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Evaluation of Atomic Fluorescence Spectrometry as a Sensitive Detection Technique for Arsenic Speciation

J. L. Gomez-Ariza,[1]* D. Sánchez-Rodas,[1] R. Beltran,[1] W. Corns[2] & P. Stockwel[2]
[1]Departamento de Química y Ciencia de los Materiales, Escuela Politécnica Superior, Universidad de Huelva, Huelva, Spain
[2]PS Analytical Ltd, Arthur House, Unit 3, Crayfields Industrial Estate, Main Road, St Pauls Cray, Orpington, Kent BR5 3HP, UK

The potential of coupling anion-exchange high-performance liquid chromatography, hydride generation and atomic fluorescence spectrometry (HPLC–HG–AFS) for arsenic speciation is considered. The effects of hydrochloric acid and sodium tetrahydroborate concentrations on signal-to-background ratio, as well as argon and hydrogen flow rates, were investigated. Detection limits for arsenite, dimethylarsinic acid (DMA), monomethylarsonic acid (MMA) and arsenate were 0.17, 0.45, 0.30 and 0.38 $\mu g\, l^{-1}$, respectively, using a 20-μl loop. Linearity ranges were 0.1–500 ng for As(III) and MMA (as arsenic), and 0.1–800 ng for DMA and As(V) (as arsenic). Arsenobetaine (AsB) was also determined by introducing an on-line photo-oxidation step after the chromatographic separation. In this case the limits of detection and linear ranges for the different species studied were similar to the values obtained previously for As(V). The technique was tested with a human urine reference material and a volunteer's sample. © **1998 John Wiley & Sons, Ltd.**

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* Correspondence to: J. L. Gomez-Ariza, Departamento de Química y Ciencia de los Materiales, Escuela Politécnica Superior, Universidad de Huelva, Huelva, Spain.

INTRODUCTION

The toxicity and biochemical behaviour of arsenic species rely on their chemical forms.[1,2] The presence of these species in the environment is due to both natural and anthropogenic sources. The toxic inorganic arsenic species (arsenite and arsenate) can be biomethylated by bacteria, fungi, algae, invetebrates and man to yield monomethylarsonic acid (MMA) and dimethylarsinic acid (DMA), which are considered less toxic than the inorganic forms. Other organic compounds, such as arsenobetaine (AsB) and arsenocholine (AsC), and tetramethylarsonium (Me_4As^+) are believed to be the most important organoarsenic compounds in marine invertebrates and fish. They are considered virtually non-toxic and can be found in human urine because they are present in dietary sources.

The speciation of arsenic compounds has been achieved with the use of hyphenated techniques, combining separation processes with a suitable detector. High-performance liquid chromatography (HPLC) is usually preferred as a separation technique rather than gas chromatography (GC) because the latter requires a previous derivatization step to produce volatile substances, which is not always feasible. The separation of arsenic species with HPLC has usually been accomplished with the use of either ion-exchange or ion-pair reverse-phase columns.[3,4,5] HPLC has been coupled with different atomic spectrometry techniques in order to improve the sensitivity. Direct coupling between HPLC and inductively coupled plasma atomic emission spectrometry (ICP–AES)[6] provides limits of detection for the different species of arsenic between 19 and 41 ng. Coupling HPLC directly with inductively coupled plasma mass spectrometry (ICP–MS)[7] improves the absolute detection limits to between 50 and 300 pg although this coupling is susceptible

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to interference from samples with high chloride content, such as urine or marine samples.

Another approach is based in the introduction of a hydride generation (HG) step after the chromatographic separation, with conversion of the arsenic compounds into volatile arsines. Limits of detection between 3.5 and 21.3 $\mu g\,l^{-1}$ have been reported for the HPLC–HG–ICP–AES coupling[8] (using a 100-l sample loop), and between 1.0 and 4.7 $\mu g\,l^{-1}$ for HPLC–HG–AAS[9] (with a 50-µl loop). These levels are sometimes not low enough to detect the arsenic species present in water or biological samples. Better results are obtained with the HPLC–HG–ICP–MS[10] coupling, with a limit of detection for As(III) of 0.46 $\mu g\,l^{-1}$.

There are also some non-reducible organic compounds of arsenic, such as arsenobetaine (AsB), that do not form volatile hydrides, and which have been identified mainly in marine organisms,[11] but also in human urine, due to the ingestion of marine products.[12] In order to detect them, different authors have proposed on-line oxidation of these compounds based on the use of microwave[13] or ultraviolet[8] radiation in the presence of an oxidant medium.

