

Short communication

Characterization of arsenic (V) and arsenic (III) in water samples using ammonium molybdate and estimation by graphite furnace atomic absorption spectroscopy

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Abstract

Arsenic (V) is known to form heteropolyacid with ammonium molybdate in acidic aqueous solutions, which can be quantitatively extracted into certain organic solvents. In the present work, 12-molybdoarsenic acid extracted in butan-1-ol is used for quantification of As (V). Total arsenic is estimated by converting arsenic (III) to arsenic (V) by digesting samples with concentrated nitric acid before extraction. Concentration of As (III) in the sample solutions could be calculated by the difference in total arsenic and arsenic (V). The characterization of arsenic was carried out by GFAAS using Pd as modifier. Optimization of the experimental conditions and instrumental parameters was investigated in detail. Recoveries of (90–110%) were obtained in the spiked samples. The detection limit was $0.2 \mu\text{g l}^{-1}$. The proposed method was successfully applied for the determination of trace amount of arsenic (III) and arsenic (V) in process water samples.

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1. Introduction

Arsenic is a ubiquitous element, which occurs, in the form of various chemical species. It has been shown that both trivalent and pentavalent inorganic arsenic compounds in solution are readily absorbed after ingestion. The toxicity of arsenic is well documented and that it depends on its valence state (zero-valent, trivalent or pentavalent), its form (inorganic or organic), and the physical aspects governing its absorption and elimination is well established [1,2]. General, inorganic arsenic is more toxic than organic arsenic, and trivalent arsenite is more toxic than pentavalent and zero-valent arsenic. Quantification of the different species remains a challenge as the concentrations in real samples remain at the lower limit of detection [3,4].

Separation and preconcentration of total arsenic by distillation of trichloride or bromide, extraction of silverdiethyldithiocarbamate, molybdenum blue complex, coprecipitation with

Fe (III) hydroxide, Ce, Zr hydroxides, thioanilide and Nipyrrolidinedithio carbamate [5–10] have been reported.

Many analytical techniques like HG AAS [12], HG-AFS [13], ICP-AES [4], ETAAS [11,12], EDXRF [19], NAA [17], photometric analysis [18], IC-ICP-AES [20,21], IC, HPLC [24], ICP-MS [22,23], cathodic and anodic stripping voltammetry [14–16] have been used for the determination of low levels of arsenic. Gas phase Chemiluminescence Analyser is presented by Toda and co-workers [27], for field estimations of waterborne arsenic. ICP-MS is known to have superior detection [25] limits but it also has instrumental limitations in addition to being expensive. GFAAS is a sensitive technique and has been commonly used for the determination of trace impurities in a variety of matrices. The long residence times and efficient sample delivery enable the detection limits to surpass even those of ICP-MS [25].

Wadelin and Mellon [26] developed a procedure for the colorimetric estimation of arsenic by measurement of its 12-molbdoarsenic acid. It is known that only As (V) forms this complex, but not As (III). We have used this idea and developed a sensitive, accurate and rapid method for the quantification of

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As (V) and As (III) in natural and process water. The arsenic is then characterised by GFAAS.

2. Experimental

2.1. Instrumentation

GBC 906AA AAS unit with deuterium correction, GF 3000 Electro Thermal Atomiser and PAL 3000 auto sampler were used in the present investigation. Pyrolytic graphite coated furnaces were used in all the studies. The elemental hollow cathode As $\lambda_{193.7}$, lamp manufactured by GBC Australia was used.

All containers and glassware were cleaned by soaking successively in three baths of 10, 1 and 0.1% double distilled nitric acid in nanopure water. All glassware was stored in 0.1% nitric acid baths till further use.

A ceramic top Thermolyne Barnstead hot plate was used for sample treatment. All dilutions, dissolutions were carried out in an Ultra Trace Analytical Facility provided with Class 100 LAF working benches.

