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FLAMELESS ATOMIC ABSORPTION DETERMINATION OF BERYLLIUM IN THE PRESENCE OF VARIOUS ANIONS AND CATIONS

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Environmental Sciences and Waste Control
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FLAMELESS ATOMIC ABSORPTION DETERMINATION OF BERYLLIUM IN THE PRESENCE OF VARIOUS ANIONS AND CATIONS

Jeffrey A. Hurlbut and Dale L. Bokowski

Abstract. A method for determining trace amounts of beryllium in the presence of various anions and cations is described. The method involves use of a Perkin-Elmer Model 503 spectrophotometer equipped with an HGA-2100 graphite furnace. The absorption signal from 20 ng/ml of beryllium varies significantly from acid to acid, and both 5% (V/V) nitric acid and 5% (V/V) sulfuric acid were studied as possible analysis solvents. Absorption signal enhancement and suppression caused by the presence of other chemicals appears similar in either solvent. Concentrations of more than 0.1M hydrochloric and hydrofluoric acid suppress the signal in both solvents. Group II cations, lanthanum, cerium, chromium, molybdenum, tungsten, manganese, aluminum, and silicon, when present in concentrations of 100 μg/ml, enhance the beryllium signal. The addition of 100 μg/ml of lanthanum increases the signal over two fold and masks the signal enhancement caused by the other listed elements; however, hydrochloric and hydrofluoric acids still interfere. The recovery of 20 ng/ml of beryllium in the presence of 100 μg/ml of lanthanum and in the presence of 100 μg/ml each of thirty elements tested is 20 ng/ml with a relative standard deviation of 4% and a range of 19 to 22 ng/ml. The presence of lanthanum permits direct detection of less than 1 ng/ml of beryllium in urine.

INTRODUCTION

Beryllium and beryllium compounds are highly toxic chemicals that are frequently handled by workers in the aerospace, nuclear, and metal alloy industries. One hazard in this work may manifest itself in the form of either acute or chronic beryllium disease.[1] A useful diagnostic tool for these diseases is verification of beryllium in biological tissues and fluids, but the determination of submicrogram amounts of beryllium in biological samples is difficult and time consuming.[1-5]

Besides being useful for diagnostic purposes, trace-beryllium analysis techniques may be relied upon in future beryllium-exposure bioassays;[1] consequently, any analytical procedure used should be rapid and capable of detecting less than nanogram amounts of beryllium in biological samples.

A search of the literature revealed that three beryllium analysis procedures fit the above criteria: gas chromatography, flame atomic absorption spectrometry (AAS), and flameless AAS.[1] Flameless AAS appeared the most promising of the three procedures.

Sighinolfi used flameless AAS to determine beryllium in rock samples.[6] Siemer, Lech, and Woodriff utilized porous graphite cup filtration and flameless AAS to determine the beryllium content of air samples.[7] Siemer and Woodriff continued the porous graphite cup work in 1974.[8] Janouskova, Sulcek, and Sychra,[9] in addition to Chapman, Dale, and Kelley,[10] used flameless AAS to detect beryllium in water samples. Hurlbut analyzed urine for beryllium by flameless AAS.[11] Hurlbut and Bokowski investigated the recovery of nanogram amounts of beryllium from air filter samples by flameless AAS[12] as did Bettger, Ficklin, and Rees.[13] Owens and Gladney used flameless AAS in analyzing coal, orchard leaves, fly ash, and bovine liver for beryllium.[14] Runnels, Merryfield, and Fisher investigated the effect of carbide-forming elements on the atomization of beryllium by the HGA-70 graphite furnace.[15]

Several of the papers referenced above indicate that variations in the sample matrix often cause either enhancement or suppression of the absorption signal. Because of interferences, attempts to directly analyze biological samples for beryllium were unsuccessful; therefore, a study was made to identify and to eliminate these interferences. This paper describes the results of that study.

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 10, 20, and 50 µl 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, and the external argon flow rate was 50 cm^3/min. The lamp current was 30 mA, slit width was 0.7 nm, and the wavelength was 235 nm. Absorbance signals were measured both with the recorder and with the 503 peak reader. To use the peak reader, the baseline had to be equivalent to zero absorbance after the char stage.