Atomic fluorescence spectrometry (AFS) has been used as analytical technique since 1964 and numerous papers has been focused on the use of this technique because of its flexibility in single- and multi-elemental determinations with a wide variety of light sources, atomizers, optical designs and electronics.[14] However, a lack of commercially available spectrometers has caused the application of AFS to be restricted in the field of element-specific detection for chromatography by interfacing commercially available AAS or ICP–AES spectrometers with the chromatograph. Generally, a remarkable difference between detection limits is peculiar to AFS, depending on both the atomizer and light source selected. The use of cold vapour or hydride generation allows very low detection limits, as do intense light sources such as microwave-excited or radio-frequency Electrodeless Discharge Lamp EDLs[15] available for As, Sb, Bi, Se, Te, Sn, Pb and Hg. In addition, flame AFS with boosted-discharge hollow-cathode lamps[16,17] (BDHCLs) is comparable with ICP–AES for many elements.

Atomic fluorescence spectrometry has been used for the detection of arsenic hydrides in the ultraviolet spectral region, due to the small background emission produced by the relatively cool hydrogen diffusion flame. The technique can now be used for arsenic speciation by interfacing HPLC with commercially available AFS spectrometers based on the BDHCL.[16] Woller *et al.*[18] proposed the use of ultrasonic nebulization to convert the arsenic species separated in the HPLC device into aerosols, which are introduced into a hydrogen–argon flame. With this approach, detection limits between 20 to 50 ng were obtained (for a 250-µl injection). Le *et al.*[19] coupled ion-pair HPLC with AFS for arsenic speciation using hydride generation for sample introduction into the detector, and applied the procedure to biological samples. However, no data were provided about either hydride generation optimization or the performance of the procedure.

In this paper we propose the use of a strong anion-exchange chromatographic separation for the speciation of four arsenic compounds (arsenite, arsenate, monomethylarsonate, dimethylarsinate) followed by hydride generation with hydrochloric acid (HCl) and sodium tetrahydroborate ($NaBH_4$) gas–liquid separation of the volatile arsines and detection by atomic fluorescence spectrometry in a hydrogen–argon diffusion flame (HPLC–HG–AFS). The effects of hydrogen and argon flows on the net signal-to-background ratio (SBR), as well as the effect of HCl and $NaBH_4$ concentrations, were investigated. Linear ranges, detection limits and reproducibility are also reported. In order to determine arsenobetaine, we introduced an on-line photo-oxidation step after the chromatographic separation, by adding a basic solution of potassium persulphate in a reaction coil wrapped around a low-pressure mercury lamp that emits UV radiation (HPLC–UV–HG–AFS). The method has been tested on a commercial lyophilized urine sample and urine from a volunteer.

EXPERIMENTAL

Instrumentation

A Spectra Physics 1000 HPLC pump and a six-port 7125 injection valve (Rheodyne, CA, USA) were used in conjuction with a strong anion-exchange column (Hamilton PRP X-100). A manually controlled electrical valve made it possible to perform a gradient program. Hydride generation was carried out with a peristaltic pump (PS Analytical, Kent, UK). Arsines were detected by an AFS detector (PSA Excalibur: PS Analytical, UK) equipped with an arsenic boosted-discharge hollow cathode lamp (Super lamp; Photron, Victoria, Australia). Measurements were performed

Table 1 Instrumental parameters for the HPLC–HG–AFS coupling

HPLC parameters	
Column	Hamilton PRP-X100 (250 mm × 4.1 mm i.d., 10 μm particle size)
Mobile phase	10 mmol l^{-1} and 60 mmol l^{-1} potassium phosphate (K_2HPO_4 and KH_2PO_4) adjusted to pH 5.75
Injected volume	20 μl
Flow rate	1 ml min^{-1}
Gradient elution	0 to 2.1 min: 10 mmol l^{-1} phosphate 2.1 to 6.1 min: 60 mmol l^{-1} phosphate 6.1 to 12.0 min: 10 mmol l^{-1} phosphate
Photo-oxidation	
$K_2S_2O_8$	2% (w/v) in 2% (w/v) NaOH; 0.3 ml min^{-1}
UV source	Low-pressure mercury lamp, 15 W
HG parameters	
Acid solution	1.5 mol l^{-1} HCl or 8 M (with photo-oxidation); l ml min^{-1}
Reducing agent	1.5% (w/v) $NaBH_4$ in 1% (w/v) NaOH; 1 ml min^{-1}.
Main Ar flow rate	200 ml min^{-1} at the gas–liquid separatator
Auxiliary Ar flow rate	100 ml min^{-1}
AFS parameters	
Hydrogen flow rate	60 ml min^{-1}
Wavelengths	197.3 nm, 193.7 nm, 189.0 nm
Bandwidth	20 nm
Primary current	27.5 mA
Boost current	35.0 mA

at three resonance wavelengths of arsenic, viz. 197.3, 193.7 and 189.0 nm, with a spectral bandpass of 20 nm. Argon was used as carrier gas in a glass gas–liquid separator and was dried with a hygroscopic membrane drying tube (Perma Pure Products, Farmingdale, NJ, USA). Air was used as the drying gas at a flow rate of 2.5 l min^{-1}. A lateral auxiliary flow of argon was also used, to improve the separation. The signal output of the AFS was recordered with either a potentiometer chart recorder or a computer with chromatographic software (Ezchrom: Scientific Software Ltd, CA, USA). The optional on-line photo-oxidation step was performed with the aid of a low-pressure mercury lamp (TNN 15/32, 15 W: Heraeus, Germany). Optimal instrumental parameters are given in Table 1.

