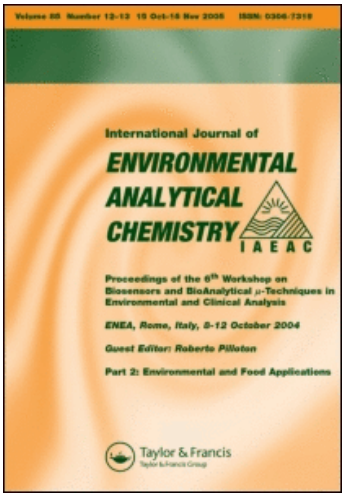

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

Photooxidation Of Arsenobetaine And Arsenocholine To Generate Arsines Previous To Icp-Oes Measurement

R. Rubio[a]; J. Albertí[a]; G. Rauret[a]
[a] Departament Química Analítica, Universitat de Barcelona, Barcelona, Spain

To cite this Article Rubio, R. , Albertí, J. and Rauret, G.(1993) 'Photooxidation Of Arsenobetaine And Arsenocholine To Generate Arsines Previous To Icp-Oes Measurement', International Journal of Environmental Analytical Chemistry, 52: 1, 203 — 213
To link to this Article: DOI: 10.1080/03067319308042861
URL: http://dx.doi.org/10.1080/03067319308042861

Intern. J. Environ. Anal. Chem., Vol. 52, pp. 203-213
Reprints available directly from the publisher
Photocopying permitted by license only

PHOTOOXIDATION OF ARSENOBETAINE AND ARSENOCHOLINE TO GENERATE ARSINES PREVIOUS TO ICP-OES MEASUREMENT

R. RUBIO, J. ALBERTÍ and G. RAURET

Departament Química Analítica, Universitat de Barcelona, Avda. Diagonal, 647, 08028 Barcelona, Spain

(Received, 15 June 1992; in final form, 9 October 1992)

A photolytic method, which uses UV irradiation (254 nm) and $K_2S_2O_8$ in alkaline media has been optimized for the speciation of arsenite, arsenate, monomethylarsonic and dimethylarsinic acid, arsenobetaine and arsenocholine. Under these conditions it is possible to obtain not only simple species from arsenobetaine and arsenocholine with good yields, but also to establish the optimum conditions to carry out the process on-line with HG-ICP/OES for the determination of these species.

The products obtained in the photolytic reaction are introduced into the reduction chamber to form arsines. According to the results obtained from the ICP measurements, the recoveries obtained are about 100% and the procedure has a good reproducibility.

KEY WORDS: Arsenic speciation, UV oxidation, arsenobetaine, arsenocholine, hyphenated techniques, hydride generation.

INTRODUCTION

Arsenic occurs in the environment in several forms, among them arsenite, arsenate, monomethylarsonic acid (MMAA), dimethylarsinic acid (DMAA), arsenobetaine (AsBet) and arsenocholine (AsChol) are of main interest.

Some of the arsenic species are introduced into the environment as inorganic forms (arsenite and arsenate), whereas some organic species (MMAA and DMAA) are generated from biomethylation processes. Some marine animals and algae are able to transform inorganic arsenic into higher molecular weight species such as AsBet, AsChol, and arsenosugars [1-3].

The different arsenic species show toxic effects depending on their molecular structure. Thus, the toxicity decreases in the order As(III)> As(V)> MMA> DMA, whereas arsenobetaine and arsenocholine are relatively non toxic, although it has been reported [4] that under specific conditions arsenobetaine present in marine biomass could be transformed

into trimethylarsine, a toxic specie, also often present in natural gas and in petroleum. Consequently, it is of high interest to carry out arsenic speciation in samples to ascertain their real or potential toxicity. In environmental analytical chemistry there has been increasing interest in the last years in the analysis of different contents of arsenic species in environmental samples from the aquatic media, namely water, marine organisms and sediments. This kind of study leads to a better understanding of the behaviour, transport and diagenesis of arsenic through the different compartments of the aquatic cycle.

To carry out arsenic speciation some of the most suitable methods proposed in the literature use coupled techniques such as HPLC-AAS or HPLC-ICP/OES, which achieve good separation and sensitivity. Arsenic, like other elements able to be reduced to hydride, shows highest sensitivity when the original arsenic species are reduced to the corresponding arsines before detection by spectroscopy [5–8]. In previous papers [9,10] we have optimized the reduction conditions for the generation of arsines, as well as the separation conditions, in which speciation of arsenite, arsenate, MMA and DMA in waters can be achieved.

