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Determination of Arsenic in Urine and Feces by Dry Ashing, Atomic Absorption Spectrometry

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A dry ashing flameless atomic absorption procedure was used to determine fish-arsenic in human urine and feces. Samples were dry ashed with $\text{Mg}(\text{NO}_3)_2\text{--MgO}$ and dissolved in 6N HCl. Arsine was generated by the addition of NaBH_4 and swept into a thermally heated silica tube furnace. Recoveries of several arsenic compounds added to samples ranged from 85 to 117%. The detection limit was about 3 ppb as for 10 g sample. Effects of the presence of common cations, anions and acids were studied.

KEY WORDS: Arsenic, urine, dry ashing, AAS.

INTRODUCTION

Trace levels of arsenic can be determined by emission spectrometry¹⁻³ or more commonly by hydride generation atomic absorption spectrometry.⁴⁻⁸ These methods involve wet digestion using H_2SO_4 , HClO_4 or HNO_3 singularly or in combination to destroy the organic matter followed by generation of arsine by sodium borohydride in acidic solution. These acids at high concentrations interfere with arsenic recovery in the determinative step.⁹ Continuous attention is also required during the digestion period due to the use of potentially explosive HClO_4 . A simple dry ashing method used to decompose biological samples, including samples of marine origin, was found to give good precision and recovery for determination of arsenic by colorimetry.^{10,11} The dry ashing procedure is simpler, easier to perform and less time consuming than the wet digestion procedure. Moreover, many samples can be handled simultaneously without difficulty in dry ashing. However, the colorimetric method cannot be used to determine arsenic and its metabolites in biological samples due to its low sensitivity. It is thus advisable to

combine the simple dry ashing procedure for decomposition of the samples with the more sensitive hydride-generation atomic absorption spectrometry for measurement of arsenic. This has been seldom investigated.¹² This study investigates the dry ashing, flameless atomic absorption procedure for determination of arsenic, especially in human urine and feces. The effects of the ashing aid, a mixture of magnesium nitrate and magnesium oxide, acids and common ions were studied.

EXPERIMENTAL

Apparatus

The Varian Techtron vapor generation accessory model 64 was used for generation of arsine. It consisted of a glass cylinder (1.5" × 6") and a teflon stopper with a slip-valve allowing a mixture of N₂ and H₂ to either flow through the reaction cylinder or directly to the furnace. The flow rates of N₂ and H₂ were adjusted to 1200 and 200 mL/min, respectively. A trap filled with cotton wool soaked with lead acetate solution and dried was installed between the reaction cylinder and the furnace.

The Vycor furnace tube was 1.5 cm id by 15 cm long, wrapped with 5 m of 26 ga chromel wire and maintained at ~970°C with a variable transformer. The furnace was wrapped outside with a layer of asbestos strings for insulation. It was held in the light path of a Varian AA120 spectrometer equipped with an arsenic hollow cathode lamp. Parameters were set up according to manufacturer's suggestion. The peak height was recorded using a Varian 25 recorder and used for calculation.

Reagents

All reagents were analytical reagent grade unless otherwise stated.

Several sources of commercial analytical grade MgO were found to be contaminated with arsenic. However, high-purity MgO could be prepared by ashing analytical grade Mg(NO₃)₂ · 6H₂O in a muffle furnace at 500°C overnight and grinding to a fine powder. The ashing aid was prepared by dissolving 80 g Mg(NO₃)₂ · 6H₂O in 200 mL deionized water. Ten g MgO was then added to it.

Arsenic standard stock solution was prepared from high-purity arsenic trioxide (Alfa Chemical). The dilute standard solutions containing 0, 10, 20, 40, 60, 80, and 100 ng As in 20 mL 6N HCl were prepared by stepwise dilution of the stock solution.

Ashing and determination procedure

A sample (1–10 g) was mixed with 10 mL ashing aid and dry ashed

overnight at 500°C (11). The ashed sample was dissolved and made up to 50.0 mL in 6N HCl. Duplicate aliquots containing less than 100 ng As were pipetted into the hydride-generation tubes. An appropriate volume of 6N HCl was added to bring the final volume to 20 mL. One mL 30% KI solution was added to reduce arsenate to arsenite. Three mL 3% NaBH₄ solution were injected to the solution 20 min later to generate the arsine gas.