Reagents

Stock standard solutions were prepared as follows. A 1000 mg l^{-1} arsenite solution was prepared by dissolving 1.320 g of arsenic trioxide (Merck) primary standard in NaOH (4 g l^{-1}) solution. Arsenate, MMA and DMA solutions (each at 1000 mg l^{-1}) were prepared by dissolving in water the appropriate amounts of $Na_2HAsO_4{\cdot}7H_2O$ (Merck), $CH_3AsO(ONa)_2{\cdot}6H_2O$ (Carlo Erba) and $(CH_3)_2AsHO_2$ (Sigma), respectively. Arsenobetaine (AsB; $(CH_3)_3As^+ \cdot CH_2COO^-$) was supplied by Dr Foulkes (University of Plymouth, UK). Deionized water (Elga Ltd, High Wycombe, UK) was used to prepare the solutions. Working diluted solutions were prepared daily.

Potassium dihydrogen phosphate and dipotassium hydrogen phosphate (Aldrich), hydrochloric acid (Analar, BDH), potassium persulphate (Aldrich), NaOH (Merck) and $NaBH_4$ (Aldrich) were of analytical grade or better. The $NaBH_4$ solution was not filtered before use, and was prepared daily. Samples were filtered through a 0.45-μm PTFE membrane (Minisart SRP 15: Sartorius AG, Germany).

Procedure

For the analysis of reducible species, a 20 μl portion of sample solution was injected into the HPLC strong anion-exchange column and subjected to a gradient of 10–60 mmol l^{-1} phosphate solution, following the gradient conditions recommended by Rubio *et al.*[20] for this type of column. Samples were filtered through a 0.45-μm PTFE filter. The separation of the different arsenic species took places in less than 10 min, with a mobile phase flow rate of 1 ml min^{-1}. The hydride generation of the arsines was carried out by adding 1.5 M HCl and 1.5% (w/v) $NaBH_4$ in 1.0% (w/v) NaOH with a peristaltic pump, both at a 1 ml min^{-1} flow rate. The volatile arsines passed to the gas–liquid separator where an argon flow of 200 ml min^{-1} carried them to the detector. Before the detection,

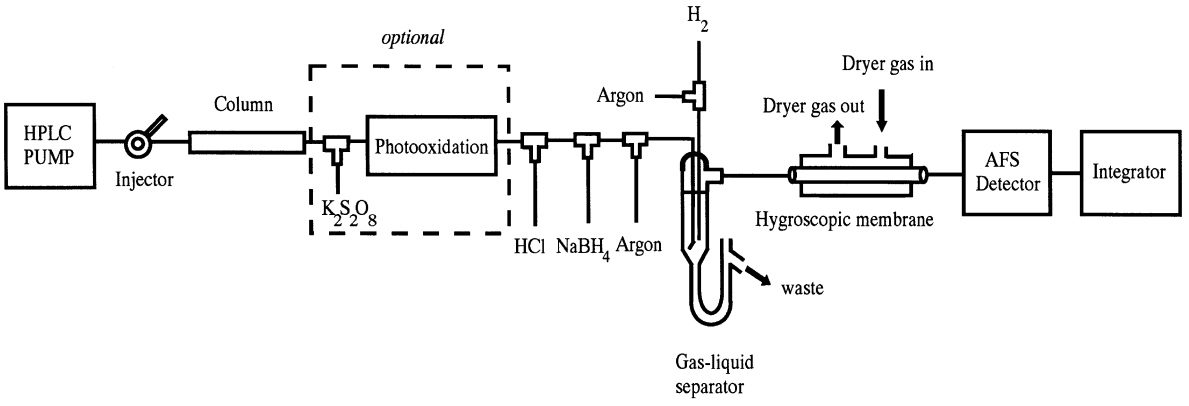

Figure 1 Operating scheme for the HPLC–HG–AFS coupling.

the argon stream was dried with a hygroscopic membrane drying tube. A lateral flow of argon of 100 ml min^{-1} after the hydride generation improved the transport of the arsines to the gas–liquid separator. A flow of 60 ml min^{-1} hydrogen was added at the gas–liquid separator in order to maintain the argon–hydrogen diffusion flame. Peak heights or peak areas were considered during the different experiments. The operating scheme is shown in Fig. 1.

