 µg/m³ (suspect carcinogen)

PROPERTIES: hard, light metal; valence +2;
MP 1284 to 1300 °C

SYNONYMS: Vary as to compound.

SAMPLING		MEASUREMENT	
SAMPLER:	FILTER (0.8 µm cellulose ester membrane)	TECHNIQUE:	ATOMIC ABSORPTION, GRAPHITE FURNACE
FLOW RATE:	1 to 4 L/min	ANALYTE:	beryllium
VOL-MIN:	25 L @ 2 µg/m ³	ASHING REAGENTS:	HNO ₃ , 10 mL; H ₂ SO ₄ , 1 mL
-MAX:	1000 L	CONDITIONS:	150 °C until brown fumes disappear; 400 °C to dense fumes of H ₂ SO ₄
SHIPMENT:	routine	FINAL SOLUTION:	2% Na ₂ SO ₄ /3% H ₂ SO ₄ ; 10 mL
SAMPLE STABILITY:	stable	GRAPHITE FURNACE:	110 °C dry 20 sec; 900 °C char 10 sec; 2800 °C atomize 18 sec
BLANKS:	2 to 10 field blanks per set	WAVELENGTH:	234.9 nm
ACCURACY		BACKGROUND CORRECTION:	D ₂ or H ₂ continuum
RANGE STUDIED:	2.7 to 11.8 µg/m ³ [1] (40-L samples)	INJECTION VOLUME:	10 µL
BIAS:	- 0.39%	CALIBRATION:	Be ²⁺ in 2% Na ₂ SO ₄ /3% H ₂ SO ₄
OVERALL PRECISION ($\hat{S}_{r,T}$):	0.064 [1]	RANGE:	0.05 to 1 µg per sample [2]
ACCURACY:	± 12.42%	ESTIMATED LOD:	0.005 µg per sample [2]
		PRECISION (\hat{S}_r):	0.008 [2]

APPLICABILITY: The working range is 0.5 to 10 mg/m³ for a 90-L air sample. The method is applicable to ceiling measurements using a 25-L air sample.

INTERFERENCES: Calcium interference is masked by 3% (v/v) sulfuric acid. Sodium, potassium, and aluminum enhance beryllium absorbance; this effect is overcome by addition of 2% (w/v) sodium sulfate to both standards and samples. Perc hloric, phosphoric, and hydrofluoric acids produce interfering non-atomic peaks. These must be removed by digesting to dryness.

OTHER METHODS: This revises Method P&CAM 288 [2], which replaced Method S339 [3]. Flame atomic absorption and plasma emission (ICP-AES) are not sensitive enough for beryllium at these concentrations.

REAGENTS:

1. Nitric acid, conc., reagent grade or better.
2. Sulfuric acid, conc., reagent grade or better.
3. Sodium sulfate, reagent grade.
4. Sodium sulfate, 2% (w/v)/3% sulfuric acid (v/v). Add 10 g sodium sulfate and 15 mL H₂SO₄ to deionized water. Dilute to 500 mL.
5. Calibration stock solution, 1000 µg Be/mL,* commercially available, or dissolve 1.000 g Be metal in a minimum volume of 1:1 HCl, dilute to 1 L with 1% (v/v) HCl
6. Argon, prepurified.
7. Water, distilled or deionized.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler: mixed cellulose ester membrane filter, 0.8-µm pore size, 37-mm diameter in two-piece cassette filter holder.
2. Personal sampling pump, 1 to 4 L/min, with flexible connecting tubing.
3. Atomic absorption spectrophotometer with graphite furnace and background corrector.
4. Beryllium hollow cathode lamp.
5. Pressure regulator, two-stage, for Argon.
6. Beakers, Phillips, 125-mL.*
7. Watchglasses.*
8. Volumetric flasks, 10-mL.*
9. Pipets, 10-mL volumetric, with pipet bulb.*
10. Automatic pipettor with tips, 10-µL and assorted sizes for standards.
11. Hotplate, 150 to 400 °C.
12. Waterbath, 60 to 70 °C.
13. Bottles, polyethylene, 25-mL.

