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METHOD 104—DETERMINATION OF BERYLLIUM EMISSIONS FROM STATIONARY SOURCES

NOTE: This method does not include all of the specifications (*e.g.*, equipment and supplies) and procedures (*e.g.*, sampling and analytical) essential to its performance. Some material is incorporated by reference from methods in appendix A to 40 CFR part 60. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods: Method 1, Method 2, Method 3, and Method 5 in appendix A, part 60.

1.0 Scope and Application

1.1 Analytes.

Analyte	CAS No.	Sensitivity
Beryllium (Be)	7440-41-7	Dependent upon recorder and spectrophotometer.

1.2 Applicability. This method is applicable for the determination of Be emissions in ducts or stacks at stationary sources. Unless otherwise specified, this method is not intended to apply to gas streams other than those emitted directly to the atmosphere without further processing.

1.3 Data Quality Objectives. Adherences to the requirements of this method will enhance the quality of the data obtained from air pollutant sampling methods.

2.0 Summary of Method

2.1 Particulate and gaseous Be emissions are withdrawn isokinetically from the source and are collected on a glass fiber filter and in water. The collected sample is digested in an acid solution and is analyzed by atomic absorption spectrophotometry.

3.0 Definitions [Reserved]

4.0 Interferences

4.1 Matrix Effects. Analysis for Be by flame atomic absorption spectrophotometry is sensitive to the chemical composition and to the physical properties (*e.g.*, viscosity, pH) of the sample. Aluminum and silicon, in particular, are known to interfere when present in appreciable quantities. The analytical procedure includes (optionally) the use of the Method of Standard Additions to check for these matrix effects, and sample analysis using the Method of Standard Additions if significant matrix effects are found to be present (see Reference 2 in Section 17.0).

5.0 Safety

5.1 Disclaimer. This method may involve hazardous materials, operations, and equipment. This test method may not address all of the safety problems associated with its use. It is the responsibility of the user of this test method to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to performing this test method.

5.2 Corrosive reagents. The following reagents are hazardous. Personal protective equipment and safe procedures are useful in preventing chemical splashes. If contact occurs, immediately flush with copious amounts of water at least 15 minutes. Remove clothing under shower and decontaminate. Treat residual chemical burn as thermal burn.

5.2.1 Hydrochloric Acid (HCl). Highly toxic. Vapors are highly irritating to eyes, skin, nose, and lungs, causing severe damage. May cause bronchitis, pneumonia, or edema of lungs. Exposure to concentrations of 0.13 to 0.2 percent can be lethal to humans in a few minutes. Provide ventilation to limit exposure. Reacts with metals, producing hydrogen gas.

5.2.2 Hydrogen Peroxide (H₂O₂). Irritating to eyes, skin, nose, and lungs.

5.2.3 Nitric Acid (HNO₃). Highly corrosive to eyes, skin, nose, and lungs. Vapors cause bronchitis, pneumonia, or edema of lungs. Reaction to inhalation may be delayed as long as 30 hours and still be fatal. Provide ventilation to limit exposure. Strong oxidizer. Hazardous reaction may occur with organic materials such as solvents.

5.2.4 Sodium Hydroxide (NaOH). Causes severe damage to eyes and skin. Inhalation causes irritation to nose, throat, and lungs. Reacts exothermically with limited amounts of water.

5.3 Beryllium is hazardous, and precautions should be taken to minimize exposure.

6.0 *Equipment and Supplies*

6.1 Sample Collection. Same as Method 5, Section 6.1, with the exception of the following:

6.1.1 Sampling Train. Same as Method 5, Section 6.1.1, with the exception of the following:

6.1.2 Probe Liner. Borosilicate or quartz glass tubing. A heating system capable of maintaining a gas temperature of 120 ±14 °C (248 ±25 °F) at the probe exit during sampling to prevent water condensation may be used.

NOTE: Do not use metal probe liners.

6.1.3 Filter Holder. Borosilicate glass, with a glass frit filter support and a silicone rubber gasket. Other materials of construction (*e.g.*, stainless steel, Teflon, Viton) may be used, subject to the approval of the Administrator. The holder design shall provide a positive seal against leakage from the outside or around the filter. The holder shall be attached immediately at the outlet of the probe. A heating system capable of maintaining the filter at a minimum temperature in the range of the stack temperature may be used to prevent condensation from occurring.

