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Final Report

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U. S. DEPARTMENT OF COMMERCE, Frederick B. Dent, Secretary
NATIONAL BUREAU OF STANDARDS, Richard W. Roberts, Director

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ABSTRACT

Techniques are described for the preparation of reference materials useful for evaluating the accuracy and precision of analytical methods for measurement of beryllium emissions from stationary sources. These reference materials consist of membrane filters upon which are deposited microgram quantities of high-fired beryllium oxide and ampoules containing soluble beryllium and suspended beryllium oxide. Methods for measurement of the beryllium content of such materials by atomic absorption spectrometry and by spectrofluorimetry are described.

1. INTRODUCTION

This report describes work done to prepare reference materials for evaluating analytical methods in the measurement of beryllium emissions from stationary sources. In National Emission Standards for Hazardous Air Pollutants (1), beryllium is identified as a hazardous material and a reference method, Method 104, is designated for its measurement. A specific objective of the work described in the present report is to provide reference materials for use in the evaluation of Method 104 by collaborative interlaboratory testing.

In Method 104, beryllium emissions are isokinetically sampled from the source and the collected sample is digested in an acid solution and analyzed by atomic absorption spectrometry. A sampling train containing both a filter and liquid impingers is used. The critical steps that affect the accuracy and precision of the analysis are considered to be the calibration of the atomic absorption instrument, the dissolution of the particulate material, and the measurement of the resulting solutions. It was decided that three types of reference samples were needed, namely a filter sample, a slurry representing washings from a probe, and a soluble sample of beryllium. The filter sample and slurry were to be prepared from high-fired beryllium oxide to evaluate the dissolution step.

in the measurement. Three filter samples containing approximately 3, 7, and 15 μg , respectively, of the oxide were to be prepared while similar sets of slurries and soluble samples also were required.

2. PREPARATION OF REFERENCE MATERIALS

2.1 Materials Used

Samples of high-fired beryllium oxide were kindly furnished by the National Beryllia Corporation. The material consisted of finely ground powder with a particle size of less than 5 μm . The analysis of the material showed a BeO assay of >99 percent.

Solutions of beryllium were prepared as described later from high-purity beryllium metal (>99.9 percent) regularly used in this laboratory as an analytical standard.

Water and acids, prepared in the Analytical Chemistry Division and regularly used for trace elemental analysis, were used for the preparation of solutions and in the confirmatory analysis of the reference materials.

2.2 Preliminary Experiments

In an initial study, 40 mg of high-fired beryllium oxide were dispersed in 200 ml of various supporting media and evaluated for uniformity of particle size and reproducibility of sampling. The material formed large particles or clottlets that quickly settled to the bottom of the containing vessel in the various supporting media. To overcome this difficulty, the samples were treated with ultrasonic radiation which dispersed the large particles or conglomerates. Addition of 0.5 percent gum tragacanth was found to be beneficial in that the fine material would remain suspended for many hours. For the final preparation of the filter reference samples, an aliquot of the suspended BeO could be transferred to a membrane filter and dried.

For the aqueous solutions, a 0.01 percent solution of high-purity beryllium metal in 0.5 N HCl was prepared. Dilutions of this master stock solution were made as needed to give the final desired concentration. The final reference samples could be prepared by transferring an aliquot with an automatic pipet to a 2-ml ampoule.

2.3 Soluble Beryllium Reference Samples

A 0.01 percent beryllium solution was prepared by dissolving 100 mg of high-purity metal in HCl. To prevent any

loss of material during dissolution, the sample was transferred to a Teflon beaker and covered with water. Then, 5 ml of acid was added dropwise and heated gently until solution occurred. The solution was transferred to a liter flask and diluted to the calibrated volume with 0.5 N HCl. Aliquots of the master stock solution were taken to give final concentrations of 1.5, 3.8 and 8.0 $\mu\text{g}/\text{ml}$ in 0.25 N HCl.