* Clean all glassware with conc. nitric acid and rinse thoroughly before use.

SPECIAL PRECAUTIONS: Beryllium is very toxic and a suspected human carcinogen [4]. Perform all acid digestions in a fume hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative filter in line.
2. Sample at an accurately known flow rate between 1 and 4 L/min for a sample size of 25 to 1000 L. Do not exceed 2 mg total dust loading on the filter.

SAMPLE PREPARATION:

3. Open cassettes and transfer filters to clean Phillips beakers.
4. Add 10 mL conc. HNO₃ and 1 mL conc. H₂SO₄. Cover with watchglass.
5. Heat in fume hood on hotplate (150 °C) until brown fumes of HNO₃ disappear, then at 400 °C until dense fumes of H₂SO₄ appear.

NOTE: Verify that the compounds in the samples are soluble with this ashing procedure, e.g., ore or mining samples will require HF in the digestion. If additional ashing acids are used (e.g., HF, HClO₄, or H₃PO₄), evaporate to complete dryness at this point.

6. Cool and rinse watchglass and sides of beaker with distilled water and evaporate just to dryness. Remove beaker immediately and air-cool.
7. Pipet 10.0 mL 2% Na₂SO₄/3% H₂SO₄ solution into beaker and cover.
NOTE: Start sulfate reagent blanks at this step.
8. Heat in 60 to 70 °C waterbath for 10 min. Allow to stand overnight before analysis to ensure complete dissolution of BeSO₄.

CALIBRATION AND QUALITY CONTROL:

9. Calibrate daily with at least six working standards over the range 0.005 to 1 µg Be per sample.
 - a. Use serial dilutions of known amounts of calibration stock solution in 2% Na₂SO₄/3% H₂SO₄ to prepare working standards. Store in polyethylene bottles. Stable at least four weeks.
 - b. Analyze together with samples and blanks (steps 11 and 12).

NOTE: Analyze working standards alternately with the samples to compensate for the increasing Be signal as the graphite tube ages.
10. Analyze three quality control blind spikes and three analyst spikes.

MEASUREMENT:

11. Set spectrophotometer and graphite furnace according to manufacturer's recommendations and to conditions on page 7102-1.
12. Inject 10-µL aliquots of samples into graphite tube. Record absorbance (peak height mode).

CALCULATIONS:

13. Read absorbance of samples, A; average media blanks, A_b; average sulfate reagent blanks, A_r; and working standards, A_s.
14. Using the working standard, C_s (µg/mL), analyzed adjacent to the sample of interest, calculate concentration, C (µg/m³), of Be in the air volume sampled, V (L):

$$C = \frac{(A - A_b) \cdot C_s \cdot 10^4}{(A_s - A_r)V}, \mu\text{g}/\text{m}^3.$$

EVALUATION OF METHOD:

This method was evaluated using NTIS Standard Reference Material No. 2675 for Be over the range of 0.1 to 0.4 µg Be/filter (equivalent to one-half to two times the OSHA PEL). Beryllium recovery was 98.2% with a measurement precision, S_r, of 0.008 [2]. This method is an improvement of S339 [3], which was validated over the range of 2.68 to 11.84 mg/m³ using a 40-L sample. Mean recovery was 106.9% with overall precision of 0.064 [1].

REFERENCES:

- [1] Documentation of the NIOSH Validation Tests, S339, U.S. Department of Health, Education and Welfare, Publ. (NIOSH) 77-185 (1977).
- [2] NIOSH Manual of Analytical Methods, 2nd ed., V. 5, P&CAM 288, U.S. Department of Health, Education and Welfare, Publ. (NIOSH) 79-141 (1979).
- [3] Ibid., V. 3, S339, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-C (1977).
- [4] Criteria for a Recommended Standard...Occupational Exposure to Beryllium, U.S. Department of Health, Education and Welfare, Publ. (NIOSH) 72-10268 (1972); and as revised in August, 1977 in NIOSH testimony at OSHA hearing.

METHOD REVISED BY:

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