Interference studies

Different amounts of conc. inorganic acids, cations and anions were added to a solution containing 50 ng As and 0.2 g MgO. The final volume was adjusted to 20 mL in 6N HCl. Arsine was then generated as mentioned above.

RESULTS AND DISCUSSION

Effect of Ashing Aid

Since Mg(NO₃)₂·6H₂O and MgO were used to decompose the sample, the ashed solution used for atomic absorption determination contained a large amount of magnesium ion (12 mg/mL). The effect of this large amount of Mg⁺⁺ on the recovery of arsenic was studied by adding different amounts of purified MgO to a standard arsenic solution containing 50 ng As in 20 mL 6N HCl. The recoveries are shown in Table I. The 0.2 g MgO added was equivalent to the amount of MgO in 10 mL of the dissolved ashed sample which had a total volume of 50 mL. No interference was observed with this amount of MgO. The recovery of arsenic decreased with larger amounts of MgO. Thus, it was decided to limit the volume of ashed solution used to a maximum of 10 mL.

Effect of Acids and Common Ions

Even though only HCl was used to dissolve the ashed sample, the effect of other acids was also studied. Table II shows the effect of HClO₄, H₂SO₄ or HNO₃ on the recovery of arsenic. No interference was observed for HClO₄ up to 25% (v/v). Higher concentrations of H₂SO₄ reduced the recovery of arsenic. It appeared that the larger amount of H₂SO₄ in the solution slowed down the production of arsine after NaBH₄ addition.⁹ As for HNO₃, the high positive effect is probably due to the reduction of HNO₃ to NO₂ and NO which showed a nonspecific absorption interference at 193.7 nm. This enhancement effect was in contradiction to the suppression effect reported by Kang⁹ and Pierce and Brown¹³ who used

TABLE I
Recovery of arsenic (50 ng) using different amounts of MgO

Amount of MgO added (g)	Arsenic found ^a (ng)	Arsenic Recovery (%)
0	50	
0.02	50	100
0.10	50	100
0.20	50	100
0.30	43	86
0.40	36	72

^aAverage of duplicate analyses.

TABLE II
Effect of acids on recovery of 50 ng arsenic

Acid	Vol. of acid/vol. of 6N HCl (mL)	Arsenic found ^a (ng)	Arsenic found (%)
HClO ₄	0.5–5.0/19.5–15.0	50 ^b	100
H ₂ SO ₄	0.5/19.5	50	100
	1.0/19.0	45	90
	2.5/17.5	38	76
	5.0/15.0	31	62
HNO ₃	0.2/20.0	50	100
	0.5/19.5	> 100	
	2.0/18.0	≥ 100	

^aAverage of duplicate analyses.

^bAverage of eight analyses.

more dilute solutions of HCl and less NaBH₄. Nevertheless, the effect of HNO₃ would not be observed since no HNO₃ would be present after dry ashing or wet digestion with a mixture of acids containing H₂SO₄ or HClO₄. It is concluded that samples for arsine generation, atomic absorption spectrometry should never be prepared in H₂SO₄ or HNO₃ media, and HCl would be the proper choice.

No interferences on the recovery of 50 ng As were observed in the presence of up to 500 μg Na⁺, K⁺, Ca⁺⁺, Fe⁺⁺, Fe⁺⁺⁺, Co⁺⁺, Ni⁺⁺, Cu⁺⁺, Zn⁺⁺, Cd⁺⁺, Pb⁺⁺, CO₃⁼, PO₄⁼, MnO₄⁼, Cr₂O₇⁼, or CrO₄⁼. Five hundred μg SeO₃⁼ or SeO₄⁼ reduced the recovery of arsenic by 20%. No suppression was observed for 250 μg selenite or

selenate. The presence of 100 μg antimony or bismuth reduced the recovery by more than 50%. These results agree generally with those reported by Pierce and Brown.^{13,14} The above studies showed that the sample matrix after dry ashing was suitable for hydride-generation atomic absorption spectrometry.

