



Beryllium and Compounds (as Be)

| | |
|---|---|
| Method Number: | 1023 |
| Version: | 1.0 |
| Target Concentration: | 0.2 $\mu\text{g}/\text{m}^3$ |
| OSHA PEL: | 0.2 $\mu\text{g}/\text{m}^3$ 8-hour time-weighted average (TWA) 2.0 $\mu\text{g}/\text{m}^3$ short-term exposure (STEL) |
| ACGIH TLV: | 0.00005 mg/m^3 (8-hour TWA) Skin; dermal sensitizer; respiratory sensitizer |
| Procedure: | Collect air samples by drawing workplace air through a 37-mm diameter, 0.8 micron pore size, mixed-cellulose ester (MCE) filter contained in a closed-face polystyrene cassette, using a personal sampling pump. Collect wipe samples on Smear Tabs. Bulk samples may also be collected. Digest the samples in nitric acid using microwave digestion and analyze by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) instrumentation. |
| Recommended Sampling Time and Sampling Rate: | 240 minutes at 2 L/min (480 L) 15 minutes at 2 L/min (30 L) STEL |
| Reliable Quantitation Limit: | 0.03 $\mu\text{g}/\text{m}^3$ |
| Standard Error of Estimate at the Target Concentration: | 5.4% |
| Status of the Method: | Fully validated. This method has been subjected to the established validation procedures of the Methods Development Team. |

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1. General Discussion

For assistance with accessibility problems in using figures and illustrations presented in this method, please contact the Salt Lake Technical Center (SLTC) at (801) 233-4900. This procedure was designed and tested for internal use by OSHA personnel. Mention of any company name or commercial product does not constitute endorsement by OSHA.

1.1 Background

1.1.1 History

Previous data indicated that nitric acid alone was not effective for complete digestion of beryllium, particularly calcined beryllium oxide (referred to as “high-fired”) such as NIST SRM 1877.¹ Sulfuric acid has historically been used by OSHA for digestion of beryllium compounds.² As nitric acid is the preferred acid matrix for ICP-OES as well as ICP-MS³, a nitric acid digestion procedure capable of digesting beryllium oxide is ideal. Data presented in this method show that microwave technology used to heat samples to high temperatures is effective in digestion of beryllium oxide without the use of sulfuric acid. Microwave procedures capable of heating nitric acid to 215 °C in a closed vessel can achieve sufficient digestion. Because this method uses only nitric acid for digestion, it is ideally suited for analyses by other instrumentation.

In January 2017, OSHA published its final rule Occupational Exposure to Beryllium and Beryllium Compounds in the Federal Register. The new 8-hour time-weighted average (TWA) permissible exposure limit (PEL) for beryllium is 0.2 µg/m³ and the new short term exposure limit (STEL) over a 15-minute sampling period is 2.0 µg/m³.

1.1.2 Toxic effects (This section is for information only and should not be taken as the basis of OSHA policy.)

Exposure to beryllium can lead to beryllium sensitization, chronic beryllium disease/berylliosis, and lung cancer. These health effects have been identified with beryllium (dust, fume, mist, or solutions) exposure via inhalation or skin contact.⁴

1.1.3 Workplace exposure⁵

Approximately 62,000 workers are exposed to beryllium in the workplace. Exposures include work conducted with abrasive blasting operations using beryllium containing slags, beryllium metal and ceramic production, non-ferrous foundries, and fabrication of beryllium alloy products. Engineering and work practice controls along with personal protective clothing and equipment have been used to protect workers from harmful exposure to beryllium for years.

¹ Oatts, T. J.; Hicks, C. E.; Adams, A. R.; Brisson, M. J.; Youmans-McDonald, L. D.; Hoover, M. D.; Ashley, K. Preparation, certification and interlaboratory analysis of workplace air filters spiked with high-fired beryllium oxide. *J. Environ. Monit.* **2012**, *14*, 391.

² Septon, J.; Abel, R.; Simmons, M. Metal and Metalloid Particulates in Workplace Atmospheres (OSHA Method ID-125G), 2002. United States Department of Labor, Occupational Safety & Health Administration Web site. <https://www.osha.gov/dts/sltc/methods/inorganic/id125g/id125g.html> (accessed April 2018).

³ Thomas, R. *Practical Guide to ICP-MS: A Tutorial for Beginners*; Marcel Dekker, Inc.: New York, 2004; p 154.

⁴ Beryllium Health Effects, 2015. United States Department of Labor, Occupational Safety & Health Administration Web site. <https://www.osha.gov/SLTC/beryllium/healtheffects.html> (accessed April 2018).

⁵ Final Rule to Protect Workers from Beryllium Exposure, 2017. United States Department of Labor, Occupational Safety & Health Administration Web site. <https://www.osha.gov/berylliumrule/index.html> (accessed April 2018).

1.1.4 Physical properties and descriptive information^{6,7}

Properties listed in this section are for beryllium metal. Physical properties for beryllium compounds vary. The major forms of beryllium encountered industrially are: beryllium metal, beryllium alloys (mainly aluminum or copper), and beryllium compounds (beryllium fluoride, beryllium hydroxide, and beryllium oxide).

Beryllium

| | |
|----------------------------|---|
| Synonyms: | elemental beryllium (Be); glucinum (Gl) |
| Solubility: | insoluble in water |
| IMIS number ⁸ : | 0360 |
| CAS number: | 7440-41-7 |
| Molecular weight: | 9.01218 |
| Boiling point: | 2500 °C, extrapolated |
| Melting point: | 1287 °C |
| Molecular formula: | Be |
| Appearance: | grayish-white, hard light metal |
| Specific gravity: | 1.8477 g/cm ³ |

2. Sampling Procedure

All safety practices that apply to the work area being sampled should be followed. The sampling equipment should be attached to the worker in a manner that will not interfere with work performance or safety.

