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DETERMINATION OF BERYLLIUM IN
URINE, HAIR, FINGERNAIL, AND FECAL SAMPLES
BY FLAMELESS ATOMIC ABSORPTION SPECTROMETRY

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Environmental Sciences and Waste Control
ENVIRONMENTAL CONTROL

SUBJECT DESCRIPTORS

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Flameless
Beryllium

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Abstract. Methods for determining trace amounts of beryllium in urine, hair, fingernail, and fecal samples are described. These methods involve use of a Perkin-Elmer Model 503 spectrophotometer equipped with an HGA-2100 graphite furnace. Lanthanum was used as a masking and enhancing agent, and recoveries were determined by direct comparison with aqueous standards. The hair and fingernail samples were degraded readily in a nitric acid-perchloric acid mixture, and the feces were digested rapidly using a ferrous ion, hydrogen peroxide method. The urine samples were run by two methods: (1) direct and (2) coprecipitation. Nanogram-per-gram levels of beryllium were recovered from all tissues and fluids. All recoveries varied from 90 to 110% with relative standard deviations of less than 13%.

INTRODUCTION

Attempts to analyze for trace amounts of beryllium in biological samples by flameless atomic absorption spectrometry (AAS) led to erratic recoveries; consequently, the effects of various cations and anions on the absorption signal were investigated.¹ It was learned that Group II cations, aluminum, silicate, and other elements interfere with the signal. If the samples contain small amounts of any of these elements, then good recoveries are possible,² but urine and fecal samples contain some of the interfering elements in large amounts.

Lanthanum in 5% (V/V) nitric acid is an effective masking and enhancing agent^{1, 3} and was used in analyzing biological samples. This paper describes the procedures involved and gives results for the rapid determination of beryllium in biological tissues and fluids by flameless AAS.

EXPERIMENTAL

Apparatus

All samples were analyzed on a Perkin-Elmer Model 503 atomic absorption spectrophotometer equipped with an HGA-2100 graphite furnace and a deuterium background corrector. The absorbance signals were recorded on a 10 mV, 0.4 sec response time, Servo/Riter II recorder.* Argon was used as the purge gas. Injections of 20 and 50 μ l were made with Eppendorf pipettes.

Controls of the graphite furnace were set to dry for 50 sec at 100 °C, to char for 60 sec at 1000 °C, and to atomize for 10 sec at 2600 °C. The internal argon flow was constantly blocked. The external argon flow rate was 50 cm³/min, lamp current was 30 mA, slit width was 0.7 nm, and the wavelength was 235 nm.

Reagents

Reagent-grade chemicals were used. Concentrated acids and the singly distilled water were free of picogram quantities of beryllium. All glassware was washed with dilute nitric acid, and the dilute beryllium standards were prepared from a 1000-ppm Ventron, Alfa Inorganics Standard. All dilute beryllium stock solutions (2000, 1000, 500, and 100 ng/ml) were 1% (V/V) in nitric acid and were stable for weeks. A 10,000 μ g/ml lanthanum solution was prepared from lanthanum oxide (La₂O₃) and was 5% (V/V) in nitric acid.

*Product of Texas Instruments Inc., Dallas, Texas.

Digestion Procedures

Method A—This was a direct urine method. Urine was made 5% (V/V) in nitric acid and 100 µg/ml in lanthanum. The urine was then spiked with an appropriate amount of beryllium and was pipetted directly into the graphite tube.

Method B—A one hundred-millilitre sample of urine was acidified with nitric acid to 5% (V/V). This sample was spiked with the appropriate amount of beryllium, placed in two 90-ml centrifuge tubes, made basic with an excess (about 15 ml) of concentrated ammonium hydroxide, stirred until mixed, and centrifuged for 10 minutes. The solution then was decanted, the precipitates were transferred to a 50-ml beaker, and the centrifuge tube was rinsed with concentrated nitric acid. The nitric acid was subsequently removed by evaporation on a hot plate, and exactly 5.0 ml of 5% (V/V) nitric acid, which was 100 µg/ml in lanthanum, was pipetted into each beaker. The solutions were warmed briefly to about 80 °C, and then pipetted into the graphite furnace.

Method C—Hair was cut into about 1-cm lengths, stirred twice (10 min each time) with acetone, rinsed with distilled water, and boiled for 30 min in 2% (W/V) Alconox^{*} detergent. The samples then were rinsed with distilled water, boiled in 1% (V/V) nitric acid for 30 min, rinsed with distilled water, and each sample stirred twice (10 min each time) with acetone.^{4, 5}

After the hair dried, one-gram samples were transferred to 150-ml beakers, and 10 ml of concentrated nitric acid was added. After carefully evaporating the mixture to dryness, 10 ml of 1:1 nitric acid-perchloric acid was added, and again the mixture was brought to dryness. Five millilitres of nitric acid were then added and evaporated to help remove all of the perchloric acid. Exactly 5.0 ml of 5% (V/V) nitric acid, which was 100 µg/ml in lanthanum, was added, and an aliquot of this solution was pipetted into the graphite furnace.