2.2. Reagents

Supra pure nitric acid 65%, Supra pure hydrochloric acid 35% from E. Merck Darmstadt, Germany was used for all sample treatment. Nanopure water of 18.3 M Ω delivered from Barnstead Thermolyne Water Purification System was used for all dilutions. Standard solutions of As (V) were prepared by suitable dilution of certified AAS standard solution (1 mg ml⁻¹) from E. Merck Darmstadt. Arsenic (III) solution was prepared by dissolving sodium arsenite in 5% hydrochloric acid. Palladium nitrate and nickel nitrate were prepared by dissolving weighed quantities in nitric acid and making up to volume. Ammonium molybdate, G.R. Sarabhai M Chemicals Ltd.: 1% solution was prepared. This solution was cleaned by extraction with 20 ml butan-1-ol. Butan-1-ol, Analar Grade, Glaxo Ltd., was used without any purification. Argon gas was used as a carrier and sheath gas for AAS.

2.3. Procedure

A suitable aliquot of sample solution (50–200 ml, containing 5–50 ng As) was taken in a beaker and solution was made 2 M wrt nitric acid. Ten milliliters of the cleaned 1% ammonium molybdate solution was added. The sample solution was transferred to 250 ml separating funnel. Ten milliliters of butan-1-ol is added and the contents briskly shaken. The two phases were allowed to separate. The lower aqueous phase was rejected and the organic phase was transferred to a standard flask.

The same aliquot of sample solution was transferred to another beaker, acidified with nitric acid and warmed on hot plate and extracted as above. Blank was run through the same protocol.

Standard As solution was carried through the same protocol.

All analysis was carried out on GBC 906AA AAS. The sample butan-1-ol extract and standard arsenic butan-1-ol extract were injected into the graphite furnace using an auto sampler.

Table 1a
Instrumental conditions for arsenic

Element	Arsenic
Wavelength (nm)	193.7
Lamp current (mA)	8.0
Slit width (nm)	1.0
Argon carrier gas (L/min)	2

Table 1b
Optimised graphite furnace parameters

Process	Final temperature °C	Ramp time (s)	Hold time (s)	Gas type
Drying	90	10	5	Inert
	120	10	10	
	300	10	10	
	600	5	5	
Ashing	1300	5	5	None
	1300	0	1	
Atomization	2300	1	2	Inert
Tube clean	2500	1	2	

Aqueous arsenic standards were also run directly along with the organic extracts. The required amounts of each were adjusted using the auto mix function of the auto sampler. Twenty micrograms palladium was used as modifier in the estimation of volatile As. Optimized furnace programme was employed for carrying out the analysis (Tables 1a and 1b).

3. Results and discussion

In order to optimize the analytical procedure, the possible effects of several variable factors were studied.

3.1. Effect of acidity

The effect of varying acidity of aqueous solutions of 12-molybdoarsenic acids was first studied. Acidity of the solution was varied from 0.2 to 4 M using HCl in synthetic water samples containing 10 ng ml⁻¹ of As (V) and 10 ml of 1% ammonium molybdate was added to sample solutions and then it was extracted using 10 ml butane-1-ol. The absorbance was plotted against the concentration of HCl (Fig. 1). It can be seen that at absorbance value is increasing with the concentration of HCl up to 2 M and remains constant thereafter.

The effect of varying concentration of nitric acid on extraction efficiency was determined, using of equivalent amounts of HNO₃. It was observed that it could be used interchangeably with HCl without affecting the results. Therefore, for further investigation, acidity was maintained to 2 M.