The 2-ml ampoules were washed, rinsed in distilled water and dried in an oven. An automatic delivery pipet was adjusted to deliver approximately 2.0 ml of solution to an ampoule. A series of ampoules were filled to contain nominally 3.0, 7.6 and 16 μg of beryllium, and flame sealed.

2.4 Particulate Beryllium Samples

Two types of particulate samples were prepared. One consisted of the material deposited on a membrane filter. The second consisted of a suspension of the oxide in dilute acid.

Samples of 8.1, 20.8, and 40.4 mg of high-fired beryllium oxide were transferred to 250 ml bottles. The samples were diluted to 50 ml with water and then treated with ultrasonic radiation for 10 minutes.

A one percent solution of gum tragacanth was prepared by dissolving one gram of material in warm water. To remove any insoluble residue, the solution of gum tragacanth was filtered under reduced pressure through quartz wool. An equal volume (50 ml) of the filtered gum tragacanth was added to each slurry of beryllium oxide and mixed thoroughly with a Teflon coated stirring bar and a magnetic stirrer.

For the filter samples, a 100 μl aliquot was transferred with an automatic pipet to a membrane filter, type MF-AA (mixed ester of cellulose) 55 mm diameter, mean pore size of 0.8 μm , white, plain and air dried. The dried samples were then transferred to plastic petri dishes to serve as containers for each individual filter.

2.5 Suspended Beryllium Oxide Samples

Suspended beryllium oxide samples were prepared by transferring 100 μl of suspended particles (2.4.1) to previously cleaned 2-ml ampoules. Then two ml of distilled water was added with the automated pipet, and the ampoules were flame sealed.

3. CONFIRMATORY ANALYSIS

The reference materials were analyzed by two techniques, atomic absorption spectrometry and spectrofluorimetry.

3.1 Dissolution of High-Fired Beryllium Oxide

The procedure used to dissolve the suspended solids and filter samples was a modification of that described in the Federal Register (1). An individual filter was removed with tweezers from the plastic petri dish and transferred to a clean 30 ml beaker. Then 2 ml of HNO_3 , 1 ml of HClO_4 and 1 ml of H_2SO_4 were added followed by digestion on a hot plate at approximately 80°C for 30 minutes. The temperature of the hot plate was then increased and the samples were evaporated to 0.5 ml. After allowing the samples to cool, the sides of the beaker were rinsed with water and the sample was transferred to a 10-ml volumetric flask and diluted to the calibrated volume with water.

Before transferring, each ampoule was examined. If liquid was present in the top or neck of the ampoule, the ampoule was tapped gently until the top was free of solution. The top was carefully snapped from the body of the ampoule. The slurry was transferred from the ampoule to a 30-ml beaker with a disposable Pasteur capillary pipet. To ensure a quantitative transfer of sample, the top and body of the ampoule were rinsed with five-0.5 ml portions of 6 N HCl . Then 2 ml of HNO_3 and 1 ml of H_2SO_4 were added and the samples were digested as described above.

3.2 Atomic Absorbtion Spectrometric Analysis

The procedure used for analysis of the beryllium content of the reference solutions is described in the following sections.

3.2.1. Preparation of Standard Solutions

Beryllium, 10.00 mg Be/ml - Dissolve 1.000g of high-purity beryllium metal in 25 ml of 2 N HCl . Transfer the solution to a 100-ml volumetric flask and dilute to the calibrated volume with water. Prepare appropriate dilutions from this stock solution as needed in 5 percent H_2SO_4 .