Unfortunately, neither AsBet nor AsChol, two arsenic species of environmental interest, are able to generate volatile arsine by reduction.

The most attractive way to produce simpler molecules from AsBet and AsChol, potentially able to generate volatile arsines seems to be photooxidation. In the literature, methods are described for AsBet and AsChol is decomposition to obtain simpler arsenic species, which are able to form hydride species before final measurement. Decomposition in alkaline medium at 85°C has been studied [11], but only AsBet is degraded in the conditions described, and the process is too slow to be coupled on line. Thermochemical hydride generation of AsBet and AsChol is also carried out in a coupled system between HPLC separation and AAS measurement [12].

Some authors have proposed UV irradiation to treat AsBet, MMA and DMA to obtain As(V) [13,14]. Nevertheless, the long period of time (hours) required for quantitative photolysis of AsBet prevents inclusion in an on-line system.

UV irradiation in the presence of $S_2O_8^=$ is proposed as a means to oxidize organic matter where radical species are involved [15]. This method has been used for Arsenobetaine, MMA, DMA and As(V) determination in an HPLC-UV-HG-AAS system [16].

In this paper we have established the photooxidation conditions in which we obtain simpler species from AsBet and AsChol. Under these conditions good yields and precisions are obtained. The photooxidation is carried out by means of UV irradiation in the presence of persulphate, the resulting species easily produce the corresponding arsines. The suitability of the method for the on-line determination of the different As species, using HPLC-UV-HG-ICP/OES, is demonstrated.

EXPERIMENTAL

Instrumentation

Two different UV sources were assayed: A low-pressure Hg vapour lamp (Sylvania, 254

nm, o.d. 1.5 cm, length 30 cm, 8W), used to visualize solutes on TLC fluorescent plates, and a low-pressure Hg vapor lamp Heraeus TNN 15/32 (254 nm, o.d. 2.5 cm, length 17 cm, 15W).

Photoreactor: The UV lamps were placed into PVC tubes (i.d. 7.5 cm) with the inner wall and the ends covered with an aluminum foil and wrapped with PTFE tubing (i.d. 0.5 mm, length 2m).

Peristaltic pump: Gilson Minipuls 3.

HPLC System: A gradient Perkin Elmer 250 LC binary pump was used, equipped with Hamilton PRP X-100, 10 μm particle size (250 mm × 4.1 mm) and Supelcosil LC-SAX, 5 μm particle size (250 mm × 4.6 mm) anionic exchange columns. Injection was performed with a Reodyne 100 μL loop.

Hydride generation system: Varian model VGA-76 with gas-liquid separator.

ICP/OES: 'Plasmatherm' source, inductively coupled to a high frequency (27.12 MHz) magnetic field, operating at 1 kW. A Jobin-Ivon thermoregulated monochromator with a holographic grating, 2400 grooves/mm, focal length 1 m, 0.1Å resolution. Argon was used as coolant and carrier gas. Wavelength: 193.696 nm. An IBM PS/2 was used for data acquisition.

Reagents

Stock solutions of arsenic compounds containing 1000 mg/L were prepared as follows:

Arsenite: As_2O_3 (Merck) primary standard, dissolved in NaOH (4g/L). Arsenate: $Na_2HAsO_4.7H_2O$ (Carlo Erba) dissolved in water. MMA: $CH_3AsO(ONa)_2{\cdot}6H_2O$ (Carlo Erba) dissolved in water. DMA: $(CH_3)_2AsNaO_2.3H_2O$ (Fluka), dissolved in water. Arsenocholine: $(CH_3)_3As^+CH_2\text{-}CH_2OHBr^-$ and arsenobetaine: $(CH_3)_3As^+\text{-}CH_2COO^-$, were supplied by Service Central d'Analyse from CNRS (Vernaison, France) and solutions of 1000 mg/L of both were prepared in water.

Mobile phases: Phosphate buffers from NaH_2PO_4. H_2O and $Na_2HPO_4.2H_2O$, of 20 and 100 mM in water.

Other reagents were: $K_2S_2O_8$ 99.5% (Fluka). NaOH (Carlo Erba). $NaBH_4$ 1% (Alfa Venton) in NaOH 0.5%. HNO_3 (Merck 65% pro analysi).

All solutions were prepared using double deionized water Culligan Ultrapure GS 18.3 Mohms. cm^{-1} resistivity.

Procedure

Photooxidation of Arsenocholine and Arsenobetaine:.