3.2. Effect of molybdate concentration

The effect of changing ammonium molybdate concentration was studied by preparing similar synthetic samples. The procedure was same as used for studying effect of acidity. Acidity was maintained constant to 2 M. Amount of 1% ammonium molyb-

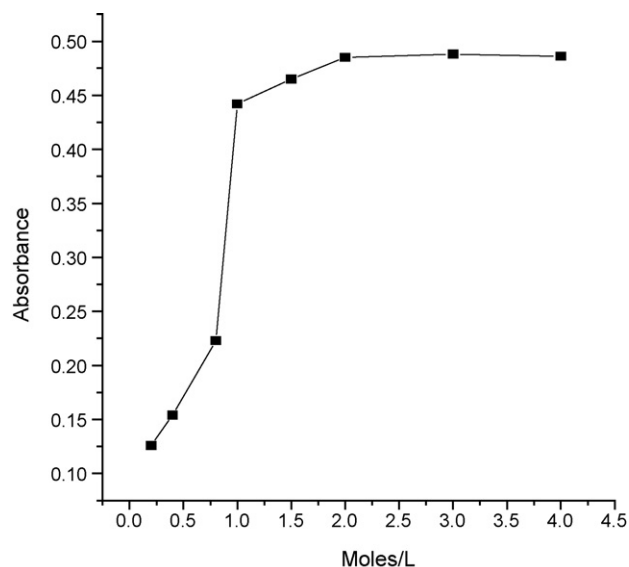


Fig. 1. Optimization of HCl concentration. Experimental conditions as given in Tables 1a and 1b. Concentration of As (V) 10 ng ml^{-1} .

date varied from 10 to 50 ml. It was observed that the absorbance for 10 ng ml^{-1} of As (V) remains constant. Therefore, 10 ml of 1% ammonium molybdate was used for analysis.

3.3. Estimation by GFAAS

3.3.1. Optimization of furnace ashing and atomization temperature

Optimization of furnace conditions were important so that the maximum ashing temperature and minimum atomization temperature was arrived at, so that minimum matrix effect and extended life of tube could be effected. Volatility of arsenic compounds ensures the use of matrix modifiers to obtain reproducible analyte signals. Therefore, it was felt necessary to reestablish the conditions for 12-molybdoarsenic acid in butan-1-ol. $20 \mu\text{g}$ Pd was used as modifier in all our studies.

In the present work, we are injecting an organic solvent into the furnace. In order to avoid spitting and bubbling causing loss of analyte we have used a four step drying cycle, 90, 120, 300 and 600°C with a 35 s ramp mode and 30 s hold mode.

To optimize the ashing temperature the recommended atomization temperature of 2300°C was chosen and the ashing temperature was varied in steps of 100°C , starting from 600 to 1600°C . In the peak area mode the absorbance values showed a decline in absorbance from 600 to 1000°C after which there was a rise which remained constant from 1200 to 1400°C , after which there was a decrease in the analyte signal. In the peak height mode there was no significant change in absorbance with an increase in atomization temperature. Keeping the ashing temperature at 1300°C the atomization temperature was then varied in steps of 100°C from 2000 to 2500°C . Fig. 2 shows that in the peak area mode the analyte signal reached a well defined plateau between 2200 and 2400°C after which a decrease in signal was seen. The peak area mode gave better calibration linearity. In the peak height mode it was observed the absorbance

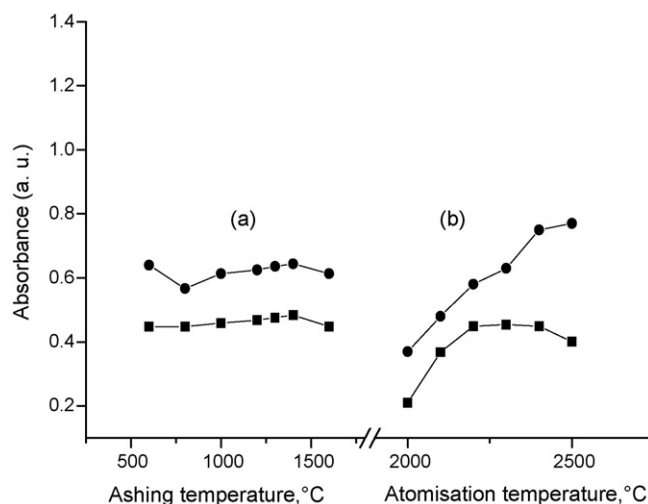


Fig. 2. (a and b): Optimization of heating temperature and absorbance's of arsenic. Ashing time: 76 s, atomization time: 3 s. Each point represents absorbance for a 10 ng ml^{-1} As (●) peak height absorbance (■) peak area absorbance.

slightly increased with increase in temperature. Ashing temperature of 1300°C , atomization temperature of 2300°C and peak area mode was used in all further studies. Instrument settings and optimised graphite furnace parameters are as shown in Tables 1a and 1b.