Optionally, for the analysis of arsenobetaine, a photo-oxidation step was introduced after the chromatographic separation, using a similar device to that described by Rauret *et al.*,[8] adding a 0.3 ml min^{-1} flow of a 2% (w/v) potassium persulphate solution [in 2% (w/v) NaOH] at the outlet of the column. The different arsenic species were oxidized to arsenate in an 8 m Teflon tube (i.d. 0.3 mm) wrapped around a low-pressure mercury lamp that emitted UV radiation at 254 nm.

RESULTS AND DISCUSSION

Effects of HCl and $NaBH_4$ concentrations on the SBR

The hydride generation step was optimized by changing the concentration of HCl and $NaBH_4$ while keeping the other parameters constant. These fixed parameters were 80 ml min^{-1} hydrogen, 200 ml min^{-1} argon as principal carrier and 100 ml min^{-1} argon as auxiliary flow. The flow rates of HCl and $NaBH_4$ were kept at 1 ml min^{-1}.

Optimization of HCl concentration was carried

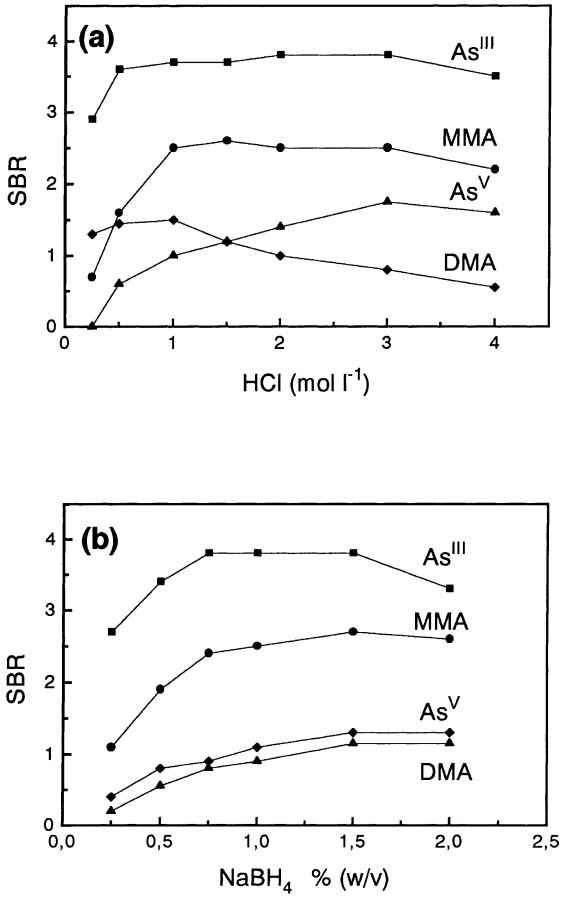

Figure 2 Effect of experimental variables on arsine generation from a mixture of As(III), DMA, MMA and As(V) containing 50 μg l^{-1} of each: (a) Influence of HCl concentration; (b) influence of $NaBH_4$ concentration.