2.1 Equipment

Mixed-cellulose ester (MCE) filters, 37-mm diameter, 0.8 micron pore size, with support pads (SKC 225-5)

Two-piece polystyrene cassettes

Plastic end plugs

Gel bands

Flexible pump tubing

Personal sampling pump

Whatman Smear Tabs, catalog number 1450-993 (SKC 225-24)

Glass scintillation vials, 20-mL

Proper PPE, including disposable gloves (not powdered)

Form OSHA-21 seals

⁶ American Conference of Governmental Industrial Hygienists, Inc. *Documentation of the Threshold Limit Values and Biological Exposure Indices*, 7th ed.; Cincinnati, OH, 2014; Beryllium and compounds, pp 1-14.

⁷ Sax, N. I. *Dangerous Properties of Industrial Materials*, 5th ed.; Van Nostrand Reinhold Company, New York, 1979; p. 412.

⁸ Beryllium and Beryllium Compounds (as Be) (Chemical Sampling Information), 2012. United States Department of Labor, Occupational Safety & Health Administration Web site. https://www.osha.gov/dts/chemicalsampling/data/CH_220600.html (accessed April 2018).

2.2 Reagents

Deionized water for wipe sampling

2.3 Technique

2.3.1 Air samples

Wear clean gloves while handling media. Do not use powdered gloves due to the potential contamination of metals which cause interference during analysis. Cassettes preassembled with MCE filters are recommended for collecting air samples. If preassembled cassettes are not used, assemble each two-piece cassette with an MCE filter on top of a support pad; the support pad on the bottom cassette piece. Apply a gel band to the cassette and secure plugs in the top and bottom. Assemble all components of cassettes in the proper order and direction, with cassette pieces completely seated against each other. Loose or crooked assembly may result in low sample collection due to material bypassing the filter; contaminated support pads are not analyzed.

Label each cassette with a unique identification number.

Samples are collected using a personal sampling pump calibrated to within $\pm 5\%$ of the recommended flow rate with the sampling device in-line. Remove the bottom plug from a prepared cassette, attach the calibrated personal sampling pump (the support pad should face the pump) with flexible tubing, and position the apparatus in the appropriate workplace area or in the worker's breathing zone. Remove the top (inlet) plug from the cassette and draw air directly into the inlet. The air being sampled should not pass through any hose or tubing before entering the cassette. Care should be taken to avoid overloading the filter.

Sample, closed-face, for 240 min at 2 L/min (480 L) to collect TWA samples.

Sample, closed-face, for 15 min at 2 L/min (30 L) to collect short-term samples.

After sampling, replace the plugs at both ends of the cassette. Seal each sample by attaching a Form OSHA-21 seal over both plugs as soon as possible.

Submit at least one field blank sample with each set of samples. Open the field blank in a clean area at the sampling site. Blank samples should be handled, stored and shipped in the same manner as other samples; however, no air is drawn through them.

Record sample air volume (liters), sampling time (min) and sampling rate (L/min) for each sample, along with any known substance present or potential interferences on the Form OSHA-91A.

Submit the samples to the laboratory for analysis as soon as possible after sampling.

2.3.2 Wipe samples

Prepare a sufficient number of vials, label each with a unique identification number. It may be convenient to preload vials with the moist Smear Tabs.

Wear clean, impervious, disposable gloves while handling media or collecting wipe samples. Change gloves between samples to minimize cross-contamination. Do not use powdered gloves.

Moisten Smear Tabs with deionized water prior to use.

Record the sample vial number and the location where the sample is taken. Withdraw the Smear Tab with gloved fingers or clean forceps.

Wipe a 10-cm by 10-cm surface area in a horizontal side-to-side pattern, applying firm pressure. If possible, fold the wipe in half with the exposed-side in, and use it to wipe the same area again in a vertical up-and-down pattern.

Transfer the wipe to a 20-mL scintillation vial. Cap the vial securely and seal with vinyl or electrical tape. Securely wrap the vial with a Form OSHA-21 seal.

Submit at least one field blank sample with each set of samples. Blank samples should be handled, stored and shipped in the same manner as other samples.

Note any known substance present or potential interferences on the Form OSHA-91A.

2.3.3 Bulk samples

Collect representative material for bulk samples. Ideally 0.2 – 1 gram of material should be collected in a 20-mL scintillation vial. Cap the vial securely, identify with a unique number and seal with vinyl or electrical tape. Securely wrap the vial with a Form OSHA-21 seal.

Note any known substance present or potential interferences on the Form OSHA-91A.

Ship all bulk samples separate from air samples.

3. Analytical Procedure

3.1 Equipment

ICP-OES (A PerkinElmer Optima 7300 DV ICP-OES was used for validation data.)

Laboratory microwave system, capable of reaching and maintaining samples at a temperature of 215 °C, without sample loss (A CEM Discover SP-D Microwave was used for validation data.)

Analytical balance (0.01 mg)

Water purification system for deionized water or better (A Barnstead Nanopure Diamond system was used for generating reverse osmosis (RO) water with minimum resistivity of 18 MΩ.)

Microwave vessels and trays, 35-mL Pyrex pressure vessels (CEM 909036) and Teflon caps (CEM 909350)

Syringes, Luer-Lock plastic, 10-mL syringes, Thermo Scientific S751510 (Fisher Scientific 03-377-29)

Filters, EMD Millipore Millex, 25-mm, 0.8-µm MCE syringe filters with PVC housing (EMD Millipore SLAA025NK)

Class-A graduated cylinder, 100-mL, TD

50-mL polypropylene DigiTUBE containers, meeting Class-A requirements, with caps, (SCP Science 010-500-263) or other equivalent Class-A, volumetric glassware

Bottle top dispenser capable of dispensing 5-mL aliquots

Vials for sample analysis, 10-mL glass culture tubes (Fisher Scientific 14-961-29) or 15-mL Falcon plastic centrifuge tubes by Corning Inc. catalog number 352096 (Fisher 14-959-49B)

Whatman Smear Tabs, Whatman catalog number 1450-993 (SKC 225-24)

Laboratory wash bottles

Weighing boats or paper

Forceps

3.2 Reagents

Beryllium standard solution, 1,000 $\mu\text{g/mL}$ in water with dilute nitric acid, Ultra Scientific

RO water, 18 M Ω

Concentrated nitric acid (69-70%), [CAS no. 7697-37-2], for trace metal analysis: J.T. Baker Intra-Analyzed Reagent grade was used (9598-34). Ultra-pure nitric acid with Be \leq 0.1 ppb is recommended.