Step 1: A solution of AsBet or AsChol in appropriate concentration of $K_2S_2O_8$ solution, in neutral, acidic (HNO_3) or alkaline media (NaO4) is prepared.

Step 2: These solutions are aspirated to the photoreactor by means of the peristaltic pump, the UV irradiation time is regulated by the pump speed control. After irradiation, 5 mL of

the resulting solution is collected in a polyethylene container after rejecting the first mL. This must be analyzed quickly (if this cannot is possible, the solution can be stored at 4°C in darkness for four hours).

Step 3: The resulting solution from step 2 is filtered through a 0.22 μm nylon membrane filter. 100 μL of this solution is injected into the HPLC-HG-ICP coupled system, with gradient elution. A Hamilton PRP X-100 anion exchange column was used and elution conditions were: Sol.1 (Buffer 20 mmol/L Na_2HPO_4/NaH_2PO_4 pH 5.75) and Sol.2 (Buffer 100 mmol/L Na_2HPO_4/NaH_2PO_4 pH 5.75). 100% Sol. 1 for 2 minutes, decreasing to 50% Sol. 1/50% Sol.2 in 0.1 min. and maintaining this ratio for 3 minutes, then 100% Sol. 1 is reached again in 0.1 minutes and maintained for 7 minutes (10), at a flow-rate of 1mL.min.

Hydride generation conditions: H_2SO_4 2 mol/L and $NaBH_4$ 1% in NaOH 0.5%.

RESULTS AND DISCUSSION

Photoreactor design

First the design of photoreactor was studied using low-pressure mercury vapour lamps and PTFE tubs. These lamps (8W and 15W loading) emit intense radiation on the mercury resonance line (wavelength 254 nm) and persulphate is decomposed (absorbs at 235 nm), giving hydroxyl radicals which convert organic matter into CO_2. A great advantage of this kind of lamps in photochemical reactions is that they do not need to be cooled.

PTFE tubing is highly suitable for the construction of an on-line photoreactor, owing to

Table 1 Recovery values of DMA, MMA and As(V) obtained from 2 mg/L AsChol (a) and 2 mg/L AsBet (b) photooxidation with 30 s. UV irradiation time (8W UV lamp) in neutral and acidic media.

a) *Medium*	*% DMA*	*% MMA*	*% AS(V)*
0.025% $K_2S_2O_8$	52.5	19.7	8.1
0.1% $K_2S_2O_8$	0	16.8	86.8
0.5% $K_2S_2O_8$	0	8.0	88.7
0.5% $K_2S_2O_8$ - 0.1M HNO_3	62.1	20.7	24.5
b) *Medium*	*% DMA*	*% MMA*	*% As(V)*
0.025% $K_2S_2O_8$	27.1	32.0	39.6
0.1% $K_2S_2O_8$	0	14.1	83.7
0.5% $K_2S_2O_8$	0	6.6	92.1
0.5% $K_2S_2O_8$ - 0.1M HNO_3	54.2	13.3	22.8

its low cost, the availability of various sizes and diameters, ease of handling and high transmittance of UV light between 200-300 nm due to internal reflection mechanisms [17–19].

Photolysis in presence of persulphate in different media

The effect of medium (neutral, acidic or alkaline) on UV photolysis of Arsenocholine and Arsenobetaine in the presence of potassium persulphate was studied. A concentration of 2 mg/L and 30 s. UV irradiation time was established. Four arsenic species were formed during the process. We identified DMA, MMA and As(V) by means of their retention times against standards using two different anionic exchange columns (Hamilton PRP X-100 and Supelcosil LC-SAX). An unknown As compound was also formed in photooxidation, which could be a trimethylarsenic oxide (TMAO), as expected from its retention time and its low yield in hydride generation.

Tables 1-2 show the variation in recoveries of the resulting species after UV irradiation for AsBet and AsChol. The method followed is described in procedure and the recoveries are expressed according to:

$$\% \text{ resulting species} = [\text{Conc. resulting species (expressed as As)/Conc. AsChol or AsBet in initial solution (expressed as As)}] * 100$$

Asbet and AsChol show a very similar behaviour in the conditions assayed. In each case four species are formed. The results show that the best recoveries are obtained in neutral and alkaline media; in acidic medium the reaction proceeds very slowly. Although neutral medium provides slightly better results, the alkaline medium was chosen because our HPLC separation system, which is the previous step in a coupled system, uses an acidic mobile phase, and it is difficult to adjust pH to neutrality in an on-line system. Thus, alkaline medium has been studied in more detail. Table 2 shows that the recovery of As(V) increases with NaOH concentration.