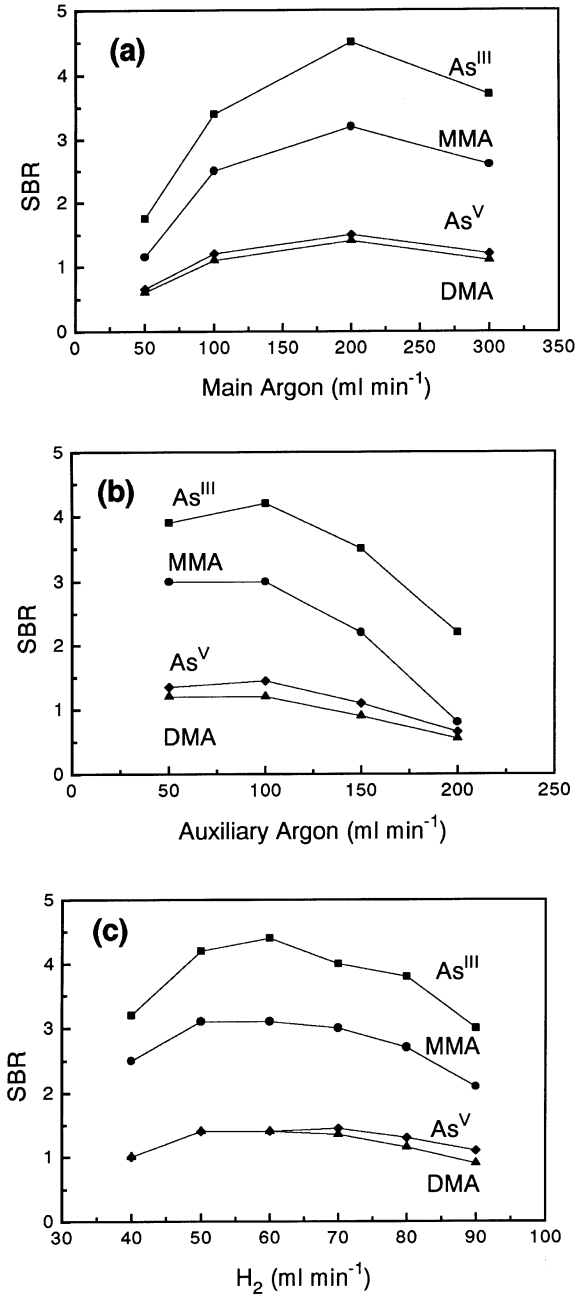

Figure 3 Effect of experimental variables on arsine generation from a mixture of As(III), DMA, MMA and As(V) containing 50 μg l^{-1} of each: (a) influence of main argon flow; (b) influence of auxiliary argon flow; (c) influence of hydrogen flow.

out up to the maximum value of 4 mol l^{-1} recommended by the manufacturers for inorganic arsenic with the AFS detector. Figure 2(a) shows the effect of different concentrations of HCl on the signal-to-background ratio (SBR) for As(III), DMA, MMA and As(V), each at a 50 μg l^{-1} concentration (as As), when using a 1.5% (w/v) $NaBH_4$ [in 1% (w/v) NaOH] solution. The signal for DMA decreases with the acidity and the corresponding signal of As(V) increases. The responses of As(III) and MMA show high values of SBR for HCl concentrations from 1 to 4 mol l^{-1}. Therefore, a compromise concentration of 1.5 mol l^{-1} HCl was chosen.

The same experiment was performed with the $NaBH_4$ concentration while maintaining the acid concentration at 1.5 mol l^{-1}. All $NaBH_4$ solutions tested were stabilized in 1% (w/v) NaOH. Figure 2(b) shows that DMA, MMA and As(V) have higher SBR values when the $NaBH_4$ concentration is increased. A value of 1.5% (w/v) was chosen as the optimal concentration. At concentrations above this value a considerable increase in the flame noise was observed.

Effect of the argon flow rates on the SBR

Gas–liquid separation of the arsines has an important influence on the signal. Two argon flows reached the gas–liquid separator: the main one carried the arsines to the detector, while an auxiliary flow of argon was added after the hydride generation step in order to obtain fast transportation of the arsines to the separator, reducing the noise of the net signal and baseline and thus improving the shape of the peaks. Figure 3(a) shows that a flow of 200 ml min^{-1} gives the optimal SBR value when keeping a fixed auxiliary flow of 100 ml min^{-1}.

The auxiliary argon flow was optimized following a similar procedure (Fig. 3b), fixing the value of the main argon flow at 200 ml min^{-1}. The background was found to increase slightly with higher rates, but the net signal decreased sharply. Hence, the auxiliary flow was kept at 100 ml min^{-1}.

Effect of the hydrogen flow rate on the SBR

Hydrogen was found to be an important source of the background (Fig. 3c). Flow rates above 70 ml min^{-1} produced a significant increase in the background while the net signals were maintained for the four species studied, thus lowering the SBR values. On the other hand, flow rates lower than 50 ml min^{-1} resulted in poor net signals and also made the flame rather unstable. Therefore, a flow of

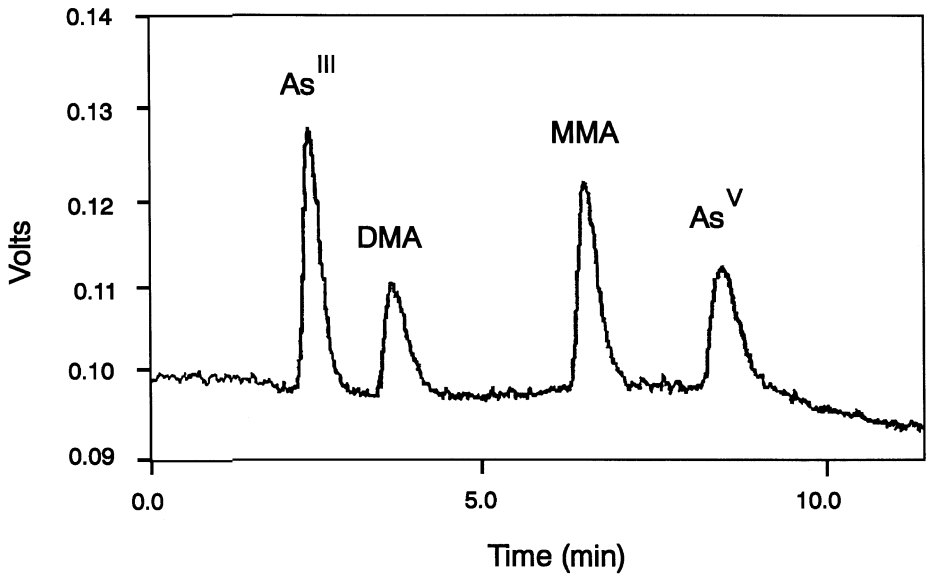

Figure 4 Chromatogram obtained with the instrumental conditions described in Table 1. Amount of each compound injected, 5 μg l^{-1} (as As).