Sample diluent: 20% (v/v) nitric acid/water solution

Instrument rinse: 5% (v/v) nitric acid/water solution

3.3 Standard preparation

Prepare analytical working standards by diluting (v/v) a beryllium stock standard solution to the desired concentrations, matching the acid matrix of the digested samples. Suggested concentrations for working standard are 0.001, 0.05, and 1 $\mu\text{g/mL}$ Be in 20% (v/v) nitric acid. Prepare standards every six months.

3.4 Sample preparation

3.4.1 MCE filters

Carefully transfer any loose dust from the cassette into a 35-mL Pyrex microwave digestion vessel. Use forceps to transfer the filter to the same vessel. Wipe the interior of the cassette top with a clean Smear Tab, moistened with 18 M Ω water, and add it to the same vessel. (Other interior surfaces of the cassette should be wiped if visibly contaminated.) Contaminated support pads are not analyzed.

3.4.2 Wipes (smear tabs only)

Carefully transfer each sample into a 35-mL Pyrex microwave digestion vessel using forceps. If material remains in the scintillation vial, rinse with a small amount (up to 2 mL) of 18 M Ω water into the same vessel.

3.4.3 Bulks

Weigh 20 to 50 mg of sample material (less if high beryllium content is relatively certain) and carefully transfer all the weighed sample material into a 35-mL Pyrex microwave digestion vessel. If any material remains on the weighing-boat or paper, rinse it into the vessel with a small amount (up to 2 mL) of 18 M Ω water. Alternatively,

sample material may be weighed directly into the digestion vessel with an appropriate balance.

3.4.4 Microwave procedure for all samples

Add approximately 2 mL of 18 MΩ water. Add 5 mL of concentrated nitric acid. A minimum liquid volume of 7 mL is needed to digest material that may be above the liquid level. (This will completely digest a filter placed on the side wall at the bottom of the vessel.) Cap the vessel and place it in the microwave sample tray. Treat blank samples in the same manner as other samples. Note the location of each sample.

Program the microwave to ramp the temperature in 10 minutes to 215 °C and hold at 215 °C for 10 minutes.

The SP-D microwave customized program is shown below.

| Stage | Temp. | Ramp Time | Hold Time | Pressure | Power |
|-------|--------|-----------|-----------|----------|-------|
| 1 | 215 °C | 10 min | 10 min | 250 psi | 300 W |

Programmed pressure stages (sets events to release pressure by venting vessels) are shown below. The program also includes a venting for a sudden change in pressure, as Delta Pressure = 25 °C.

| Stage | Pressure Set Point (psi) | Vent Times at Set Point |
|-------|--------------------------|-------------------------|
| 1 | 225 | 2 |
| 2 | 250 | 2 |
| 3 | 275 | 2 |
| 4 | 300 | 2 |
| 5 | 350 | 100 |

After samples have cooled, quantitatively transfer each solution to a Class-A container using water in a rinse bottle. Dilute each sample solution to a final volume of 25 mL. Cap the container and stir or shake each sample several times.

3.5 Analysis

Sample aliquots used for instrumental analysis should be free of particulate. Filter each solution as necessary. Pour an aliquot of each sample into an appropriate vial for analysis. Label each vial with unique identification. Analyze samples by ICP-OES, using the instrument rinse solution between samples. Optimize analytical conditions for each analytical instrument.

When a sample concentration exceeds the highest working standard, dilute the sample with the sample diluent to a concentration within the standard range and analyze. The diluted sample matrix must match the acid matrix of the working standards.

3.5.1 Analytical conditions

Follow manufacturer's instructions for instrument conditions and optimization. Settings will vary for each instrument. An example of ICP operating conditions is listed below.

Spectrometer

Spectral settings: Normal Purge Gas Flow
 No Spectral Profiling
 High Fixed Resolution

Read parameters: Automated Time, 2-10 sec
60 sec Delay Time
2 Replicates

Sampler

Plasma: 15 sec Source Equilibration Delay
Plasma Conditions: Vary by Element

| Plasma (L/min) | Aux. (L/min) | Neb. (L/min) | Power (watts) | View Distance |
|-------------------|-----------------|-----------------|------------------|------------------|
| 20 | 0.2 | 0.60 | 1300 | 15.0 |

Plasma View Axial for Be
Plasma View varies (Axial or Radial) for interfering analytes

Peristaltic pump: 1.20 mL/min Sample Flow Rate
24 sec Flush Time
2 Replicates

Auto-sampler: Wash after every sample + extra time if sample concentration exceeds set limits
2.50 mL/min Rate
48 sec Normal wash time
200 sec Extra time

| Processing: | Analyte | λ (nm) | Peak Algorithm | Pts/Peak | BGC |
|-------------|---------|----------------|----------------|----------|---------|
| | Be | 313.1 | MSF | N/A | N/A |
| | Be | 234.9 | Peak Area | 2 | 1-Point |

3.5.2 Calibration

Calibrate the instrument with a blank and beryllium standards at three different levels. The suggested standard concentrations are 0.001, 0.05, and 1 $\mu\text{g/mL}$ Be. Use a weighted linear curve equation ($w_i = 1/x^2$) with blank correction. The relative standard deviation (RSD) of the beryllium (313.1 nm) replicates for the high standard should be less than 2%.