6.1.4 Impingers. Four Greenburg-Smith impingers connected in series with leak-free ground glass fittings or any similar leak-free noncontaminating fittings. For the first, third, and fourth impingers, use impingers that are modified by replacing the tip with a 13 mm-ID (0.5 in.) glass tube extending to 13 mm (0.5 in.) from the bottom of the flask may be used.

6.2 Sample Recovery. The following items are needed for sample recovery:

6.2.1 Probe Cleaning Rod. At least as long as probe.

6.2.2 Glass Sample Bottles. Leakless, with Teflon-lined caps, 1000 ml.

6.2.3 Petri Dishes. For filter samples, glass or polyethylene, unless otherwise specified by the Administrator.

6.2.4 Graduated Cylinder. 250 ml.

6.2.5 Funnel and Rubber Policeman. To aid in transfer of silica gel to container; not necessary if silica gel is weighed in the field.

6.2.6 Funnel. Glass, to aid in sample recovery.

6.2.7 Plastic Jar. Approximately 300 ml.

6.3 Analysis. The following items are needed for sample analysis:

6.3.1 Atomic Absorption Spectrophotometer. Perkin-Elmer 303, or equivalent, with nitrous oxide/acetylene burner.

6.3.2 Hot Plate.

6.3.3 Perchloric Acid Fume Hood.

7.0 *Reagents and Standards*

NOTE: Unless otherwise indicated, it is intended that all reagents conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available; otherwise, use the best available grade.

7.1 Sample Collection. Same as Method 5, Section 7.1, including deionized distilled water conforming to ASTM D 1193-77 or 91 (incorporated by reference—see §61.18), Type 3. The Millipore AA filter is recommended.

7.2 Sample Recovery. Same as Method 5 in appendix A, part 60, Section 7.2, with the addition of the following:

7.2.1 Wash Acid, 50 Percent (V/V) Hydrochloric Acid (HCl). Mix equal volumes of concentrated HCl and water, being careful to add the acid slowly to the water.

7.3 Sample Preparation and Analysis. The following reagents and standards and standards are needed for sample preparation and analysis:

7.3.1 Water. Same as in Section 7.1.

7.3.2. Perchloric Acid (HClO₄). Concentrated (70 percent V/V).

7.3.3 Nitric Acid (HNO₃). Concentrated.

7.3.4 Beryllium Powder. Minimum purity 98 percent.

7.3.5 Sulfuric Acid (H₂SO₄) Solution, 12 N. Dilute 33 ml of concentrated H₂SO₄ to 1 liter with water.

7.3.6 Hydrochloric Acid Solution, 25 Percent HCl (V/V).

7.3.7 Stock Beryllium Standard Solution, 10 µg Be/ml. Dissolve 10.0 mg of Be in 80 ml of 12 N H₂SO₄ in a 1000-ml volumetric flask. Dilute to volume with water. This solution is stable for at least one month. Equivalent strength Be stock solutions may be prepared from Be salts such as BeCl₂ and Be(NO₃)₂ (98 percent minimum purity).

7.3.8 Working Beryllium Standard Solution, 1 µg Be/ml. Dilute a 10 ml aliquot of the stock beryllium standard solution to 100 ml with 25 percent HCl solution to give a concentration of 1 mg/ml. Prepare this dilute stock solution fresh daily.

8.0 *Sample Collection, Preservation, Transport, and Storage*

The amount of Be that is collected is generally small, therefore, it is necessary to exercise particular care to prevent contamination or loss of sample.

8.1 Pretest Preparation. Same as Method 5, Section 8.1, except omit Section 8.1.3.

8.2 Preliminary Determinations. Same as Method 5, Section 8.2, with the exception of the following:

8.2.1 Select a nozzle size based on the range of velocity heads to assure that it is not necessary to change the nozzle size in order to maintain isokinetic sampling rates below 28 liters/min (1.0 cfm).

8.2.2 Obtain samples over a period or periods of time that accurately determine the maximum emissions that occur in a 24-hour period. In the case of cyclic operations, perform sufficient sample runs for the accurate determination of the emissions that occur over the duration of the cycle. A minimum sample time of 2 hours per run is recommended.

