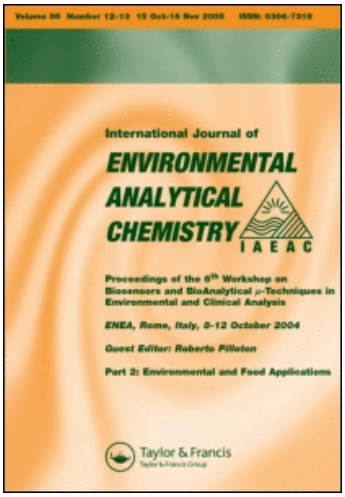

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Zeeman Effect Electrothermal Atomic Absorption Spectrophotometry with Matrix Modification for the Determination of Arsenic in Urine

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Zeeman Effect Electrothermal Atomic Absorption Spectrophotometry with Matrix Modification for the Determination of Arsenic in Urine

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Arsenic was determined in urine by electrothermal atomic absorption spectrophotometry using Zeeman Effect background correction and after matrix modification with 5% nickel nitrate. Mean recovery of urine samples spiked with 100 $\mu g . L^{-1}$ dimethylarsinic acid was 97.9 $\mu g . L^{-1}$. Within-run CV was 2.4%, between-run CV was 7.3% and the detection limit was determined to be 10.0 $\mu g . L^{-1}$. The method can be used for the rapid screening of urine samples for elevated arsenic levels.

KEY WORDS: Electrothermal atomic absorption spectrophotometry, urine, Zeeman effect, arsenic.

INTRODUCTION

The difficulties encountered in the direct determination of arsenic in biological samples by Electrothermal Atomic Absorption Spectrophotometry (ET-AAS) due to wisespread interferences have been documented.[1] The determination of arsenic in urine can be performed but usually only through the use of such methods as hydride generation[2] or extraction followed by ET-AAS.[3] Furthermore, with deuterium background corrected systems spectral interference at the primary arsenic wavelength (193.7 nm) from the presence of calcium phosphate, which is present in large amounts in urine, can affect the accuracy of the measurement.[4] However, the elimination of this interference by the use of Zeeman effect background correction has recently been reported.[5]

The use of nickel as a matrix modifier to enhance the recovery of arsenic was first reported by Ediger[6] and has since gained widespread use. Also, Saeed and Thomassen,[4] working with selenium, have reported that large amounts of nickel can reduce the error caused by the spectral interference of calcium phosphate with deuterium background corrected systems.

Dimethylarsinic acid (DMA) has been identified as the major constituent of arsenic in human urine, even 24 hours after ingestion of large doses of inorganic arsenic.[3] Therefore, this metabolite was selected to develop a method for the direct determination of arsenic in urine by ET-AAS using large amounts of nickel matrix modifier and Zeeman effect background correction. This procedure can be used as a simple and rapid means of testing for elevated urinary arsenic. If high levels are detected, other methods[3] can be used for the speciation of the arsenic as required.

EXPERIMENTAL

Spectrophotometer

The ET-AAS analyses were performed on an Hitachi Model 180-80 Zeeman Effect Atomic Absorption Spectrophotometer equipped with a graphite furnace autosampler, and using pyrolytically coated graphite tubes (All from Hitachi, Tokyo, Japan). A Hamamatsu (Tokyo, Japan) hollow cathode lamp was operated at 7 ma.

Reagents

Inorganic arsenic standards were prepared from stock 1000 mg. L^{-1} atomic absorption standard (Canlab, Toronto, Ontario M8Z 2H4). DMA standards were prepared from sodium dimethylarsinic acid (J. T. Baker Chemical Co., Phillipsburg, N.J. 08865) dissolved in 0.1 N NaOH, and a stock 20%(w/v) nickel nitrate (BDH, Toronto, Ontario M8Z 1K5) solution (Analar grade, Lot No. 9199001) was prepared, as were all aqueous solutions, with distilled water passed through a Milli-Q system (Millipore Ltd., Mississauga, Ontario L4V 1M5).

Ortho Control Urine II (Ortho Diagnostics, Raritan, N.J. 08869) Lot No. 095X01 was reconstituted in accordance with the manufacturer's instructions.

Sample preparation

Urine samples were collected in acid-washed polyethylene bottles. For each analysis 0.5 ml of urine was pipetted directly into an autosampler cup followed by 0.25 ml of 20% nickel nitrate solution to give a final concentration of 5% nickel nitrate or approximately 10,000 mg. L^{-1} elemental Ni. The sample was then made up to 1.0 ml with arsenic spike and/or water.