60 ml min^{-1} was selected as optimum. Figure 4 shows a typical chromatogram of the four species studied (each at a concentration of 5 μg l^{-1} as As) after optimization of the different variables. Sensitivity was in general very high, although lower responses were obtained for DMA and As(V), probably because of the poor efficiency of hydride generation for these two species.

Calibration graphs, precision and limits of detection

One of the main advantages of using AFS is that the linear range for arsenic compounds covers five orders of magnitude. Therefore the Excalibur detector has four amplification ranges, allowing detection of absolute arsenic mass values between picogram and nanogram levels. Table 2 summarizes calibration data in different ranges using peak areas and employing five points for each calibration. The relative standard deviation (R.S.D.) for ten replicates at the lower standard of each calibration line are also given. Detection limits were calculated as 3 × standard deviation (σ_{n-1}) for ten replicates of known low concentration (1 μg l^{-1} standard solution for each arsenic compound). Linearity was calculated with a least-squares fit, with square correlation coefficient $r^2 = 0.99$ or better. Linear behaviour was found between 0.1 and 500 ng (absolute As mass) for

Table 2 Precision and detection limits[a]

		Correlation coefficient, r^2				Peak area lowest-standard R.S.D. ($n = 10$)			
Range of signal amplication	Calibration range (ng)	As(III)	DMA	MMA	As(V)	As(III)	DMA	MMA	As(V)
1 × 1	100–500	0.9974	0.9968	0.9975	0.9999	3.2	5.9	3.3	5.0
1 × 5	10–100	0.9997	0.9991	0.9993	0.9992	3.8	5.2	3.3	3.5
10 × 5	1–10	0.9998	0.9992	0.9998	0.9990	3.4	5.8	4.5	4.8
100 × 5	0.1–1	0.9999	0.9999	0.9999	0.9999	4.2	6.2	3.1	6.2
LOD(μg l^{-1}) = $3\sigma_{n-1}$ (slope for lowest range)						0.17	0.45	0.30	0.38
Absolute LOD (pg) = $3\sigma_{n-1}$ (slope for lowest range)						3.4	8.9	6.0	7.5

[a] Precison was calculated injecting 10 times the lowest standard of each calibration range. Limit of detection was calculated as three times the standard deviation ($3\sigma_{n-1}$) of a 1 μg l^{-1} standard solution of each species injected 10 times in a 20-μl loop, divided by the slope of the calibration line for the lowest range (0.1–1 ng).

Table 3 Arsenic species found in urine samples.

Sample	Concentration[a] ($\mu g\,l^{-1}$)					
	AsB	As^{III}	DMA	MMA	As^{v}	Total As
Without photo-oxidation						
Seronorm™ Urine, no. 009024	—	n.d.[b]	8.3 ± 0.4	n.d.	99.5 ± 2.1	107.8 ± 2.5
Volunteer's sample	—	n.d.	5.2 ± 0.6	0.8 ± 0.3	n.d.	6.0 ± 0.9
With photo-oxidation						
Seronorm™ Urine, no. 009024	87.3 ± 2.6	n.d.	8.4 ± 0.8	n.d.	97.2 ± 2.6	192.9 ± 6.0
Volunteer's sample	35.2 ± 1.5	n.d.	5.3 ± 0.3	0.7 ± 0.1	n.d.	41.2 ± 1.9

[a] Each value is the mean of three replicates ± standard deviation.
[b] Not detected.

As(III) and MMA, and between 0.1 and 800 ng (absolute As mass) for DMA and As(V). Loss of the linear behaviour was found near the microgram level due to fluorescence self-absorption processes, as described previously.[11]

On-line photo-oxidation

When the on-line photo-oxidation step was introduced, it was necessary to increase the HCl concentration to $8\,mol\,l^{-1}$ in order to counteract the basicity imported by the persulphate solution. The limits of detection (LODs) and linear ranges for all the species studied under these conditions (LOD $0.38\,\mu g\,l^{-1}$, linear range 0.1–800 ng) are similar to those values previously obtained for As(V), due to oxidation of all these species to arsenate.