8.3 Preparation of Sampling Train. Same as Method 5, Section 8.3, with the exception of the following:

8.3.1 Prior to assembly, clean all glassware (probe, impingers, and connectors) by first soaking in wash acid for 2 hours, followed by rinsing with water.

8.3.2 Save a portion of the water for a blank analysis.

8.3.3 Procedures relating to the use of metal probe liners are not applicable.

8.3.4 Probe and filter heating systems are needed only if water condensation is a problem. If this is the case, adjust the heaters to provide a temperature at or above the stack temperature. However, membrane filters such as the Millipore AA are limited to about 107 °C (225 °F). If the stack gas is in excess of about 93 °C (200 °F), consideration should be given to an alternate procedure such as moving the filter holder downstream of the first impinger to insure that the filter does not exceed its temperature limit. After the sampling train has been assembled, turn on and set the probe heating system, if applicable, at the desired operating temperature. Allow time for the temperatures to stabilize. Place crushed ice around the impingers.

NOTE: An empty impinger may be inserted between the third impinger and the silica gel to remove excess moisture from the sample stream.

8.4 Leak Check Procedures, Sampling Train Operation, and Calculation of Percent Isokinetic. Same as Method 5, Sections 8.4, 8.5, and 8.6, respectively.

8.5 Sample Recovery. Same as Method 5, Section 8.7, except treat the sample as follows: Transfer the probe and impinger assembly to a cleanup area that is clean, protected from the wind, and free of Be contamination. Inspect the train before and during this assembly, and note any abnormal conditions. Treat the sample as follows: Disconnect the probe from the impinger train.

8.5.1 Container No. 1. Same as Method 5, Section 8.7.6.1.

8.5.2 Container No. 2. Place the contents (measured to 1 ml) of the first three impingers into a glass sample bottle. Use the procedures outlined in Section 8.7.6.2 of Method 5, where applicable, to rinse the probe nozzle, probe fitting, probe liner, filter holder, and all glassware between the filter holder and the back half of the third impinger with water. Repeat this procedure with acetone. Place both water and acetone rinse solutions in the sample bottle with the contents of the impingers.

8.5.3 Container No. 3. Same as Method 5, Section 8.7.6.3.

8.6 Blanks.

8.6.1 Water Blank. Save a portion of the water as a blank. Take 200 ml directly from the wash bottle being used and place it in a plastic sample container labeled "H₂O blank."

8.6.2 Filter. Save two filters from each lot of filters used in sampling. Place these filters in a container labeled "filter blank."

8.7 Post-test Glassware Rinsing. If an additional test is desired, the glassware can be carefully double rinsed with water and reassembled. However, if the glassware is out of use more than 2 days, repeat the initial acid wash procedure.

9.0 QUALITY CONTROL

Section	Quality control measure	Effect
8.4, 10.1	Sampling equipment leak checks and calibration	Ensure accuracy and precision of sampling measurements.
10.2	Spectrophotometer calibration	Ensure linearity of spectrophotometer response to standards.
11.5	Check for matrix effects	Eliminate matrix effects.

10.0 Calibration and Standardization

NOTE: Maintain a laboratory log of all calibrations.

10.1 Sampling Equipment. Same as Method 5, Section 10.0.

10.2 Preparation of Standard Solutions. Pipet 1, 3, 5, 8, and 10 ml of the 1.0 µg Be/ml working standard solution into separate 100 ml volumetric flasks, and dilute to the mark with water. The total amounts of Be in these standards are 1, 3, 5, 8, and 10 µg, respectively.

10.3 Spectrophotometer and Recorder. The Be response may be measured by either peak height or peak area. Analyze an aliquot of the 10-µg standard at 234.8 nm using a nitrous oxide/acetylene flame. Determine the maximum absorbance of the standard, and set this value to read 90 percent of the recorder full scale.

10.4 Calibration Curve.

10.4.1 After setting the recorder scale, analyze an appropriately sized aliquot of each standard and the BLANK (see Section 11) until two consecutive peaks agree within 3 percent of their average value.

10.4.3 Subtract the average peak height (or peak area) of the blank—which must be less than 2 percent of recorder full scale—from the averaged peak heights of the standards. If the blank absorbance is greater than 2 percent of full-scale, the probable cause is Be contamination of a reagent or carry-over of Be from a previous sample. Prepare the calibration curve by plotting the corrected peak height of each standard solution versus the corresponding total Be weight in the standard (in µg).