Effect of persulphate concentration and irradiation time in photolysis

The recoveries of the three main compounds formed (DMA, MMA and As(V)), as a function of UV irradiation time and persulphate concentration can be observed for AsBet (Table 3) and AsChol (Table 4).

Table 2 AsBet photooxidation in alkaline media. Conditions: 2 mg/L AsBet, 0.5% $K_2S_2O_8$ and 30 s. UV irradiation time (8W UV lamp).

NaOH conc. (%)	*% DMA*	*% MMA*	*% As(V)*
0	0	11.3	84.4
0.1	0	49.7	56.3
0.2	0	41.8	61.9
0.5	0	17.6	77.4
1	0	7.9	91.4

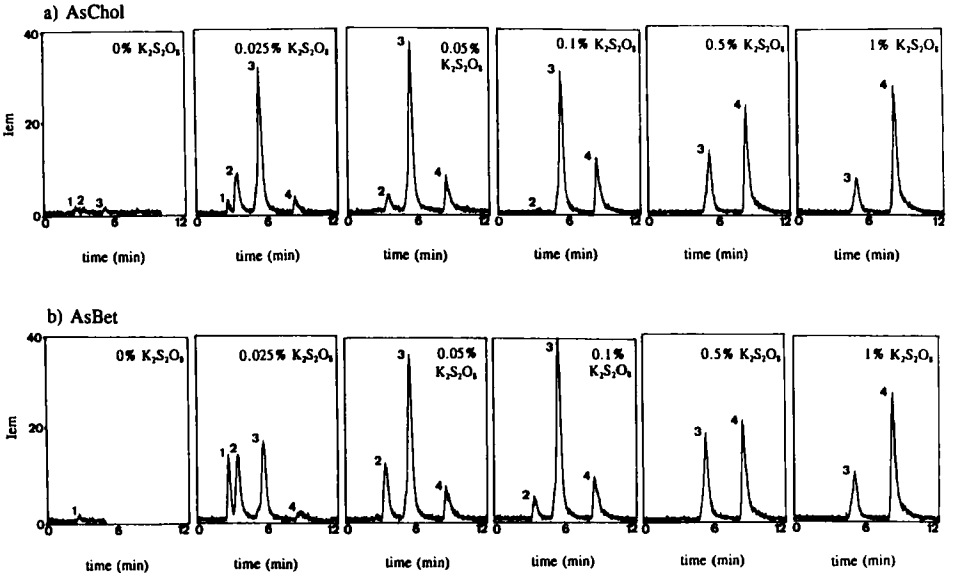

Figure 1 AsChol 2 mg/L (a) and AsBet 2 mg/L (b) decomposition by photolysis using different persulphate concentrations in 0.5% NaOH and 30 s. UV irradiation (8W UV lamp). Chromatograms obtained by HPLC-HG-ICP using the conditions described in Procedure, step 3. Injection volume:100 µL.
Compounds: 1. Unknown compound, 2. DMA, 3. MMA,4. As(V).

Table 3 Arsenocholine photooxidation. Recovery values of DMA, MMA and As(V) obtained from 2 mg/L AsChol with different persulphate concentration and UV irradiation time (8W UV lamp), in 0.5% NaOH.

t UV	*$K_2S_2O_8$ concentration (%)*					
(s)	*0*	*0.025*	*0.05*	*0.1*	*0.5*	*1*
			% DMA			
0	0	0	0	0	0	5.2
15	0	22.9	21.6	20.5	6.6	0
30	0	21.3	12.4	0	0	0
60	0	16.0	0	0	0	0
120	0	14.8	0	0	0	0
			% MMA			
0	0	0	0	0	0	0
15	0	30.6	34.1	37.1	37.2	31.2
30	0	54.2	62.5	51.4	27.3	17.0
60	0	65.4	52.7	43.8	16.6	6.1
120	0	63.1	30.5	13.9	0	0
			% As(V)			
0	0	0	0	0	0	0
15	0	10.7	11.6	12.2	23.4	28.9
30	0	12.5	24.8	35.3	68.7	74.7
60	0	29.0	39.0	58.9	82.5	91.6
120	0	46.7	78.1	83.5	100.3	100.6

Table 4 Arsenobetaine photooxidation. Recovery values of DMA, MMA and As(V) obtained from 2 mg/L AsBet with different persulphate concentration and UV irradiation time (8W UV lamp), in 0.5% NaOH.