3.2.2 Preparation of Calibration Curve and Measurement of Beryllium Concentrations

Prepare a series of standard beryllium solutions in 5 percent H_2SO_4 . (NOTE: The concentration of standards will depend upon the level of beryllium in the unknown. For the 3, 8 and 16 μg levels of beryllium, standards were prepared containing 0.2, 0.3,

and 0.4; 0.6, 0.8 and 1.0; 1.0, 1.5 and 2.0 $\mu\text{g Be/ml}$, respectively. Turn on the electronics of the atomic absorption instrument and allow the beryllium hollow-cathode lamp to warm-up for 15 minutes. Set the wavelength control to 2348 \AA and adjust the output of the amplifier so that the readout is 100 percent transmission or 0.000 absorbance. Install a 5-cm single-slot head on the burner. Light the burner using air-acetylene gas and then convert to a nitrous oxide-acetylene flame using the recommended procedure by the burner manufacturer. Adjust the acetylene flow rate until the pink plume is 3.8 mm (1 1/2 in.) in height. Nebulize water into the flame for 15 minutes to permit the instrument and burner to stabilize. Nebulize the highest of the three beryllium standards into the flame. Adjust the absorbance to read 0.500 or greater using scale expansion. Then nebulize the lower standard solutions into the flame and record the absorbance. Nebulize water between each standard solution. Repeat the nebulization of standards and water until the absorbance reading for a standard solution does not deviate by more than ± 0.5 percent. Nebulize the unknown solutions and record the absorbance. Repeat the nebulization of a standard solution between each unknown and record the absorbance.

To check for molecular absorption or scattered radiation, remove the beryllium hollow-cathode lamp and insert a rhenium hollow-cathode lamp. Set the wavelength control to 2365 \AA and adjust the output of the amplifier to read 100 percent transmission or 0.000 absorbance. (NOTE: Do not adjust burner height, oxidant-fuel ratio, slit width or scale expansion). Nebulize the unknown solution as well as a standard solution and record the absorbance. Subtract the absorbance obtained at 2365 \AA from the values obtained at 2348 \AA . (NOTE: A continuum source or a double-beam instrument with background correction capabilities may be substituted.)

Plot on rectilinear graph paper the net absorbance of the beryllium standard solutions as the ordinate versus the concentration of the standards, $\mu\text{g/ml}$, as the abscissa and determine the beryllium concentration of the unknown solution. If a computer is available, determine the concentration of the unknown samples using a least square fit on the computer.

3.2.3 Results and Discussion

The analytical results obtained by atomic absorption spectrometry are summarized in column 3 of Table 1. Atomic absorption spectrometry is a simple and relatively sensitive analytical technique for the determination of beryllium.

The sensitivity of the method for aqueous solutions is 0.03 $\mu\text{g/ml}$ /1 percent absorption. A detection limit of 0.002 $\mu\text{g/ml}$ is obtainable under ideal instrumental conditions. Extensive studies of chemical interferences in atomic absorption have been reported (2-6). At concentration ratios greater than 1000:1 Al, Mg and Si are reported to suppress the absorption of beryllium. However, these interferences can be corrected by the method of standard addition. In the presence of mineral acids the absorbance of beryllium may be enhanced. To eliminate this possibility, standard solutions of beryllium were prepared in the same acid medium as the unknowns (5 percent H_2SO_4). Because of the high ionization potential of beryllium (9.32 eV), no ionization interference would be expected in a nitrous oxide-acetylene flame, nor was any found in the studies conducted.

3.3 Fluorimetric Analysis

The basic fluorimetric methodology used was a combination of procedures reported by Kirkbright, et al (7) and Burke and Christopher (8).

3.3.1 Experimental Details:

A. Instrumentation: A spectrofluorimeter with excitation and emission monochromators was used: $\lambda_{\text{ex}} = 373 \text{ nm}$, $\lambda_{\text{em}} = 460 \text{ nm}$.

B. Reagents: Reagent-grade materials were used unless otherwise specified.

1. Beryllium Standards: Dissolve 0.1000 g Be metal in 2 ml dilute HCl (1:4, HCl:H₂O, v:v). Care should be taken with the dissolution since foaming occurs. Heat the solution (~50°C) until dissolution occurs, add 5 ml conc. HClO₄, and continue heating the solution at elevated temperatures until fumes of HClO₄ are observed. Quantitatively rinse the solution into a one liter volumetric flask, add 5 ml conc. HClO₄ and dilute to the calibrated volume, giving a Be stock solution of 100 $\mu\text{g/ml}$ in HClO₄ with a pH \approx 1. Dilutions are made as necessary to give a working solution of 1 $\mu\text{g/ml}$ Be in ~1 percent HClO₄. A fresh working solution is prepared daily.