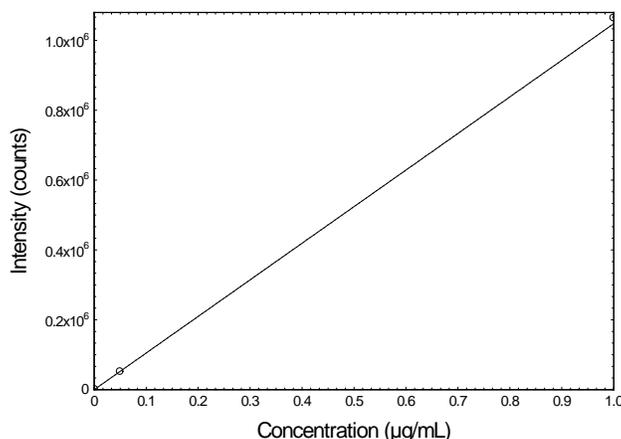


Figure 3.5.2. Example calibration curve for Be 313.1 nm ($y = 1048000x + 23.1$, $w_i = 1/x^2$).

3.6 Interferences and corrections

Calibrate each interfering element with a blank and one standard. Aluminum, calcium, cerium, chromium, iron, molybdenum, niobium, titanium, and vanadium were identified as potential interferences with beryllium at 313.1 nm or 234.9 nm. Where high levels of other elements are suspected or anticipated, perform tests to identify spectral interferences. Perform these tests according to instrument manufacturer's guidelines. Also use the instrument manufacturer's guidelines to set up the instrument to correct for the spectral interferences. Spectral corrections may require frequent checks or updates due to the low reporting limit, instrument sensitivity, and variability of peak shapes related to interfering elements. For more information, see Section 4.9 Analytical Interferences.

Interferences with beryllium at 313.1 nm were corrected using Multicomponent Spectral Fitting (MSF). Corrections for beryllium at 234.9 nm were made by Inter-Element Correction (IEC). Results at 313.1 nm with MSF applied were generally found to be more accurate. Results at 234.9 nm were only used for verification of the 313.1 nm beryllium results.

3.7 Calculations

3.7.1 Air samples

$$C_a = \frac{C_s V_s}{V_a} DF$$

Where C_a is the concentration of beryllium found in the sampled air (mg/m^3)
 C_s is the beryllium concentration of the sample, as reported by the analytical instrumentation ($\mu\text{g}/\text{mL}$)
 V_s is the final diluted volume of the digested sample solution (mL)
 DF is any additional dilution factor applied for analysis
 V_a is the volume of air sampled (L)

3.7.2 Wipe samples

$$m = C_s V_s DF$$

Where m is the total mass of beryllium found in the sample (μg)
 C_s is the beryllium concentration of the sample, as reported by the analytical instrumentation ($\mu\text{g}/\text{mL}$)
 V_s is the final diluted volume of the digested sample solution (mL)
 DF is any additional dilution factor applied for analysis

3.7.3 Bulk samples

$$P = \frac{m}{m_s} \times 100\%$$

Where P is the beryllium total found in the sample (%)
 m is the total mass of beryllium found in the sample (μg), calculated in section 3.7.2
 m_s is the mass of bulk sample digested (μg).

4. Method Validation

General instruction for the laboratory validation of OSHA sampling and analytical methods that employ spectroscopic analysis is presented separately.⁹ These Guidelines detail required validation tests, show examples of statistical calculations, list validation acceptance criteria, and define analytical parameters.

Beryllium validation data are all reported from analyses at 313.1 nm using MSF. Data from 234.9 nm, using IEC, are used for verification. Additional elements analyzed for interference purposes were Al, Ca, Ce, Cr, Fe, Mo, Nb, Ti, and V.

4.1 Detection limit of the analytical procedure (DLAP)

The DLAP is measured as the mass per solution volume and expressed as a mass per sample equivalent, based on a 25 mL digested sample volume. Ten analytical standards were prepared with equally descending increments of beryllium (analyzed at 313.1 nm) with the highest standard containing 0.10 ng/mL. This is the sample concentration that would produce a detector response approximately 10 times the response of a reagent blank. These spiked reagents and a reagent blank were analyzed with the recommended analytical parameters listed in section 3. The data obtained were used to determine the required parameters (standard error of estimate and slope) for the calculation of the DLAP. Values of 993 and 11.25 were obtained for the slope and standard error of estimate respectively. The DLAP was calculated to be 0.034 ng/mL (0.85 ng/sample).

Table 4.1
Detection Limit of the Analytical
Procedure

| concentration (ng/mL) | intensity (counts) |
|--------------------------|-----------------------|
| 0 | 33.2 |
| 0.01 | 40.8 |
| 0.02 | 47.5 |
| 0.03 | 64.9 |
| 0.04 | 56.6 |
| 0.05 | 67.0 |
| 0.06 | 63.7 |
| 0.07 | 101.5 |
| 0.08 | 122.8 |
| 0.09 | 118.6 |
| 0.10 | 128.1 |

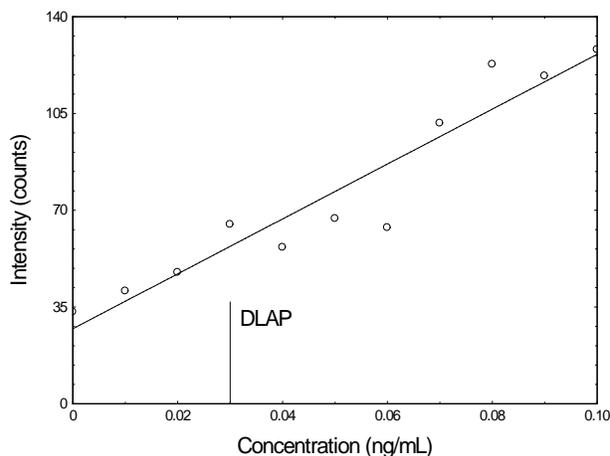


Figure 4.1. Plot of data to determine the DLAP ($y = 993x + 27.2$).