t UV	*$K_2S_2O_8$ concentration (%)*					
(s)	*0*	*0.025*	*0.05*	*0.1*	*0.5*	*1*
			% DMA			
0	0	0	0	0	0	0
15	0	6.5	23.0	26.7	1.1	0
30	0	32.4	25.9	0.9	0	0
60	0	27.1	12.0	0	0	0
120	0	14.7	0	0	0	0
			% MMA			
0	0	0	0	0	0	0
15	0	19.5	32.5	48.3	57.1	46.5
30	0	26.7	67.1	75.5	25.9	6.7
60	0	38.2	52.9	36.8	26.8	3.2
120	0	46.2	36.9	23.5	9.0	0
			% As(V)			
0	0	0	0	0	0	0
15	0	2.1	3.5	7.1	29.1	37.7
30	0	8.0	17.0	21.2	68.5	80.2
60	0	11.1	20.9	55.9	65.2	87.6
120	0	22.5	42.8	58.0	79.0	92.0

As an example, Figure 1 shows the behaviour of AsChol (a) and AsBet (b) under an UV irradiation time of 30 s. with different persulphate concentration. AsChol and AsBet decomposition occurs according to the following sequence:

$$\text{AsBet}\atop\text{AsChol} \xrightarrow{\text{fast}} \text{Unknown compound} \xrightarrow{\text{fast}} \text{DMA} \xrightarrow{\text{fast}} \text{MMA} \xrightarrow{\text{slow}} \text{As(V)}$$

From this study 120 s. and 1% persulphate are necessary for total conversion of AsBet into As(V), whereas for AsChol 0.5% persulphate is enough, which can be explained taking into account that the As content is higher in AsBet for the same concentration of AsBet and AsChol (2 mg/L).

In Figure 2, the percentage of As(V) obtained versus UV irradiation time is plotted for AsChol and AsBet with different persulphate concentrations.

Effect of the power lamp

Two different UV lamp sources (8W and 15 W respectively) have been assayed in order to determine the relationship between time reaction and power lamp.

Figure 3 shows the recoveries obtained for the three arsenic compounds formed (DMA, MMA and As(V)) at two different UV irradiation times (15 and 30 s.) and at low concentration of persulphate. As can be observed, for the higher power lamp the reaction is faster (15 s. with 15W UV lamp leads to the same as 30 s. with 8W UV lamp). In order to

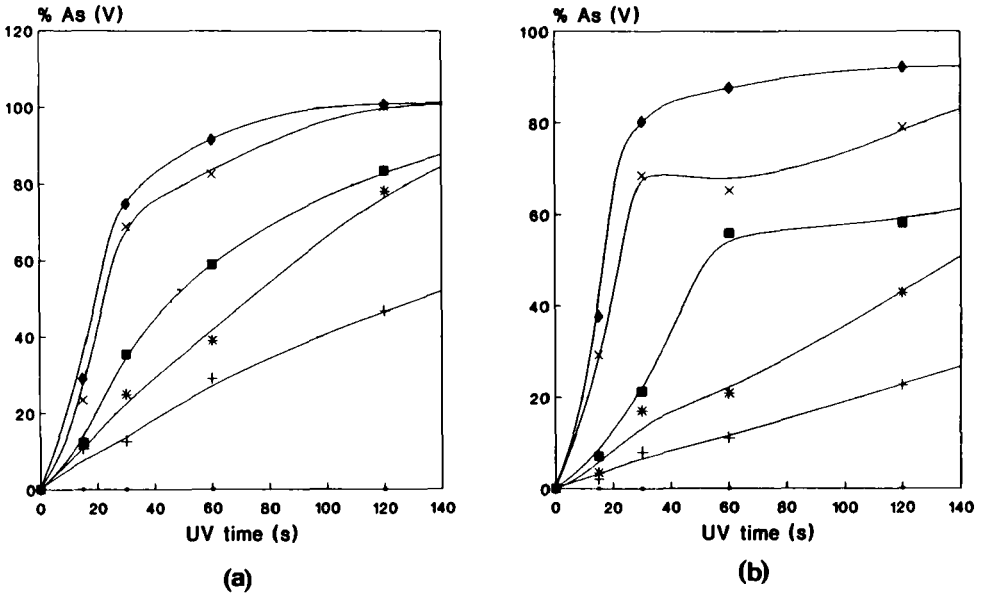

Figure 2 Percentage of As(V) obtained from AsChol 2 mg/L (a) and AsBet 2 mg/L (b) versus UV irradiation time (8W UV lamp) by photoxidation using different persulphate concentrations in 0.5% NaOH. Conditions: · 0% $K_2S_2O_8$ + 0.025% $K_2S_2O_8$ * 0.05% $K_2S_2O_8$ ■ 0.1% $K_2S_2O_8$ × 0.5% $K_2S_2O_8$ ♦ 1% $K_2S_2O_8$.