The arsenite and arsenobetaine peaks overlap under these chromatographic conditions, as has been reported elsewhere,[8] because arsenite remains as a non-charged species and arsenobetaine as a zwitterion at the working pH (5.8). Therefore, it was necessary to perform experiments with and without the photo-oxidation step to distinguish the two species.

Analysis of urine samples

The HPLC–HG–AFS system was used to analyse a volunteer's urine sample and a commercial lyophilized urine sample which contained $100\,\mu g\,l^{-1}$

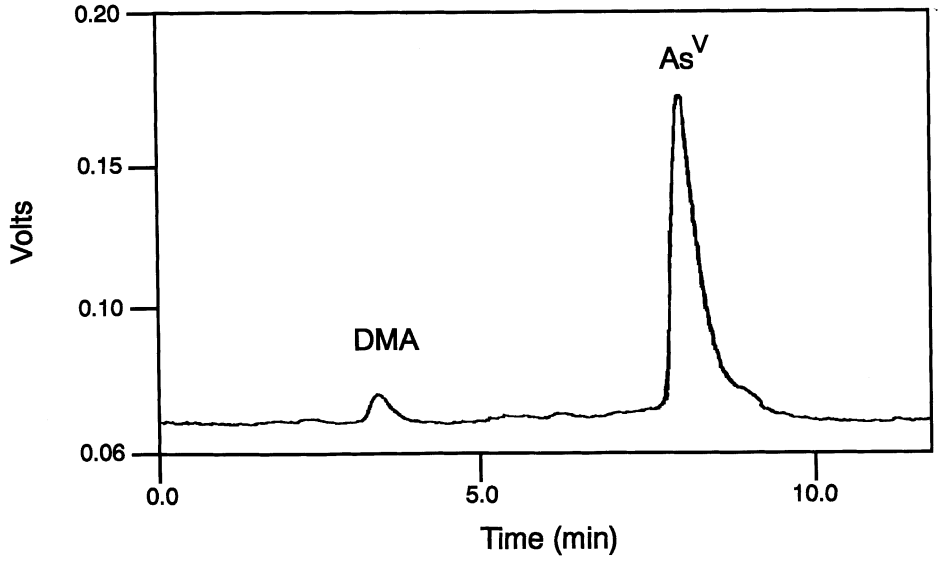

Figure 5 Chromatogram obtained for the Seronorm™ Trace Element Urine, batch no. 009024, following the conditions described in Table 1.

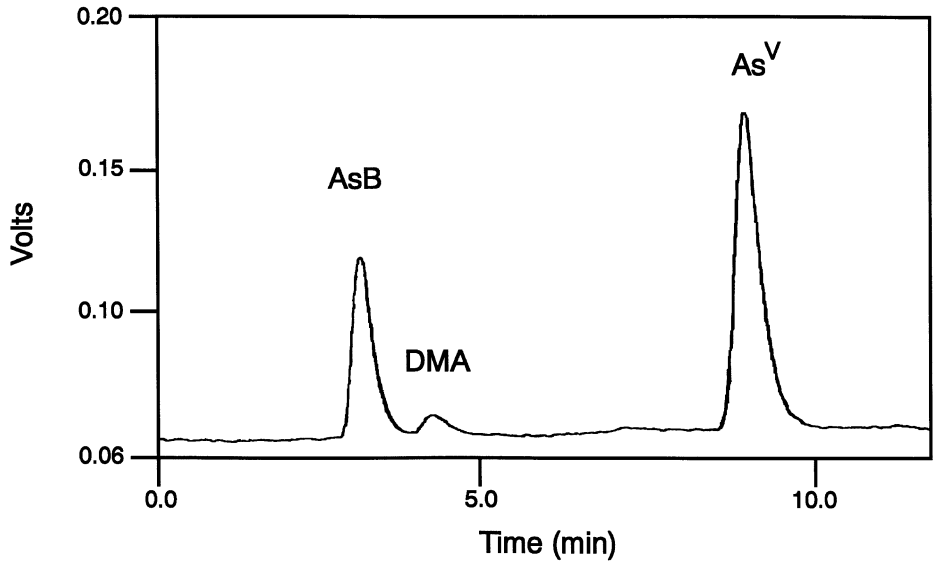

Figure 6 Chromatogram obtained for the Seronorm™ Trace Element Urine, batch no. 009024, introducing the photo-oxidation step, and following the conditions described in Table 1.