4.2 Detection limit of the overall procedure (DLQP) and reliable quantitation limit (RQL)

The DLQP is measured as mass per sample volume and expressed as mass per sample and equivalent air concentration based on a 25-mL digested sample volume and the recommended sampling volume of 480 L. Ten samplers were spiked with equally descending increments of beryllium, such that the highest sampler loading was 1.0 ng/mL. This is the amount spiked on a sample that would produce a detector response approximately 10 times the response of a sample blank. These spiked samples, and the sample blank were analyzed with the recommended analytical parameters, and the data obtained used to calculate the required

⁹ Eide, M.; Giles, P.; Simmons, M.; Hendricks, W. Evaluation Guidelines for Air Sampling Methods Utilizing Spectroscopic Analysis, 2005. United States Department of Labor, Occupational Safety & Health Administration Web site. <https://www.osha.gov/dts/sltc/methods/spectroguide/spectroguide.html> (accessed April 2018).

parameters (standard error of estimate and the slope) for the calculation of the DLOP. Values of 1297 and 79.07 were obtained for the slope and standard error of estimate respectively. The DLOP was calculated to be 0.18 ng/mL (4.5 ng/sample or 0.0094 $\mu\text{g}/\text{m}^3$).

Table 4.2
Detection Limit of the Overall Procedure

| concentration (ng/mL) | intensity (counts) |
|--------------------------|-----------------------|
| 0 | 149.8 |
| 0.1 | 287.9 |
| 0.2 | 379.9 |
| 0.3 | 518.2 |
| 0.4 | 633.9 |
| 0.5 | 752.8 |
| 0.6 | 1110.7 |
| 0.7 | 1127.6 |
| 0.8 | 1249.3 |
| 0.9 | 1252.3 |
| 1.0 | 1372.0 |

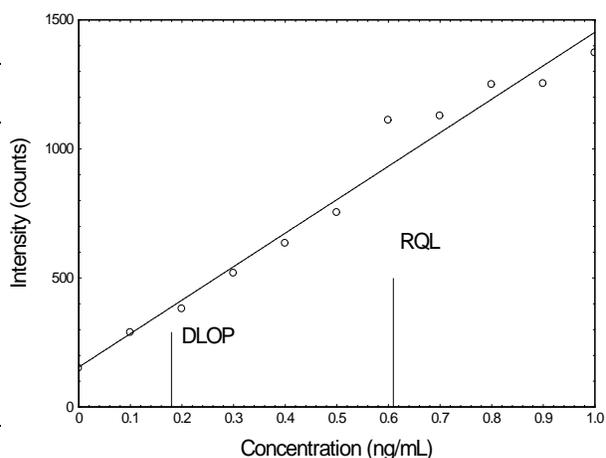


Figure 4.2. Plot of data to determine the DLOP/RQL ($y = 1297x + 154$).

The RQL is considered the lower limit for precise quantitative measurements. It is determined from the regression line parameters that were obtained for the calculation of DLOP providing 75% to 125% of the analyte is recovered. The RQL is 0.61 ng/mL (15 ng/sample or 0.031 $\mu\text{g}/\text{m}^3$). Recovery at this concentration is 123%.

When short-term samples are collected, the air concentration equivalent to the reliable quantitation limit becomes larger. For example, the reliable quantitation limit for beryllium is 0.50 $\mu\text{g}/\text{m}^3$ for a 30 L sample.

4.3 Instrument calibration, precision of the analytical instrumentation, and stability of standard solutions

The precision of the analytical instrumentation measured as the mass equivalent to the standard error of estimate determined from the linear regression of data points from standards over a range that covers 0.1 to 2 times the target concentration. The target concentration (x) is the PEL equivalent of 4 ng/mL. The standard error of estimate was 0.15 ng/mL.

Table 4.3
Precision of the Analytical Instrumentation

| x target conc. (ng/mL) | 0.1x | 0.5x | 1.0x | 1.5x | 2.0x |
|---------------------------|-------|--------|--------|--------|--------|
| intensity | 459.7 | 2171.3 | 4460.7 | 6739.7 | 9034.2 |
| (counts) | 401.7 | 2079.5 | 4413.1 | 6688.3 | 8859.6 |
| | 434.0 | 2074.4 | 4304.8 | 6504.5 | 8593.4 |

4.4 Precision (overall procedure)

The precision of the overall procedure at the 95% confidence level is obtained by multiplying the overall standard error of estimate by 1.96 (the z-statistic from the standard normal distribution at the 95% confidence level). Ninety-five percent confidence intervals are shown above and below the regression lines in the storage stability figures shown in Section 4.5.

4.4.1 MCE filter active sampler

The precision of the overall procedure at the 95% confidence level for 18-day storage test at ambient temperature (at the PEL concentration) is 10.6%. It was obtained from the overall standard error of estimate (5.39%) of the data shown in Figure 4.5.1. It contains an additional 5% for sampling pump error.

4.4.2 Recovery

The anticipated recovery derived from storage data remained above 104.3% for PEL level samples stored at ambient temperature and 100.2% for STEL level samples at the end of the storage period.

4.5 Storage stability test

Two storage stability tests were performed. Storage samples were prepared by spiking a solution of beryllium onto MCE filters at the mass equivalent to the PEL (0.1 µg) and at the mass equivalent to the STEL (0.06 µg). The PEL equivalent liquid-spiked concentration was 4 ng/mL, based on a 25-mL digested sample volume and the recommended air sampling volume of 480 L. The STEL equivalent liquid-spiked concentration was 2.4 ng/mL, based on a 25-mL digested sample volume and the recommended air sampling volume of 30 L. Eighteen storage samples were prepared at each level (PEL and STEL). Three samples at each level were analyzed on the day of preparation. Fifteen samples at each level were stored at ambient temperature. Three samples at each level were analyzed every three to four days after preparation.