Arsenic in Human Urine and Feces

The dry ashing, atomic absorption spectrometry method described above was used in a study of excretion of arsenic in human urine and feces following oral ingestion of inorganic arsenic and a meal of fish containing high natural levels of arsenic (~ 50 ppm). Recoveries of the fish-arsenic compound,¹⁵ inorganic arsenic and its metabolites (mono-methylarsonate and dimethylarsinic acid),¹⁶ added to human urine and feces ranged from 85 to 117% with a relative standard deviation of approximately 10% (Table III). The detection limit was about 3 ppb As for a 10 g sample. The method was used successfully to determine arsenic in the urine and feces of human volunteers following an oral ingestion of a meal of fish containing 10 mg As. The preliminary results (Table IV) showed that the fish-arsenic compound was completely absorbed and rapidly excreted in urine, but very little in feces. The detailed results of this study and its significance will be published shortly.

Accuracy

The application of the method, as tested by determination of arsenic in several NBS certified reference materials, showed good agreement between experimental and certified values (Table V). Furthermore, several freeze-dried marine samples were analysed for arsenic by the proposed method and the classical colorimetric method using silver diethyldithiocarbamate. The results (Table VI) showed the two methods to be in good agreement. The atomic absorption method was much more sensitive than the colorimetric method.

The dry ashing, atomic absorption procedure was also found to be applicable to a wide range of food products including apple juice, wine, fish, meat and vegetables. Recovery of arsenic was found to be 80-120%.

TABLE III
Recovery of arsenic compounds added to human urine and feces

Arsenic in urine ppb	Arsenic added ppb	Arsenic found ppb	Arsenic recovered ppb	% recovery
7.2 ± 0.2(4) ^a	15.0 (sodium arsenite)	20.0 ± 0.4(4)	12.8 ± 0.5(4)	85.3 ± 3.3(4)
	50.0 (sodium arsenite)	55.9 ± 1.8(4)	48.7 ± 1.8(4)	97.4 ± 3.6(4)
6.3 ± 0.3(4)	40.0 (sodium monomethyl arsonate)	45.3 ± 1.3(4)	39.0 ± 1.3(4)	97.5 ± 3.3(4)
6.3 ± 0.3(4)	40.0 (cacodylic acid)	47.5 ± 1.7(4)	41.2 ± 1.7(4)	103.0 ± 4.3(4)
7.9 ± 0.2(4)	15.0 (fish-arsenic compound)	25.4 ± 0.9(4)	17.5 ± 0.9(4)	116.6 ± 6.0(4)
	40.0 (fish-arsenic compound)	46.1 ± 2.8(4)	38.2 ± 2.8(4)	95.5 ± 7.0(4)
Arsenic in feces 3.9 ± 0.3(4)	15.0 (sodium arsenite)	20.1 ± 2.2(4)	16.2 ± 2.2(4)	108.0 ± 14.6(4)

^aAverage ± std. dev. (no of analyses)

TABLE IV

Excretion of arsenic in human urine and feces following an oral ingestion of a meal of fish containing 10 mg As

Day	% Excreted			
	Subject A		Subject B	
	Urine	Feces	Urine	Feces
1	49.15	0.01	45.67	0.07
2	9.81	0.13	9.83	0.15
3	4.22	0.02	6.44	0.06
4	2.52	0.01	4.90	0
5	1.82	0.01	2.65	0.01
6	1.14	0	1.69	0.06
7	0.86	0.02	1.51	0.09
8	0.79	0.01	1.02	0
Total	70.31	0.21	73.71	0.44

TABLE V

Determination of arsenic in NBS reference materials

Sample	Arsenic found ppm	Arsenic certified value ppm
NBS 1571 orchard leaves	$9.98 \pm 0.31(4)^a$	10 ± 2
NBS 1573 tomato leaves	$0.31 \pm 0.01(4)$	0.27 ± 0.05
NBS 1570 spinach leaves	$0.18 \pm 0.02(4)$	0.15 ± 0.05

^aAverage \pm std. dev. (no of analyses)

TABLE VI

Determination of arsenic by dry ashing, atomic absorption and Colorimetric method

Sample	Arsenic conc. ppm	
	A.A.	colorimetry
Cod	7.03, 7.31	7.1, 7.0
Shrimp	42.74, 43.36	44.5, 47.5
Flounder	283.3, 287.4	268, 254

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