3.3.2. Optimization of the amount of modifier

Nickel is commonly used to stabilize arsenic in furnace estimation, however, palladium is reported to have superior properties, therefore, we have investigated the effect of Ni and Pd on

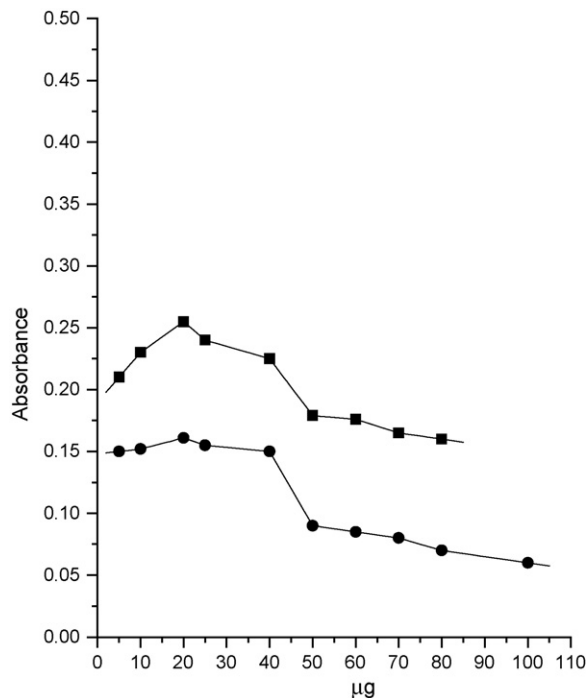


Fig. 3. Optimization of modifier concentration. Experimental conditions as given in Tables 1a and 1b. Concentration of As (V) 5 ng ml^{-1} ; (■) Pd as modifier (●) Ni as modifier.

the absorption signal of arsenic. The effect of the amount of Pd and Ni on the arsenic signal was studied using 5 ng of As (V). The amount of Pd was varied from 10 to 80 μg and that of Ni from 5 to 100 μg . It was observed that a concentration of 10–40 μg of Pd and 5–20 μg of Ni gave optimum absorbance. As depicted in Fig. 3, absorbance value observed using Pd is 1.6 times greater than signal obtained using Ni, therefore, 20 μg of Pd was used in all experiments for optimal results.

3.4. Construction of calibration curve

Standard arsenic (V) solution 5–500 ng ml^{-1} were taken in glass beakers and made up to 50 ml with 2N nitric acid, 10 ml of 1% cleaned ammonium molybdate solution was added. The solution was transferred to separating funnel, 10 ml of butan-1-ol are added and contents briskly shaken. The two phases were allowed to separate. The lower aqueous phase was rejected and the organic phase was transferred to a standard flask.

The extracted standard solutions of 5–500 ng ml^{-1} and the acidic unextracted arsenic standard solution were injected into the graphite furnace using an auto sampler. The required amounts of each were adjusted using the auto mix function of the auto sampler. Twenty micrograms palladium was used as modifier and optimized furnace programme was employed for carrying out the analysis.

Fig. 4 shows a calibration curve obtained using aqueous and extracted standards. It was found that there was no significant difference between their absorbance. The graph was linear from up to 100 ng ml^{-1} arsenic, the slope of which was 0.0036, $\sigma = \pm 0.012$, $R = 0.9966$.