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. The dilute beryllium standards were prepared from a 1000-ppm Ventron, Alfa Inorganics Standard. All dilute beryllium stock solutions (2000 ng/ml and 1000 ng/ml) were 1% (V/V) in nitric acid and were stable for weeks. Stock solutions of the cations and anions were prepared in concentrations of 1000 µg/ml and were 0.5% (V/V) in nitric acid except for tin and arsenic, which were 1% (V/V) in hydrochloric acid. The 10,000 µg/ml lanthanum solution was prepared from lanthanum oxide (La_2O_3) and was 5% (V/V) in nitric acid.

RESULTS AND DISCUSSION

Relationship between Absorbance and Concentration for Beryllium

The calibration curves are linear for beryllium concentrations between 2 and 40 ng/ml and 20 µl samples in 5% (V/V) nitric acid. The sensitivity (amount of beryllium that gives 1% absorption) is 5×10^{-12} g, which compares well with other reported values.[11-13]

Lanthanum enhances the absorption signal (see Table I), and plots of absorption versus concentration are linear from 2 to 25 ng/ml for 10 µl samples in 5% (V/V) nitric acid and 100 µg/ml of lanthanum. The sensitivity in this solution is 2×10^{-12} g.

Effects of Acids on Beryllium Recovery

Both the type and the concentration of acid are variables in graphite furnaces other than the HGA-2100;[6,12] consequently, a study on the effect of acids on absorbance was performed. The results are given in Tables II, III, and IV.

The results in Table II show that nitric acid gives the strongest absorption signal of the six acids tested. Hydrochloric and hydrofluoric acids strongly suppress the signal when present at 1M concentrations; phosphoric and perchloric acids give erratic results. These erratic results appear dependent somewhat on the condition of the graphite tube. Sulfuric acid gives a large amount of smoke during both the char and atomization steps, but the deuterium background corrector adequately compensates for this.

Sulfuric and nitric acids were chosen for further investigation. Different concentrations of these two acids have no influence on absorbance. Concentrations of these acids between 0.5M and 2.0M give essentially the same absorbances, but

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

TABLE I. Effect of various elements on the recovery of 20 ng/ml of beryllium in the presence of and in the absence of lanthanum

		Recovery of Beryllium Based on the Parent, Element-Free Standard[a, b] (ng/ml)			
Element Present 100 µg/ml	Element Source	5% HNO_3	5% HNO_3 100 µg/ml La	5% H_2SO_4	5% H_2SO_4 100 µg/ml La
–	–	20[c]	20[c]	20[c]	20[c]
Li	LiCl	19	19	18	19
Na	$NaNO_3$	21	20	21	20
K	KNO_3	21	20	23	20
Mg	$Mg(NO_3)_2$	29	20	34	20
Ca	$Ca(NO_3)_2$	39	20	41	20
Sr	$SrCO_3$	32	20	26	20
Ba	$Ba(NO_3)_2$	30	19	–[d]	–[d]
La	La_2O_3	40-80[e]	20	60-90[e]	20
Ce	$Ce(NO_3)_3$	30-80[e]	21	30-60[e]	20
V	V_2O_5	21	20	23	20
Cr	CrO_3	27	20	34	20
Mo	$(NH_4)_6Mo_7O_{24}$	29	19	22	20
W	$P_2O_5 \cdot 24WO_3$	25	20	20	20
Mn	$Mn(NO_3)_2$	24	20	26	19
Fe	$FeCl_3$	22	20	20	20
Co	$CoCO_3$	18	20	22	20
Ni	$NiCO_3$	17	20	21	20
Cu	$CuCO_3$	20	20	20	20
Ag	$AgNO_3$	20	20	19	20
Zn	$Zn(NO_3)_2$	21	21	19	20
Cd	$CdCO_3$	21	20	19	20
Hg	$Hg(NO_3)_2$	20	19	20	21
Al	$Al(NO_3)_3$	41	21	50	22
Si	Na_2SiO_3	35	20	46	22
Sn	SnO	21	19	20	20
Pb	$Pb(NO_3)_2$	20	20	–[d]	–[d]
NH_4	NH_4NO_3	20	19	22	21
As	As_2O_3	20	20	18	20
Bi	$Bi(NO_3)_3$	20	20	19	20

---

a. The sample volumes were 10 and 20 µl for solutions with and without lanthanum respectively.

b. Standards were run between all samples. The standard deviation was ±3 ng/ml in the absence of lanthanum and ±1 ng/ml in the presence of lanthanum. All of the elements at 100 µg/ml, in the absence of beryllium, gave negligible absorption signals except for silicon, which gave a small negative response.

c. This is the standard on which other recoveries in the column were based.

d. An insoluble sulfate was formed.

e. The recoveries varied from one graphite tube to another.

the smoke produced by higher concentrations of sulfuric acid is a problem.