2. Stock Ligand: (Sodium 2-hydroxy-3-naphthoate, $2 \times 10^{-3} \text{ M}$). Dissolve 0.376 g of the free acid (2-hydroxy-3-naphthoic acid) in a one liter volumetric flask by adding a molar equivalent of NaOH and 950 ml H₂O. Stir until dissolved, adjust the pH to 7.5 with dilute NaOH (or dilute HClO₄) and dilute to the calibrated volume. Dilute 50 ml of this stock solution to 500 ml using dilute NaOH (pH = 7.5) to give a working solution of $2 \times 10^{-4} \text{ M}$ in sodium 2-hydroxy-3-naphthoate. In the actual beryllium analysis, a minimum of 50-fold mole excess of ligand to Be is required (7).

3. Buffer, pH 7.5: Dilute 50 ml conc. NH_4OH to 800 ml in a large beaker. Add acetic acid (~42 ml) until a pH of 7.5 is obtained (use pH meter). Transfer this solution quantitatively to a one liter volumetric flask and dilute to the calibrated volume with water.

4. Masking Agent: [Ca^{2+} /CDTA (1,2-diaminocyclohexanetetraacetic acid)].

a. Add 3.7 g $\text{Ca}(\text{OH})_2$ to 450 ml H_2O and 2 ml HClO_4 and stir until dissolved. Adjust the pH to 5.0 with dilute HClO_4 (pH meter) and dilute to 500 ml yielding a solution that is 10^{-1}M in Ca^{2+} .

b. Add dilute NaOH to 6.925 g CDTA and 150 ml H_2O in a 200 ml volumetric flask until CDTA dissolves and a pH of 7.5 is obtained. Dilute to the calibrated volume giving a solution that is 10^{-1}M in CDTA.

c. [Ca^{2+} /CDTA]: Add 125 ml Ca^{2+} solution to 30 ml CDTA solution in a 500 ml volumetric flask and dilute to the calibrated volume with water.

5. pH Indicator, pH Range 7-8: Prepare a 0.01 - 0.1 percent phenol red solution in ethanol. Place in a dropping bottle.

3.3.2 Procedure: Take appropriate sample volumes such that the amount of Be in this volume is between 0.1 and 0.2 μg . Prepare calibration standards at the 0.10, 0.15 and 0.20 g Be levels in the same manner as the sample. (Add an equivalent amount of acid that will make the standards and the sample equivalent in solvent acidity.) Dilute to ~70 ml with water. In the analytical procedure, run the standards, blank, samples and standards in that order.

Add 5 ml Ca^{2+} /CDTA solution and 2 drops (~0.1 ml) phenol red indicator solution to the ~70 ml of samples or standards from the pre-analysis preparation and shake for 5 s. Adjust the pH to 7.5 with 6 N NH_4OH (solution turns pink). Minimize excess NH_4OH so that Be hydrolysis does not occur. Immediately add 5 ml buffer and 5 ml ligand. Shake for 20 s, allow to stand 5 min (timed using stopwatch) and read fluorescence intensity using excitation wavelength of 373 nm and emission wavelength of 460 nm. Determine unknown Be concentration by plotting the net fluorescence intensity versus concentration for the Be standards and interpolating the values for the unknown Be samples. The analytical values obtained by spectrofluorimetric analysis are summarized in column 4 of Table 1.

4. SUMMARY

Three types of reference materials have been prepared in this investigation, each type providing three levels of beryllium content. The samples are believed to simulate typical samples obtained during measurement of beryllium from a stationary source.