3.5. Optimization of sample volume and recovery studies

Optimization of sample volume was carried out by standard addition and recovery studies were carried out by spiking

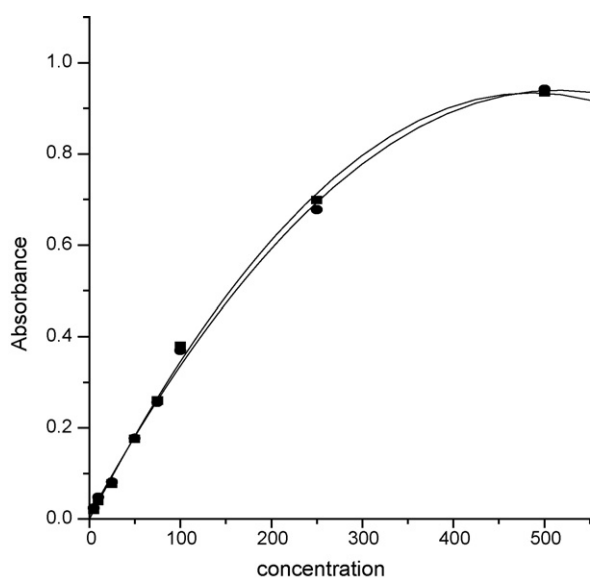


Fig. 4. Calibration plot of 12-molybdoarsenic acid. (●) Butane-1-ol (■) water; experimental conditions as given in Tables 1a and 1b.

Table 2
Standard addition and recovery studies

Element	(Sample volume 100 ml) Added (ng)	Recovered	
		Extracted (ng)	Extracted after oxidation (ng)
As (V) $n = 4$	50	48 \pm 2	49 \pm 1
	100	98 \pm 2	97 \pm 3
	200	203 \pm 3	197 \pm 2
As (III) $n = 3$	50	Nil	47 \pm 2
	100	Nil	102 \pm 2
	200	Nil	205 \pm 4
As (III) and As (V) of each $n = 3$	50	49 \pm 1	104 \pm 2
	100	101 \pm 2	216 \pm 3
	200	198 \pm 2	396 \pm 3

Table 3
Determination of As (III), (V) in process water sample

Sample No.	As (V) $\mu\text{g ml}^{-1}$	Total arsenic $\mu\text{g ml}^{-1}$	As (III) $\mu\text{g ml}^{-1}$
1	0.37 \pm 0.02	0.52 \pm 0.04	0.15 \pm 0.03
2	0.34 \pm 0.03	0.44 \pm 0.05	0.10 \pm 0.04
3	0.73 \pm 0.05	0.76 \pm 0.04	<0.01

known concentration of As (III) and As (V) to varying volumes of water sample to ensure that there was no loss and that there was quantitative crossover during the oxidation and extraction process. Fifty, 100, 200 and 500 ml sample volumes were treated and extracted with 10 ml butan-1-ol. The recovery ranged between 90 and 110%, for sample volume up to 200 ml, which is satisfactory considering the low levels of concentration measured. There was no statistically significant difference observed between obtained and expected values. In the absence of a reference standard the recovery studies adequately validate our procedure as shown in Table 2.

The detection limit, which was calculated from three times the standard deviation of 200 ml procedural blank, was 0.2 ng ml^{-1} . The concentration factor for arsenic was 20.

This procedure is routinely used to determine As (V) and As (III) in process water samples provided by Desalination Division, BARC as shown in Table 3.

4. Conclusions

We have presented a fast, reliable, sensitive and accurate method with a concentration factor of 20, for the determination of As (III) and (V) in environmental and process water samples. As (V) was separated quantitatively as 12-molybdoarsenic acid in butane-1-ol from 2 M acidic solution leaving behind As (III). After simple oxidation with nitric acid, converting As (III) to As (V), total arsenic was determined. The concentration of As (III) could be calculated by difference in the concentration between total As (V), (III) and As (V). The detection limit for arsenic was 0.2 $\mu\text{g l}^{-1}$. The standard deviation and coefficient of variation for 10 ng arsenic at 95% C.L. was ± 0.04 and 0.4% respectively.

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