The effects of 1M and 0.1M acids in both a 5% (V/V) nitric acid and a 5% (V/V) sulfuric acid solvent was investigated (see Tables III and IV). Results similar to those given in Table II were obtained. Hydrochloric, hydrofluoric, and perchloric acids, when present in 1M concentrations, interfere with the absorbance or recovery of

TABLE II. Effect of 1M acids on the recovery of 20 ng/ml of beryllium

1M Acid	Beryllium Recovery Based on 1M HNO_3 (ng/ml)^a
HNO_3	20
H_2SO_4	16
H_3PO_4	14^b
HCl	9
HF	4
$HClO_4$	16^b

a. The sample volumes were 20 μl.

b. The recovery varied considerably with respect to the condition of the graphite tube.

TABLE III. Effect of 1M acids on the recovery of 20 ng/ml of beryllium from 5% (V/V) acid solutions

Parent 5% Acid	1.0M Acid	Beryllium Recovery Based on Parent Acid No La^a (ng/ml)	Beryllium Recovery Based on Parent Acid 100 μg/ml in La^b (ng/ml)
HNO_3	–	20^c	20^d
HNO_3	H_2SO_4	18	16
HNO_3	H_3PO_4	21^e	20
HNO_3	HCl	10^e	3
HNO_3	HF	3	–^{f}
HNO_3	$HClO_4$	11	6
H_2SO_4	–	20^g	20^g
H_2SO_4	HNO_3	32	16
H_2SO_4	H_3PO_4	23^e	19
H_2SO_4	HCl	4	4
H_2SO_4	HF	1	^{f}
H_2SO_4	$HClO_4$	26^e	12

a. The sample volumes were 20 μl.

b. The sample volumes were 10 μl.

c. Standards were run between every sample. The mean and standard deviation for all of the standard runs were 20 ±2 ng/ml. The average absorption was 0.33.

d. Standards were run between every sample. The mean and standard deviation for all of the standard runs were 20 ± 1 ng/ml. The average absorption was 0.46 for the 10-μl size samples in the presence of lanthanum.

e. The recovery varied considerably with respect to the condition of the graphite tube.

f. A precipitate of lanthanum fluoride (LaF_3) was formed.

g. The standard deviation for 20-μl sized samples in the absence of lanthanum was ±2 ng/ml. The standard deviation for 10-μl sized samples, in the presence of 100 μg/ml of lanthanum, was ±1 ng/ml. These standard deviations are based on the standards that were run between every sample.

beryllium. The presence of 100 μg/ml of lanthanum does not improve the recoveries. These three acids still cause low or erratic recoveries when present at 0.1M concentrations. This interference can be removed by taking the sample to dryness and redissolving the sample in either sulfuric or nitric acid. This procedure was tried with 20 ng/ml beryllium standards in 8M hydrochloric acid. The recovery increased from 4 to 20 ng/ml.

It should be noted that the effect of acids tends to vary with respect to the type of graphite furnace used and with the internal gas flow (normal, interrupt, or constantly blocked). Results obtained with the Perkin-Elmer HGA-70,[6] the Perkin-Elmer HGA-2000,[11] the Perkin-Elmer HGA-2100, and the Varian Techtron Model 63,[12] all differ. Simple changes in the furnace parameters do not account for these differences.

Effects of Contaminants on Beryllium Recovery

Table I shows the effects of various interfering elements in the presence of different solvents and in the presence or absence of lanthanum as an interference suppressant. On all runs in the presence of lanthanum, the graphite tube was first treated with 500 μg of lanthanum (50 μl of 10,000 μg/ml lanthanum solution).[14] Standards were run between every sample. The standard deviations for all standard runs are given in the footnotes to Table I.