Method D⁶—A fecal sample was weighed into a two-litre beaker, and an amount of 5% (V/V) nitric acid equal to the sample weight was added. The material was warmed on a magnetically stirred hot plate until a slurry was produced. The slurry was then stirred. A volume of 30% hydrogen peroxide equal to twice the sample weight was added plus about 10 ml of concentrated nitric acid, and the mixture was brought to a boil while stirring. One millilitre of a solution containing 60 mg/ml of ferrous ion as ferrous chloride was then added. Heating and stirring continued until the vigorous reaction ended (about one hour). Foaming can be controlled with a squirt bottle of water, nitric acid, or octanol. The sample was evaporated to near dryness, transferred to a platinum dish by means of nitric acid, and heated in a muffle furnace. The furnace temperature should begin at about 300 °C and be increased to about 700 °C over a four-to-eight-hour period. The residue was cooled and dissolved in 100 ml of 5% (V/V) nitric acid containing 100 µg/ml of lanthanum, and an aliquot was pipetted into the graphite furnace.

The residue does not always go completely into solution with the 5% (V/V) nitric acid since ferric oxide and some silicate material may remain. To correct for this, heat and stir the mixture while obtaining the aliquot for the graphite furnace; this procedure will help ensure that a representative sample is placed in the graphite furnace. Complete dissolution can be obtained by treating the muffle furnace residue with hydrofluoric acid. The hydrofluoric acid has to be removed completely by treatment with perchloric and nitric acids.¹ This entire dissolution procedure did not alter beryllium recovery.

Method E—The fingernail samples were cleaned using Alconox, dried, and then digested as were the hair samples in Method C. The only major differences were that a 5-ml beaker was used for the nail samples, and the residue was taken up in 1.0 ml of the dilute nitric acid solution.

RESULTS AND DISCUSSION

A direct method was tried on urine samples without the lanthanum present, but the results

^{*}Trademark of Alconox, Inc., 217 Park Ave. S., New York, New York.

TABLE I. Recovery of nanogram amounts of beryllium from biological tissues and fluids

Biological Tissue or Fluid	Digestion Method	Sample Size	Beryllium Added ^a (ng)	Beryllium Recovered ^{b, c} (ng)
Urine	A	10 ml	50	50 ± 5
Urine	A	10 ml	100	101 ± 12
Urine	A	10 ml	200	190 ± 16
Urine	B	100 ml	5.0	5.5 ± 0.4
Urine	B	100 ml	10.0	9.9 ± 0.9
Urine	B	100 ml	50.0	47 ± 6
Hair	C	1.0 g	5.0	5.2 ± 0.5
Hair	C	1.0 g	10.0	10.5 ± 0.4
Hair	C	1.0 g	50.0	49 ± 2
Fingernail	E	0.10 g	2.0	2.0 ± 0.1
Fingernail	E	0.10 g	4.0	3.9 ± 0.2
Fece	D	50 g	500	540 ± 60

a. Beryllium was added to the sample before digestion.

b. Recovered beryllium was determined by a direct comparison to aqueous standards, which were 5% (V/V) in nitric acid and 100 µg/ml in lanthanum. All recoveries were corrected for blank or naturally occurring beryllium. Only fecal blanks contained significant amounts of beryllium (1 to 2 ng/g).

c. Standard deviations are based on 5 to 15 determinations.

were up to 50% higher than the expected value;¹ also, the method of standard additions yielded curved lines. The lanthanum procedure, however, gives good recoveries as seen in Table I, Method A. The practical detection limit for Method A is 0.5 ng/ml.

Method B is a coprecipitation procedure, and 5 ng of beryllium can be quantitatively recovered from 100 ml of urine as shown in Table I. This corresponds to 0.05 ng/ml.

Hair samples were reported to be from 20 to 30 ng/g in beryllium,^{7, 8} and hair samples that were washed in only acetone and water were found to be from 1 to 40 ng/g in beryllium. The wash method in Method C, however, yielded less than 0.5 ng/g of beryllium in hair. Either the beryllium leached

out of the hair during the wash⁵ or it was all surface beryllium. Less than 1 ng/g of beryllium in hair or nail samples can be detected.

Only two other investigators are known to have presented an analytical procedure for determining beryllium in feces,⁹ and they used a gamma-activation analysis method. The flameless AAS procedure coupled with Digestion Method D gives reasonable recoveries (see Table I).

Acid digestion procedures for feces was time consuming in addition to being expensive. Nitric acid digestion requires over two full days of constant work plus more than a gallon of nitric acid for a 200-g fecal sample; however, ferrous ion, hydrogen peroxide digestion is quite rapid (one day).⁶

The final solution has to contain lanthanum to mask the calcium interference, and it has to be in nitric acid because hydrochloric and hydrofluoric acids interfere.¹ Sulfuric acid yields a calcium sulfate precipitate.

Beryllium recovery from all tissues and fluids was from 90 to 110% with relative standard deviations of less than 13%. The detection limits could be lowered to less than one ng/g for all of the biological samples because only 20- and 50-µl sized furnace aliquots were used and because larger tissue sizes could be employed. All unspiked samples gave blanks of less than 0.5 ng/g except for the fecal samples. The blank (unspiked) fecal samples contained from 1 to 2 ng of beryllium per gram of feces.

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