10.5 Spectrophotometer Calibration Quality Control. Calculate the least squares slope of the calibration curve. The line must pass through the origin or through a point no further from the origin than ±2 percent of the recorder full scale. Multiply the corrected peak height by the reciprocal of the least squares slope to determine the distance each calibration point lies from the

theoretical calibration line. The difference between the calculated concentration values and the actual concentrations (i.e., 1, 3, 5, 8, and 10 $\mu\text{g Be}$) must be less than 7 percent for all standards.

11.0 Analytical Procedure

11.1 Sample Loss Check. Prior to analysis, check the liquid level in Container No. 2. Note on the analytical data sheet whether leakage occurred during transport. If a noticeable amount of leakage occurred, either void the sample or take steps, subject to the approval of the Administrator, to adjust the final results.

11.2 Glassware Cleaning. Before use, clean all glassware according to the procedure of Section 8.3.1.

11.3 Sample Preparation. The digestion of Be samples is accomplished in part in concentrated HClO_4 .

NOTE: The sample must be heated to light brown fumes after the initial HNO_3 addition; otherwise, dangerous perchlorates may result from the subsequent HClO_4 digestion. HClO_4 should be used only under a hood.

11.3.1 Container No. 1. Transfer the filter and any loose particulate matter from Container No. 1 to a 150-ml beaker. Add 35 ml concentrated HNO_3 . To oxidize all organic matter, heat on a hotplate until light brown fumes are evident. Cool to room temperature, and add 5 ml 12 N H_2SO_4 and 5 ml concentrated HClO_4 .

11.3.2 Container No. 2. Place a portion of the water and acetone sample into a 150 ml beaker, and put on a hotplate. Add portions of the remainder as evaporation proceeds and evaporate to dryness. Cool the residue, and add 35 ml concentrated HNO_3 . To oxidize all organic matter, heat on a hotplate until light brown fumes are evident. Cool to room temperature, and add 5 ml 12 N H_2SO_4 and 5 ml concentrated HClO_4 . Then proceed with step 11.3.4.

11.3.3 Final Sample Preparation. Add the sample from Section 11.3.2 to the 150-ml beaker from Section 11.3.1. Replace on a hotplate, and evaporate to dryness in a HClO_4 hood. Cool the residue to room temperature, add 10.0 ml of 25 percent V/V HCl , and mix to dissolve the residue.

11.3.4 Filter and Water Blanks. Cut each filter into strips, and treat each filter individually as directed in Section 11.3.1. Treat the 200-ml water blank as directed in Section 11.3.2. Combine and treat these blanks as directed in Section 11.3.3.

11.4 Spectrophotometer Preparation. Turn on the power; set the wavelength, slit width, and lamp current; and adjust the background corrector as instructed by the manufacturer's manual for the particular atomic absorption spectrophotometer. Adjust the burner and flame characteristics as necessary.

11.5 Analysis. Calibrate the analytical equipment and develop a calibration curve as outlined in Sections 10.4 and 10.5.

11.5.1 Beryllium Samples. Repeat the procedure used to establish the calibration curve with an appropriately sized aliquot of each sample (from Section 11.3.3) until two consecutive peak heights agree within 3 percent of their average value. The peak height of each sample must be greater than 10 percent of the recorder full scale. If the peak height of the sample is off scale on the recorder, further dilute the original source sample to bring the Be concentration into the calibration range of the spectrophotometer.

11.5.2 Run a blank and standard at least after every five samples to check the spectrophotometer calibration. The peak height of the blank must pass through a point no further from the origin than ± 2 percent of the recorder full scale. The difference between the measured concentration of the standard (the product of the corrected peak height and the reciprocal of the least squares slope) and the actual concentration of the standard must be less than 7 percent, or recalibration of the analyzer is required.

11.5.3 Check for Matrix Effects (optional). Use the Method of Standard Additions (see Reference 2 in Section 17.0) to check at least one sample from each source for matrix effects on the Be results. If the results of the Method of Standard Additions procedure used on the single source sample do not agree to within 5 percent of the value obtained by the routine atomic absorption analysis, then reanalyze all samples from the source using the Method of Standard Additions procedure.

11.6 Container No. 2 (Silica Gel). Weigh the spent silica gel (or silica gel plus impinger) to the nearest 0.5 g using a balance. (This step may be conducted in the field.)