increase the kinetics of the reaction, especially important in on-line determinations, we studied the photooxidation conditions using 15W UV lamp. In Figure 4 the results obtained in different media are presented. The behaviour of AsBet and AsChol using the 15W UV lamp is the same as the 8W UV lamp.

Finally, Table 5 shows the persulphate concentration necessary for total conversion of AsBet into As(V) with 30 s. 15W UV lamp irradiation time, which were considered adequate for an HPLC-UV-HG-ICP/OES or AAS coupled system.

Preliminary results with a HPLC-UV-HG-ICP/OES coupled system

Table 5 AsBet photooxidation (2 mg/L) with 30 s. UV irradiation lamp (15 W UV lamp) in 0.5% NaOH and different $K_2S_2O_8$ concentration.

% $K_2S_2O_8$	*% MMA*	*% As(V)*
0.5	1.5	97.3
1	0	102.0
1.5	0	99.5

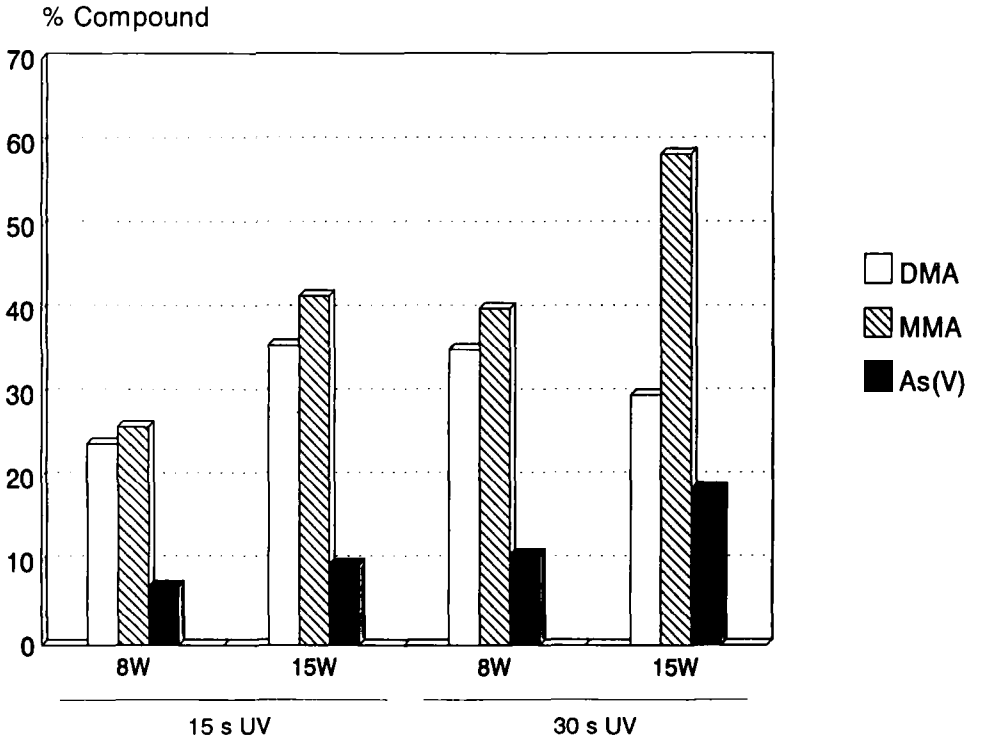

Figure 3 Effect of power UV lamp on AsBet 2 mg/L. Conditions: 0.05% $K_2S_2O_8$ in 0.5% NaOH and different UV irradiation time.

Figure 5 shows one chromatogram obtained with a HPLC-UV-HG-ICP/OES system. The photooxidation and hydride generation conditions are being now optimizated, as well as the use of other anionic exchange columns to improve separation of these arsenic compounds.