Table 4.5
Storage Test for Beryllium

| time (days) | PEL recovery (%) | | | time (days) | STEL recovery (%) | | |
|-------------|------------------|-------|-------|-------------|-------------------|-------|-------|
| 0 | 105.3 | 105.1 | 105.2 | 0 | 109.1 | 103.3 | 103.7 |
| 4 | 103.5 | 102.8 | 102.3 | 4 | 105.3 | 103.8 | 102.6 |
| 7 | 104.0 | 100.2 | 104.6 | 7 | 104.2 | 103.8 | 101.9 |
| 11 | 106.0 | 106.0 | 104.6 | 11 | 89.1 | 91.0 | 89.5 |
| 14 | 103.3 | 99.6 | 102.0 | 14 | 96.6 | 98.6 | 100.1 |
| 18 | 105.9 | 105.9 | 105.3 | 17 | 107.1 | 111.1 | 107.0 |

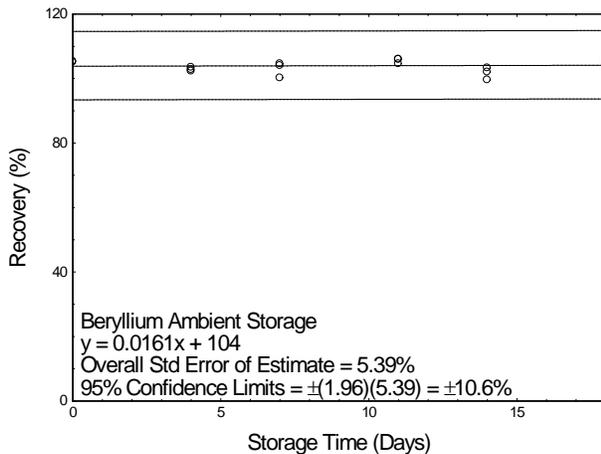


Figure 4.5.1. Storage test for beryllium at the PEL.

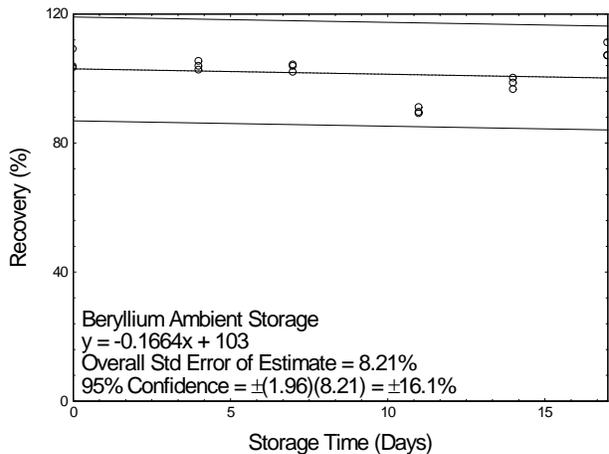


Figure 4.5.2. Storage test for beryllium at the STEL.

4.6 Reproducibility

Twelve samples were prepared by spiking MCE filters with a solution of beryllium. Six samples were spiked at the mass equivalent to the PEL (0.1 µg) and at the STEL (0.06 µg). The samples were submitted to the OSHA Salt Lake Technical Center for analysis. The samples were analyzed 2 days after being spiked. No sample result for beryllium had a deviation greater than the precision of the overall procedure determined in Section 4.4.

Table 4.6
Reproducibility Data for Beryllium
Collected on MCE Filters

| PEL | | | | STEL | | | |
|------------------|-------------|--------------|---------------|------------------|-------------|--------------|---------------|
| theoretical (µg) | result (µg) | recovery (%) | deviation (%) | theoretical (µg) | result (µg) | recovery (%) | deviation (%) |
| 0.1 | 0.1066 | 106.6 | 6.6 | 0.06 | 0.06186 | 103.1 | 3.1 |
| 0.1 | 0.1054 | 105.4 | 5.4 | 0.06 | 0.05751 | 95.8 | -4.2 |
| 0.1 | 0.1012 | 101.2 | 1.2 | 0.06 | 0.06412 | 106.9 | 6.9 |
| 0.1 | 0.1075 | 107.5 | 7.5 | 0.06 | 0.06206 | 103.4 | 3.4 |
| 0.1 | 0.1058 | 105.8 | 5.8 | 0.06 | 0.06110 | 101.8 | 1.8 |
| 0.1 | 0.1035 | 103.5 | 3.5 | 0.06 | 0.06259 | 104.3 | 4.3 |

4.7 Retention efficiency

The retention efficiency of an MCE filter was tested by spiking six filters at twice the PEL equivalent (0.2 µg Be). After drying, the filters were each placed in a two-piece cassette with the ends plugged, equipped with a support pad under the filter. Three of the filter cassettes were set aside and used as controls, with no air pulled through these cassettes. Air with approximately 75% relative humidity, at 23.8 °C, was drawn through three of the samplers, each lined up with a blank (un-spiked) sampler placed downstream, for approximately 295 minutes at 2 L/min. No analyte was detected on any of the blanks. The mean recovery for the three test filters was 102.9%. The mean recovery for the three control filters was 103.7%. The analyte was sufficiently retained on the medium.

4.8 Digestion efficiency and stability of digested samples

The digestion efficiency is dependent on the acid matrix and the digestion technique.

4.8.1 Digestion efficiency of beryllium compounds

Digestion efficiencies of beryllium compounds were determined by digesting and analyzing a known amount of solid material for three samples each of metal beryllium powder, nickel beryllium dental alloy, aluminum beryllium alloy (AlBeMet), and beryllium copper alloy chips. These samples were measured by mass onto a tared MCE filter, covered with another MCE filter which had been moistened with water, and then transferred to a digestion vessel containing a Smear Tab. (Static was an issue for weighing small amounts of powders onto the filters; an anti-static trigger gun was used regularly in an effort to minimize error from static charge.) MCE filters pre-spiked with beryllium oxide (SRM #1877) were also digested and analyzed. The data obtained are shown in Table 4.8.1.