The samples are identified as follows:

<u>Identification No.</u>	<u>Type</u>
0 - 050	Filter, blank
100 - 150	Filter, BeO
200 - 250	Filter, BeO
300 - 350	Filter, BeO
400 - 450	Ampoule, suspended BeO
500 - 550	Ampoule, suspended BeO
600 - 650	Ampoule, suspended BeO
700 - 750	Ampoule, soluble Be in 0.25 M HCl
800 - 850	Ampoule, soluble Be in 0.25 \bar{M} HCl
900 - 950	Ampoule, soluble Be in 0.25 \bar{M} HCl

Each filter should be treated as an individual sample and should be used in its entirety. Solution may be achieved by dissolving in HNO_3 , HClO_4 , and H_2SO_4 as described in the Federal Register (1) (See also Section 3.1 of this report).

Ampoule samples should also be used in their entirety and treated in the following manner. Each ampoule is prescored. Check to see if the top or neck is free of solution. If liquid is present in this portion, shake or gently tap the ampoule until the top is free of solution. Then, gently snap the top from the body. Transfer the sample (slurry or solution) to a beaker or volumetric flask, using a disposable Pasteur Capillary pipet. Rinse the ampoule with mineral acid and proceed with the analysis.

The analytical results obtained by the two measurement techniques are summarized in Table 1. Each analyst took care to optimize his calibrations and measurements. The standard deviations tabulated represent both the analytical error and any inhomogeneity of the samples.

The results obtained by the two techniques are in agreement within the 95 percent confidence interval for each. The somewhat larger standard deviations found for the fluorimetric measurements are probably due to the extra chemical steps involved in this procedure. The experimental problems can be minimized and research is in progress to improve this method.

After consideration of the measurement problems concerned with each technique, the results obtained by atomic absorption spectrometry are recommended as the assay levels for the reference samples. The fluorimetric measurements are considered to be confirmation of these values and provide an independent check for any systematic bias.

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Table 1. Summary of Analytical Results

Sample Type	Series	Be, $\mu\text{g}/\text{sample}$		
		Atomic Absorption ¹	Fluorescence ²	Recommended Values ³
Filters	100-150	2.98 \pm .06	3.27 \pm .12	2.98 \pm .05
	200-250	7.77 \pm .11	8.39 \pm .28	7.77 \pm .08
	300-350	15.2 \pm .17	14.8 \pm .38	15.2 \pm .13
Suspended	400-450	3.06 \pm .06	2.96 \pm .04	3.06 \pm .05
	500-550	7.38 \pm .22	7.41 \pm .18	7.38 \pm .16
	600-650	15.0 \pm .29	14.5 \pm .37	15.0 \pm .22
Soluble Be	700-750	3.24 \pm .03	3.06 \pm .12	3.24 \pm .02
	800-850	7.87 \pm .11	7.59 \pm .19	7.87 \pm .08
	900-950	15.8 \pm .14	16.1 \pm .4	15.8 \pm .11

¹Based on 10 determinations.

²Based on 6 determinations.

³Uncertainty represents 95 percent confidence interval, based on 9 degrees of freedom.

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<p>16. ABSTRACT (A 200-word or less factual summary of most significant information. If document includes a significant bibliography or literature survey, mention it here.)</p> <p>Techniques are described for the preparation of reference materials useful for evaluating the accuracy and precision of analytical methods for measurement of beryllium emissions from stationary sources. These reference materials consist of membrane filters upon which are deposited microgram quantities of high-fired beryllium oxide and ampoules containing soluble beryllium and suspended beryllium oxide. Methods for measurement of the beryllium content of such materials by atomic absorption spectrometry and by spectrofluorimetry are described.</p>			
<p>17. KEY WORDS (six to twelve entries; alphabetical order; capitalize only the first letter of the first key word unless a proper name; separated by semicolons)</p> <p>Air pollution; atomic absorption spectrometry; beryllium; chemical analysis; fluorimetric analysis.</p>			
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