CONCLUSIONS

With the method proposed the quantitative conversion of AsChol and AsBet into As(V) is achieved with a short reaction time. Thus, we can perform final hydride generation from AsChol and AsBet and consequently the sensitivity for these species can be drastically increased, as necessary in the analysis of environmental samples. Obviously, if DMA, MMA and As(III) are present in the initial sample, they will be transformed into As(V) under the described conditions.

The photoreactor designed can be easily made in the laboratory.

The proposed process permits on-line coupling between chromatographic separation and hydride generation with a final detection by atomic spectroscopy.

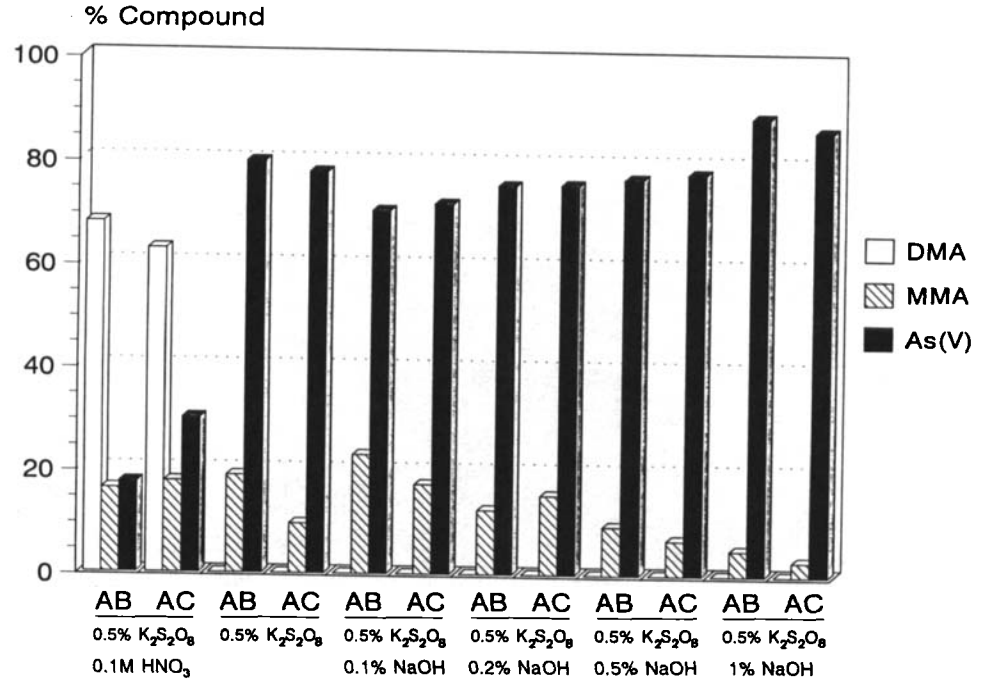

Figure 4 Recoveries obtained from AsChol 2 mg/L (AC) and AsBet 2 mg/L (AB) after 20 s. UV irradiation with 15W UV lamp in different media.