Table 4.8.1
Digestion Efficiency of Beryllium from Beryllium Metal/Alloys/Compounds

| material type | level | | | | | | % recovery by sample | | | mean % rec. |
|---------------|-----------------|-------|-------|--------------|------|------|----------------------|-------|-------|-------------|
| | total mass (mg) | | | Be mass (µg) | | | 1 | 2 | 3 | |
| Be metal | 0.843 | 0.887 | 0.221 | 843 | 887 | 221 | 94.3 | 97.8 | 89.4 | 93.8 |
| Ni-Be alloy | 1.00 | 0.24 | 0.91 | 18.6 | 4.46 | 16.9 | 105.5 | 108.2 | 107.1 | 106.9 |
| Al-Be alloy | 0.281 | 0.325 | 0.216 | 171 | 198 | 132 | 92.6 | 96.3 | 95.6 | 94.8 |
| Be-Cu alloy | 6.61 | 3.96 | 4.64 | 120 | 72.1 | 84.5 | 92.5 | 93.0 | 97.6 | 94.4 |
| BeO | N/A | N/A | N/A | 10.0 | 10.0 | 10.0 | 100.2 | 101.6 | 100.1 | 100.6 |

4.8.2 Digestion efficiency of soluble beryllium

The digestion efficiency of soluble beryllium represents the recovery of the analytical method. The digestion efficiency of soluble beryllium was determined by spiking MCE filters with a liquid solution of beryllium. Four filters were spiked at the RQL, 0.1, 0.5, 1, and 2 times the target concentration. A liquid solution was prepared at a concentration corresponding to each level of the test samples; these solutions were diluted from a beryllium solution and were not digested. Each corresponding liquid solution, used for reference, was analyzed three times (before the samples, at the mid-point of samples, and after the samples) on the same day as the samples. The mean result of each corresponding solution was used to apply a correction to the corresponding sample results. An additional test included four filters under humid conditions, spiked at the target concentration. The mean digestion efficiency over the working range of the RQL to twice the target concentration is 102%; results from the 0.1 times the target concentration were not used in the digestion efficiency calculation due to the concentration being lower than the concentration of the RQL. There is no indication of significant bias from humidity. Results in Table 4.8.2 reflect the corrected recoveries of the samples.

Table 4.8.2
Digestion Efficiency of Soluble Beryllium

| level | mass (µg) | % recovery by sample | | | | mean |
|--------|-----------|----------------------|-------|-------|-------|-------|
| | | 1 | 2 | 3 | 4 | |
| 0.1x | 0.01 | 102.1 | 103.1 | 102.7 | 102.4 | 102.6 |
| RQL | 0.015 | 99.1 | 111.1 | 98.3 | 99.1 | 101.9 |
| 0.5x | 0.05 | 103.2 | 102.5 | 101.2 | 103.4 | 102.6 |
| 1x | 0.1 | 102.8 | 102.0 | 99.6 | 103.4 | 101.9 |
| 2x | 0.2 | 101.8 | 101.3 | 101.4 | 101.4 | 101.5 |
| wet 1x | 0.1 | 102.1 | 102.1 | 103.1 | 101.4 | 102.2 |

4.8.3 Stability of digested samples

The stability of digested samples was studied by digesting four MCE filters pre-spiked with beryllium oxide at 10 µg beryllium. The digested samples were each diluted to volume in a class-A glass volumetric flask and stoppered until analysis. The filters were all analyzed on four consecutive days, beginning with the day they were prepared. For the initial analysis, only the necessary aliquot was poured into an analytical vial for the first two solutions; all of the solution was poured into vials for the last two solutions. After each analysis, the remaining solutions for the first two samples were poured from the analytical vials back into the corresponding volumetric flasks and stoppered. The last two solutions were kept in the analytical vials, in a sample rack; all of the vials were covered with one piece of plastic film, pressed tightly around all of the vials. All samples were stored at ambient temperature. The samples were always analyzed with a freshly

prepared reference standard, prepared at the same concentration of 0.4 µg/mL. These reference standards were diluted from a beryllium solution and were not digested. Each corresponding liquid solution, used for reference, was analyzed three times on the same day as the samples. The mean result of each corresponding solution was used to apply a correction to the corresponding sample results. The storage data obtained are shown in Table 4.8.3. A difference from the initial analysis is noted as “diff.” Recovery differences from storage over three days, regardless of the two storage methods, were insignificant.

Table 4.8.3
Stability of Digested Samples for Beryllium Oxide

| Stored in Volumetric Flasks | | | | | | | Stored in Vials | | | | | | |
|-----------------------------|-----------|----------|------------|----------|------------|----------|-----------------|-----------|----------|------------|----------|------------|----------|
| initial (%) | 1 day (%) | diff (%) | 2 days (%) | diff (%) | 3 days (%) | diff (%) | initial (%) | 1 day (%) | diff (%) | 2 days (%) | diff (%) | 3 days (%) | diff (%) |
| 96.6 | 98.1 | 1.5 | 99.1 | 2.5 | 100.2 | 3.6 | 96.4 | 97.3 | 0.9 | 97.6 | 1.2 | 99.4 | 3.0 |
| 97.9 | 97.7 | -0.2 | 97.8 | -0.1 | 99.5 | 1.6 | 91.8 | 91.6 | -0.2 | 92.6 | 0.8 | 93.8 | 2.0 |
| | | | (mean) | | | | | | | (mean) | | | |
| 97.2 | 97.9 | 0.6 | 98.4 | 1.2 | 99.8 | 2.6 | 94.1 | 94.4 | 0.4 | 95.1 | 1.0 | 96.6 | 2.5 |

4.8.4 Support pads

Although soluble beryllium was recovered from directly spiked support pads, the support pads did not completely dissolve. Therefore, digestion and analysis of support pads are not recommended.