The determinations were performed by the method of standard additions using 50 μg. L^{-1} and 100 μg. L^{-1} additions to the diluted sample. Triplicate injections of a blank, the sample, and each standard addition were made. The sample concentrations, which were automatically calculated by the instrument, were multiplied by the urine dilution factor (X2). The instrument, even during standard addition calibration, will print out the correlation coefficient of the curve obtained. If the correlation coefficient was not 0.9900 or above, the analysis was repeated.

AA Analyses

The analyses were performed with the instrument settings shown in Table I. Peak area mode was used for all determinations. Argon carrier gas was allowed to follow at 200 ml. $min.^{-1}$ during dry and ash cycles and was interrupted at atomization.

TABLE I

Instrument settings

Dry	50 to 90°C, 30 sec
Dry	90°C, 60 sec
Ash	400 to 1500°C, 30 sec
Ash	1500°C, 15 sec
Atomize	2800°C, 7 sec
Clean	3000°C, 3 sec
Wavelength	193.7 nm
Slit Width	2.6 nm
Sample volume	20 μL

RESULTS AND DISCUSSION

To determine the optimum level of nickel nitrate required for the analysis, the recovery of arsenic from three different urine samples (each containing arsenic concentrations below the detection limit), spiked with 100 $\mu g . L^{-1}$ DMA was compared with the absorbance of aqueous 100 $\mu g . L^{-1}$ DMA at various nickel concentrations. The analyses were performed in duplicate and some representative data are presented in Table II.

TABLE II

Recovery of arsenic at various nickel concentrations

Conc. of Nickel Nitrate (%)	100 $\mu g . L^{-1}$ Aqueous DMA	Urine 1	Urine 2	Urine 3
		(All spiked with 100 $\mu g . L^{-1}$ DMA)		
		Absorbance (SD)		
10.0	0.164(0.002)	0.226(0.008)	0.238(0.005)	0.198(0.005)
5.0	0.232(0.012)	0.218(0.007)	0.216(0.002)	0.154(0.005)
1.0	0.282(0.009)	0.050(0.004)	0.128(0.001)	0.050(0.011)
0.5	0.285(0.008)	0.035(0.006)	0.072(0.004)	0.024(0.008)

From these results, the optimum concentration of nickel nitrate was found to be 5%. It is interesting to note that although the recovery of arsenic in urine increases with increased nickel, the absorbance of aqueous arsenic alone will decrease at high nickel concentrations. Thus the 5% nickel nitrate level represents a

compromise between absorbance of aqueous arsenic and its recovery from urine.

Clearly, the purity of the nickel nitrate is paramount. The nickel used here did not give any discernible signal even at concentrations of 20% (w/v).

Despite the fact that DMA is the major metabolite of arsenic excreted in urine, it is worthwhile to compare the recoveries of DMA versus inorganic arsenic from urine. In Table III, the recovery of DMA and inorganic arsenic from five different urine samples is referenced to the absorbance of $100\,\mu g.L^{-1}$ of aqueous inorganic arsenic solution. The analyses were performed in triplicate. Especially noteworthy, but not surprising, is the wide range of recoveries evidenced by the different urine samples. The results indicate that in some urines, recovery of DMA can differ from the recovery of inorganic arsenic. Therefore, some degree of error might be expected when analysing urines containing multiple species.

TABLE III

Recoveries of inorganic arsenic and DMA from urine compared with $100\,ug.L^{-1}$ aqueous inorganic arsenic solution.

Urine	Inorganic Arsenic	DMA
	% Recovery (SD)	
1	80(4)	82(2)
2	75(2)	75(1)
3	73(3)	73(2)
4	56(2)	49(4)
5	49(4)	42(2)

Many attempts were made during this study to normalize the recoveries of DMA in different urines such as the use of various tube types with and without graphite platforms, addition of other matrix modifiers, filtration of urine specimens, and digestion.

Pyrolytic graphite tubes gave significantly higher recoveries than plain tubes or cups. Use of graphite platforms coupled with the use of an optical temperature sensor (for maximum temperature rate rise) gave slightly higher recoveries but no other clear advantage.

Other elements added as matrix modifiers at various concentrations singly and in addition to nickel included Cu, Mg, Mo, Ca, Fe, Pt, and Al. Aluminum has been identified as the source of a spectral interference at 193.7 nm[7] but our data indicate that this interference is eliminated by the Zeeman effect at the levels examined here (up to 250 mg.L^{-1}).

Other than aluminum, which offered slightly higher recoveries in the presence of 5% nickel with some urines, no advantage was found in using any of the elements tested. Although the preliminary results with aluminum were interesting, it was not considered significant enough to justify its routine use at this time.

Filtration of urine samples (0.45 μm) or digestion with HNO_3 and H_2O_2 in a Teflon bomb also did not offer any advantage in normalizing DMA recoveries in various urines.

Figure 1 illustrates the effect of ashing temperature on the absorbance and background of a urine sample spiked with 100 μg.L^{-1} DMA. An ashing temperature of 1500°C was found to be high enough to eliminate background problems and no loss of DMA was noted below 1800°C.