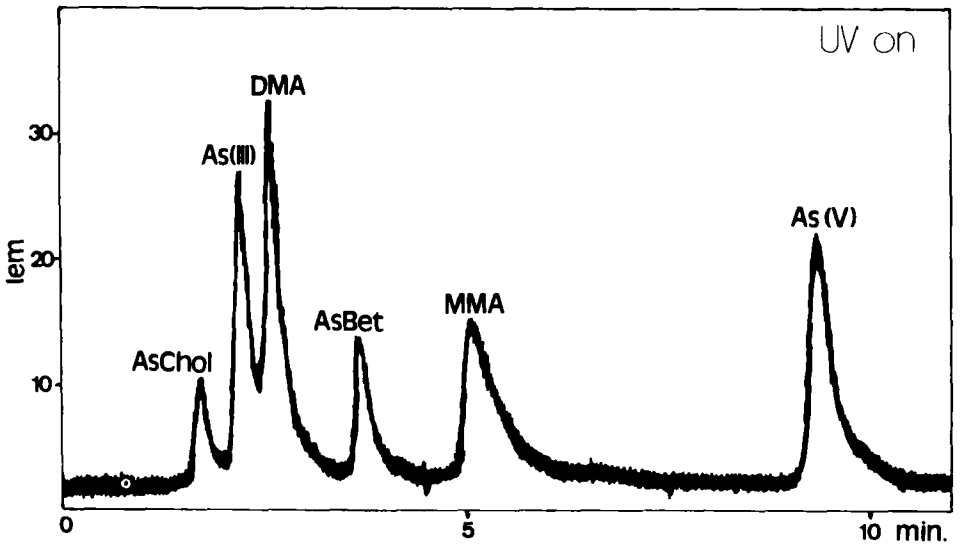

Figure 5 HPLC-UV-HG-ICP/OES separation of six arsenic species. Injection volume: 100 µL. Column: Supelcosil LC-SAX and isocratic elution with buffer 5 mmol/L Na_2HPO_4/H_3PO_4 pH 3.75 at 1 mL/min. Photoxidation step conditions: solution $K_2S_2O_8$ 3% in NaOH 2% at 0.25 mL/min. PTFE coil length 5 m. (0.35 mm i.d.) wrapping 15W UV lamp. Hydride generation conditions: HCl 6 mole/L and $NaBH_4$ 1% in NaOH 0.5%, both at 1mL/min. The concentrations of arsenic species AsChol, As(III), DMA, AsBet, MMA and As(V) are 80, 200, 200, 100, 200 and 200 µg/L as As, respectively.

A limitation of this procedure would be the use of a mobile phase of organic character in chromatographic separation, which could be decomposed during the photooxidation process and thus the yield of analytes oxidation would be decreased significantly.

The method can be applied to organometallic compounds of other elements (Hg, Sn, Ge, Se, etc) which cannot form hydrides under the normal conditions.

Acknowledgements

The authors thank CIRIT (Comissió Interdepartamental de Recerca i Innovació Tecnològica de la Generalitat de Catalunya) for the financial help received in support of this work, the Serveis Cientificotècnics de la Universitat de Barcelona the facilities in ICP/OES use and Service Central d'Analyse from CNRS, Vernaison (France) for AsChol and AsBet supply.

References

1. P. J. Craig, *Organometallic compounds in the Environment. Principles and Reactions*. (Longman Group Ltd. Leicester, U.K., 1986).
2. A. Léonard in: *Metals and their Compounds in the Environment*. (E. Merian ed., VCH Weinheim, 1991).
3. J. E. Fergusson, *The Heavy elements: Chemistry, Environmental impact and Health effects* (Pergamon Press, Oxford, 1990).
4. K. J. Irgolic and B. K. Puri in: *Metal Speciation in the Environment*, (J. A. C. Broekaert, S. Gücer and F. Adams, eds. NATO ASI Series. Series G: Ecological Sciences, *23*. Springer Verlag. Berlin, 1990).
5. A. G. Howard and L. E. Hunt, *Spectroscopy International* **3**, 26–34 (1991).
6. O. F. X. Donard and F. M. Martin, *Trends in Anal. Chem.* **11**, 17–26 (1992).
7. R. M. Harrison and R. Rapsomanikis, eds. *Environmental Analysis using Chromatography interfaced with Atomic Spectroscopy*. (Ellis Horwood. Chichester, 1989).
8. Y. U. Chau, in: *The importance of Chemical Speciation in Environmental Processes*, (M. Bernhard, F. E. Brinkman and P. J. Sadler, eds. Life Sciences Research. Report 33. Springer Verlag. Berlin, 1986).
9. G. Rauret, R. Rubio and A. Padró, *Fresenius J. Anal. Chem.* **340**, 157–160 (1991).
10. R. Rubio, A. Padró, J. Albertí and G. Rauret, *Mikrochim. Acta.* **109**, 39–45 (1992).
11. T. Kaise, H. Tamauchi, T. Hirayama and S. Fukui, *Appl. Organomet. Chem.* **2**, 339–347 (1988).
12. J. S. Blais, G. M. Momplaisir and W. D. Marshall, *Anal. Chem.* **62**, 1161–1166 (1990).
13. W. R. Cullen and M. Dodd, *Appl. Organomet. Chem.* **2**, 1–7 (1988).
14. C. I. Brockbank, G. E. Batley and C. K. C. Low, *Environ. Tech. Letters* **9**, 1361–1366 (1988).
15. R. Rosset, M. Cande, P. Sassiat and M. Dutang, *Intern. J. Environ. Anal. Chem.* **13**, 19–28 (1982).
16. R. H. Atallah and D. A. Kalman, *Talanta*, **38**, 167–173 (1991).
17. G. E. Batley, *Anal. Chem.* **56**, 2261–2262 (1984).
18. J. W. Birks and R. W. Frei, *Trends in Anal. Chem.* **1**, 361–367 (1982).
19. J. T. Stewart and W. J. Bachman, *Trends in Anal. Chem.* **7**, 106–110 (1988).