12.0 Data Analysis and Calculations

Carry out calculations, retaining at least one extra decimal significant figure beyond that of the acquired data. Round off figures only after the final calculation. Other forms of the equations may be used as long as they give equivalent results.

12.1 Nomenclature.

$K_1 = 0.3858 \text{ } ^\circ\text{K/mm Hg}$ for metric units.

$= 17.64 \text{ } ^\circ\text{R/in. Hg}$ for English units.

$K_3 = 10^{-6} \text{ g}/\mu\text{g}$ for metric units.

$= 2.2046 \times 10^{-9} \text{ lb}/\mu\text{g}$ for English units.

m_{Be} = Total weight of beryllium in the source sample.

P_s = Absolute stack gas pressure, mm Hg (in. Hg).

t = Daily operating time, sec/day.

T_s = Absolute average stack gas temperature, °K (°R).

$V_{m(std)}$ = Dry gas sample volume at standard conditions, scm (scf).

$V_{w(std)}$ = Volume of water vapor at standard conditions, scm (scf).

12.2 Average Dry Gas Meter Temperature and Average Orifice Pressure Drop, Dry Gas Volume, Volume of Water Vapor Condensed, Moisture Content, Isokinetic Variation, and Stack Gas Velocity and Volumetric Flow Rate. Same as Method 5, Sections 12.2 through 12.5, 12.11, and 12.12, respectively.

12.3 Total Beryllium. For each source sample, correct the average maximum absorbance of the two consecutive samples whose peak heights agree within 3 percent of their average for the contribution of the solution blank (see Sections 11.3.4 and 11.5.2). Correcting for any dilutions if necessary, use the calibration curve and these corrected averages to determine the total weight of Be in each source sample.

12.4 Beryllium Emission Rate. Calculate the daily Hg emission rate, R, using Equation 104-1. For continuous operations, the operating time is equal to 86,400 seconds per day. For cyclic operations, use only the time per day each stack is in operation. The total Hg emission rate from a source will be the summation of results from all stacks.

$$R = \frac{K_1 K_2 t m_{Be} P_s V_s A_s}{T_s (V_{m(std)} + V_{w(std)})} \quad \text{Eq. 104-1}$$

12.5 Determination of Compliance. Each performance test consists of three sample runs. For the purpose of determining compliance with an applicable national emission standard, use the average of the results of all sample runs.

13.0 *Method Performance. [Reserved]*

14.0 *Pollution Prevention. [Reserved]*

15.0 *Waste Management. [Reserved]*

16.0 *Alternative Procedures*

16.1 Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES) Analysis. ICP-AES may be used as an alternative to atomic absorption analysis provided the following conditions are met:

16.1.1 Sample collection, sample preparation, and analytical preparation procedures are as defined in the method except as necessary for the ICP-AES application.

16.1.2 Quality Assurance/Quality Control procedures, including audit material analysis, are conducted as prescribed in the method. The QA acceptance conditions must be met.

16.1.3 The limit of quantitation for the ICP-AES must be demonstrated and the sample concentrations reported should be no less than two times the limit of quantitation. The limit of quantitation is defined as ten times the standard deviation of the blank value. The standard deviation of the blank value is determined from the analysis of seven blanks. It has been reported that for mercury and those elements that form hydrides, a continuous-flow generator coupled to an ICP-AES offers detection limits comparable to cold vapor atomic absorption.

16.2 Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) Analysis. ICP-MS may be used as an alternative to atomic absorption analysis.

16.3 Cold Vapor Atomic Fluorescence Spectrometry (CVAFS) Analysis. CVAFS may be used as an alternative to atomic absorption analysis.

17.0 References

Same as References 1, 2, and 4-11 of Section 16.0 of Method 101 with the addition of the following:

1. Amos, M.D., and J.B. Willis. Use of High-Temperature Pre-Mixed Flames in Atomic Absorption Spectroscopy. *Spectrochim. Acta.* 22:1325. 1966.
2. Fleet, B., K.V. Liberty, and T. S. West. A Study of Some Matrix Effects in the Determination of Beryllium by Atomic Absorption Spectroscopy in the Nitrous Oxide-Acetylene Flame. *Talanta* 17:203. 1970.

18.0 Tables, Diagrams, Flowcharts, And Validation Data [Reserved]