added arsenic of (Seronorm™ Trace Elements Urine, batch 009024; Nycomed Pharma As, Norway). The analytical data recommended for this material provide two different total arsenic contents, depending on the laboratory involved in the study of the sample: 90 $\mu g\,l^{-1}$ and 106 $\mu g\,l^{-1}$, using HG–AAS in both laboratories. With the method proposed in this paper, HPLC–HG–AFS, without a photo-oxidation step, the chromatogram depicted in Fig. 5 was obtained, which shows that As(V) and DMA species are present. In the analysis of the urine of a volunteer, methylated species, DMA and MMA were also detected. Samples were filtered over a 0.45 μm PTFE filter before their analysis. Quantitative results are given in Table 3. The concentration found for total reducible arsenic species in the reference material was 107.8 $\mu g\,l^{-1}$. Of this total, 99.5 $\mu g\,l^{-1}$ corresponds to As(V) and 8.3 $\mu g\,l^{-1}$ to DMA. This indicates that the sample was spiked with an inorganic species, and DMA represents an endogenous form of arsenic in the urine. There was therefore good agreement between the analytical recommended value and the value we obtained demonstrating the accuracy and precision of the technique.

We then analysed the same samples, introducing the photo-oxidation step, with the purpose of detecting the presence of arsenobetaine in the reference material (Fig. 6) and in the volunteer's sample. The results obtained for both samples show that arsenobetaine represents the main arsenic species present in human urine. In this case, the total arsenic value obtained for the reference material (Table 3) is higher than the analytical recommended value.

CONCLUSIONS

The HPLC–HG–AFS system provides a successful method for the speciation and detection of As(III), DMA, MMA and As(V), and it can be extended to the analysis of arsenobetaine with the introduction of an on-line photo-oxidation step (HPLC–UV–HG–AFS). The absolute detection limits achieved with this system are favourably compared with other atomic detectors such as ICP–MS or quartz cuvette atomic absorption spectrometry (QCAAS), and it is quite useful for the analysis of environmental samples. The linear range was also an advantage for determining arsenic species over a wide range of concentrations. The sensitivity can be further improved by increasing the sample volume injected onto the column. Finally, the AFS detector is relatively inexpensive compared with other atomic spectrometry detectors and it is easy to couple it to the HPLC.

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REFERENCES

1. W. R. Cullen and K. J. Reimer, *Chem. Rev.* **89**, 713 (1989).
2. M. O. Andreae, Organoarsenic compounds in the environment. In: *Organometallic Compounds in the Environment*, Craig, P. J. (ed.), Longman, London, 1986, pp. 198–228.
3. W. D. Spall, J. G. Lynn, J. L. Andersen, J. G. Valdez and L. R. Gurley, *Anal. Chem.* **58**, 1340 (1986).
4. J. J. Thomson and R. S. Houk, *Anal. Chem.* **58**, 2541 (1986).
5. P. Morin, M. B. Amran, M. D. Lakkis and M. J. Leroy, *Chromatogaphia*, **33**, 581 (1992).
6. M. Morita, T. Uehiro and K. Fuwa, *Anal. Chem.* **53**, 1806 (1981).
7. D. Beauchemin, K. W. M. Siu, J. W. McLaren and S. S. Berman, *J. Anal. At. Spectrom.* **4**, 285 (1989).
8. G. Rauret, R. Rubio and A. Padró, *Fresenius' J. Anal. Chem.* **340**, 157 (1991).
9. E. Hakala and L. Pyy, *J. Anal. At. Spectrom.* **7**, 191 (1992).
10. W. C. Story, J. A. Caruso, D. T. Heitkemper and L. Perkins, *J. Chromatogr. Sci.* **30**, 427 (1992).
11. T. Kaise and S. Fukui, *Appl. Organometal Chem.* **6**, 155 (1992).
12. K. Kawabata, Y. Inoue, H. Takahashi and G. Endo, *Appl. Organometal. Chem.* **8**, 245 (1994).
13. K. J. Lamble and S. J. Hill, *Anal. Chim. Acta* **334**, 261 (1996).
14. A. D'Ulivo, Atomic fluorescence detectors. In: *Environmental Analysis using Chromatography Interfaced with Atomic Spectroscopy*, Harrison, R. M. and Rapsomanikis, S. (ed.), Ellis Horwood, Chichester, (1989), p. 126.
15. L. Ebdon, S. Hill, P. Walton and R. W. Ward, *Analyst (London)* **113**, 1159 (1988).
16. J. V. Sullivan, *Prog. Anal. Atom. Spectrosc.* **4**, 311 (1981).
17. W. T. Corns, P. B. Stockwell, L. Ebdon and S. J. Hill, *J. Anal. At. Spectrom.* **8**, 71 (1993).
18. A. Woller, Z. Mester and P. Fodor, *J. Anal. At. Spectrom.* **10**, 609 (1995).
19. X. C. Le, M. Ma and N. A. Wong, *Anal. Chem.*, **68**, 4501 (1996).
20. R. Rubio, A. Padró, J. Albertí and G. Rauret, *Mikrochim. Acta* **109**, 39 (1992).