Results for the two acid solvents are similar. Twelve of the 30 elements cause a significant enhancement of the absorption. These elements are Group II cations, lanthanum, cerium, chromium, molybdenum, tungsten, manganese, aluminum, and silicon. None of the chemicals tested caused a suppression except for the acids as indicated in Tables III and IV.

TABLE IV. Effect of 0.1M acids on the recovery of 20 ng/ml of beryllium from 5% (V/V) acid solutions

Parent 5% Acid	0.1M Acid	Beryllium Recovery Based on Parent Acid No La[a] (ng/ml)	Beryllium Recovery Based on Parent Acid 100 μg/ml in La[b] (ng/ml)
HNO_3	–	20[c]	20[d]
HNO_3	H_2SO_4	19	20
HNO_3	H_3PO_4	20	20
HNO_3	HCl	20	17
HNO_3	HF	7	_[f]
HNO_3	$HClO_4$	21	15
H_2SO_4	–	20[g]	20[g]
H_2SO_4	HNO_3	23	19
H_2SO_4	H_3PO_4	27[e]	19
H_2SO_4	HCl	15	13
H_2SO_4	HF	4	_[f]
H_2SO_4	$HClO_4$	28[e]	16

a. The sample volumes were 20 μl.
b. The sample volumes were 10 μl.
c. Standards were run between every sample. The mean and standard deviation for all of the standard runs were 20 ±2 ng/ml. The average absorption was 0.33.
d. Standards were run between every sample. The mean and standard deviation for all of the standard runs were 20 ± 1 ng/ml. The average absorption was 0.46 for the 10-μl size samples in the presence of lanthanum.
e. The recovery varied considerably with respect to the condition of the graphite tube.
f. A precipitate of lanthanum fluoride (LaF_3) was formed.
g. The standard deviation for 20-μl sized samples in the absence of lanthanum was ±2 ng/ml. The standard deviation for 10-μl sized samples, in the presence of 100 μg/ml of lanthanum, was ±1 ng/ml. These standard deviations are based on the standards that were run between every sample.

Runnels, Merryfield, and Fisher also noted and studied the enhancement of some of these elements.[14] They indicate that the above elements form a carbide coating in the graphite tube, which in turn prevents physical contact between the carbon of the tube and subsequent samples. The effect of this carbide coating is to allow the beryllium to more completely atomize and thus increase the absorbance.

The enhancement by lanthanum and cerium appears to last for nearly the lifetime of the graphite tube after just one application of the metal. Enhancement by the other cations drops off sharply, however, in the absence of these cations. The precision tends to improve if lanthanum is added to every sample at times other than just at the beginning of the run; consequently, the procedure used to obtain consistant results was to treat the graphite tube with one application of 500 μg of lanthanum at the beginning of the run and then add enough lanthanum to every sample such that the lanthanum concentration was 100 μg/ml.

Treating the graphite tube with 500 μg of lanthanum and then spiking all of the samples with lanthanum yielded complete recoveries for all of the elements tested. Recoveries were excellent in both solvents. The total, average recovery was 20 ng/ml with a relative standard deviation of ±4% and a range of 19 to 22 ng/ml.

Urine samples that were spiked with enough beryllium to make them 5.0, 10.0, and 20.0 ng/ml in concentration gave high recoveries in both 5% (V/V) nitric acid and 5% (V/V) sulfuric acid. The method of standard additions yielded curved lines so that the recoveries are also high. When the same urine samples were treated with the lanthanum, however, recoveries were good to within ±5% of the spiked amounts. Work on the recovery of beryllium in various biological tissues and fluids is reported elsewhere.[16]

Conclusion

Five percent (V/V) nitric acid or 5% (V/V) sulfuric acid are the most practical analysis solvents. Hydrochloric, hydrofluoric, and perchloric acids, when present in concentrations of 0.1M or more, interfere with the absorbance of 20 ng/ml of beryllium. This interference can be eliminated by evaporating the sample to dryness and redissolving the salts in either 5% (V/V) nitric or sulfuric acids. Several elements enhance the absorbance when present at concentrations of 100 μg/ml, but excellent recoveries are obtained by spiking the samples with 100 μg/ml of lanthanum. The addition of lanthanum gives excellent recoveries of beryllium. It also improves the sensitivity and analytical precision.

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