4.8.5 Smear Tab wipes

The digestion efficiency of soluble beryllium from liquid spiked Smear Tabs and from cassette wipes was determined at the STEL and PEL levels. Liquid was spiked onto the interior surface of a top cassette piece, allowed to dry at ambient temperature, and then wiped with a damp Smear Tab. A liquid solution was prepared at a concentration corresponding to each level of the test samples; these solutions were diluted from a beryllium solution and were not digested. Each corresponding liquid solution, used for reference, was analyzed 3 times on the same day as the samples. The mean result of each corresponding solution was used to apply a correction to the corresponding sample results. Results in Table 4.8.5.1 reflect the corrected recoveries of the samples. The digestion efficiency for Smear Tabs at the STEL is 103%. The digestion efficiency for Smear Tabs at the PEL is 102%.

Table 4.8.5.1
Beryllium Recovery from Smear Tabs

| level | mass spiked (µg) | sample recovery (%) | | | | mean (%) |
|-------|------------------|---------------------|-------|-------|-------|----------|
| | | 1 | 2 | 3 | 4 | |
| STEL | 0.06 | 103.2 | 102.4 | 103.8 | 103.9 | 103.3 |
| 1x | 0.1 | 103.3 | 102.0 | 103.4 | 100.7 | 102.4 |

Wipe efficiency was tested on six glass surface areas. Each area measured 10 cm by 10 cm square. A liquid solution was spiked at the PEL equivalent, in a spiral pattern of droplets, onto each surface and allowed to dry overnight at ambient temperature. Each surface area was wiped in an up-and-down pattern with a Smear Tab, moistened with water. The Smear Tab was folded in half, keeping the wiped side folded together, and then used to wipe the same area in a side-to-side pattern. Results are shown in Table 4.8.5.2.

Table 4.8.5.2
Beryllium Recovery from Glass

| level | mass spiked (μg) | sample recovery | | | | | | mean (%) |
|-------|----------------------------------|-----------------|-------|-------|------|-------|------|-------------|
| | | 1 | 2 | 3 | 4 | 5 | 6 | |
| 1x | 0.1 | 105.4 | 104.6 | 100.0 | 90.9 | 105.3 | 96.9 | 100.5 |

4.8.6 Recovery from wiping cassette interior

Recovery of soluble beryllium from a cassette was determined by spiking 4 cassettes each at the STEL and PEL. Liquid was spiked onto the interior surface of a top cassette piece, allowed to dry at ambient temperature, and then wiped with a damp Smear Tab. The mean recoveries at the STEL and PEL were 107% and 102% respectively. The data obtained are shown in Table 4.8.6.

Table 4.8.6
Beryllium Recovery from Cassettes

| level | mass spiked (μg) | sample recovery | | | | mean (%) |
|-------|----------------------------------|-----------------|-------|-------|-------|-------------|
| | | 1 | 2 | 3 | 4 | |
| STEL | 0.06 | 106.6 | 108.3 | 106.2 | 108.3 | 107.4 |
| 1x | 0.1 | 99.3 | 105.6 | 97.3 | 104.8 | 101.8 |

4.9 Analytical interferences

Spectral interferences were examined by evaluating two Interference Check Solution (ICSA and ICSB) mixtures as well as 10 solutions containing a single element of interest. The solutions were prepared by spiking single-element solutions to achieve the concentrations listed in Table 4.9.1.

Table 4.9.1
Spectral Interference Solution Concentrations

| element | ICSA ($\mu\text{g/mL}$) | ICSB ($\mu\text{g/mL}$) | single-element ($\mu\text{g/mL}$) |
|---------|---------------------------|---------------------------|-------------------------------------|
| Al | 50 | 50 | 500 |
| Ca | 25 | 25 | 500 |
| Ce | 1 | 1 | 10 |
| Cr | 1 | 1 | 100 |
| Fe | 50 | 50 | 200 |
| Mo | 1 | 1 | 50 |
| Nb | 1 | 1 | 10 |
| Ti | 25 | 25 | 200 |
| V | 0.5 | 0.5 | 50 |
| Be | - | 0.008 | - |

By evaluating the numerical results calculated by the instrument for beryllium and examining the spectra, aluminum, calcium, cerium, chromium, iron, molybdenum, niobium, titanium, and vanadium were identified as potentially having an inference with beryllium results at either 313.1 nm or at 234.9 nm. Calculated IEC values were used to correct for interferences with beryllium at 234.9 nm. Iron was found to have an extreme interference at 234.9 nm, which can change often with small shifts in the shape of the spectral peaks. Because the results from 313.1 nm seemed more reliable, and the corrections were more stable and consistent over time, results analyzed at 234.9 nm were only used for verification of positive identification of beryllium (by spectra and numerical values). Corrections for beryllium at 313.1 nm were all made by MSF. After applying IEC and MSF corrections, the ICSA is used to demonstrate that a solution containing reasonably high levels of interfering elements and no beryllium, results in a

beryllium value less than the reporting limit (0.001 µg/mL). The ICSB is then used to check the accuracy of beryllium, in the presence of interfering elements. Beryllium recovery in the ICSB (prepared at a concentration equivalent to an 8-hour sample) was 99.9%. Results obtained, corrected for interferences, are shown in Table 4.9.2.

Table 4.9.2
Beryllium Results for Spectral Interference Solutions

| element | ICSA (µg/mL) | ICSB (µg/mL) | single-element (µg/mL) |
|---------|------------------|--------------|------------------------|
| Al | - | - | 0.00006 |
| Ca | - | - | 0.000006 |
| Ce | - | - | 0.000006 |
| Cr | - | - | 0.000006 |
| Fe | - | - | 0.00002 |
| Mo | - | - | 0.000006 |
| Nb | - | - | -0.0005 |
| Ti | - | - | 0.000006 |
| V | - | - | 0.000006 |
| Be | 0.00007 (<0.001) | 0.00799 | - |