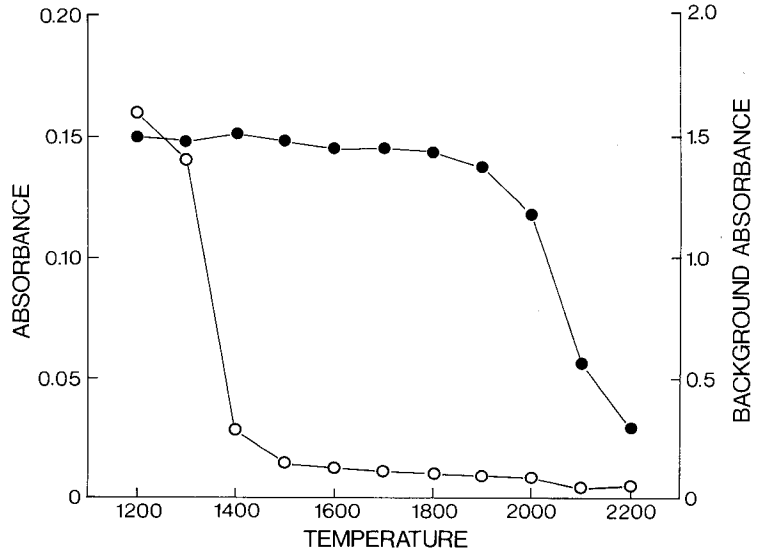

FIGURE 1 Ashing curve of 100 ug.L^{-1} DMA in urine with 5% nickel nitrate. Absorbance ●-●-●-●, Background Absorbance ○-○-○-○.

Tube life was in the order of 80-100 firings. This agrees with the finding of Chakraborti *et al*[1] who reported that high ashing temperatures dramatically extend tube life in the presence of nickel salts in arsenic determinations.

The same five urine samples from Table III, which were chosen because of their widely different recoveries, were each analyzed by the method of additions. All were found to have arsenic levels below the detection limit ($10\,\mu g.L^{-1}$). They were then spiked with $100\,\mu g.L^{-1}$ DMA each. Aliquots of each were either left at room temperature or refrigerated at 4°C. Some of the refrigerated samples developed precipitates and hence all were agitated before drawing a sub-sample. These precipitates resolubilized on addition of the nickel solution and therefore were no problem.

Each sample was then analyzed six times by the method of additions at irregular intervals over a period of ten days. This between-run evaluation yielded a mean concentration of $97.9\,\mu g.L^{-1}$ with a standard deviation of $7.1\,\mu g.L^{-1}$ and CV of 7.3%. The range was $89.0–112.8\,\mu g.L^{-1}$. No difference was observed between refrigerated and non-refrigerated samples. The mean correlation coefficient for the standard addition curves over the 30 analyses was found to be 0.9952.

Correlation coefficients for a wider range of arsenic concentrations were determined by spiking urines 1, 3 and 5 (from Table III) with DMA concentrations of 25, 100 and $500\,\mu g.L^{-1}$ each and analysing as previously described. The correlation coefficients for these standard addition curves were 0.9997, 0.9994 and 0.9992 respectively.

Within-run precision was assessed by spiking a pooled urine sample with $100\,\mu g.L^{-1}$ DMA and injecting it 30 times into the furnace and comparing the absorbance with an aqueous standard at the same concentration. No attempt was made to obtain or normalize to 100% recovery, but simply to evaluate the stability of repeated injections. The mean value obtained was $84.5\,\mu g.L^{-1}$ with a SD of $2.0\,\mu g.L^{-1}$ and CV of 2.4%. The range was 81.1 to $88.7\,\mu g.L^{-1}$.

Ortho Control Urine II—arsenic value $162\,\mu g.L^{-1}$ (arsine method) with an expected range of $\pm 50\,\mu g.L^{-1}$ was analyzed in triplicate by standard addition. A value of $173.6 \pm 2.0\,\mu g.L^{-1}$ was obtained, yielding a recovery of 107%.

The detection limit for this method was assessed by taking the

average standard deviation of several triplicate analyses made at the blank level = 2.5 $\mu g . L^{-1} \times 2$ (the urine dilution factor) $\times 2 =$ 10.0 $\mu g . L^{-1}$.

This procedure allows for the simple, direct determination of elevated arsenic in urine. Since this method will measure inorganic arsenic as well as DMA no speciation information is obtained. Therefore, because of this, and also the possibility of the presence of other compounds originating from the consumption of seafood, elevated levels that may be found in this manner should be investigated further.

The analyses of urines in triplicate allow for high precision, but for more rapid screening where high precision might not be necessary, duplicate or even single analyses could be performed.

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