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Determination of dimethylarsinic acid by hydride generation gas phase molecular absorption spectrometry

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Abstract

A method is described for the determination of dimethylarsinic and monomethylarsonous acids. The procedure involves $NaBH_4$ reduction of the arsenic compounds to the corresponding gaseous arsines. After generation, the hydrides are collected in a liquid nitrogen trap. They are revolatilized and carried to the flow cell where they are measured by gas phase molecular absorption spectrometry (GPMAS). Various parameters affecting the production and collection of the arsines, such as the sample volume, generation conditions, and analyte retention and volatilization are discussed. The spectra obtained over a wide range of wavelengths, allows the reactions which take place during arsine generation, retention and revolatilization and their effects on the analytical signal to be studied. The quality parameters (detection limits, precision and accuracy) for two arsenic species are reported.

Keywords: Hydride generation; Gas phase molecular absorption spectrometry; Methylarsine; Dimethylarsine

1. Introduction

The development of techniques for the separation and determination of organoarsenical compounds is of great interest in environmental analysis. This interest is due to the use of these compounds as herbicides (sodium and ammonium salts of the monomethylarsonic and dimethylarsonic acids) or in pharmaceutical formulations (cacodilic acid and chemotherapy preparations) together with their appearance in various living organisms in river and sea water [1]. Their use gives rise to problems of bioaccumulation and reduction by microorganisms of the constituent arsines; these are highly volatile and extremely toxic. It is also known that the different organic compounds of arsenic are produced by methylation and are interchangeable via chemical and biological processes; these compounds have been found in environmental sample [2].

The most commonly used method for the determination of organoarsenical compounds is based on their conversion to volatile hydrides, followed by their detection. The most widely used generation system is chemical reduction with sodium tetrahydroborate(III) [3,4] or sodium tetraethyl borate(III) [5]. The generation can be carried out via prior decomposition of the compounds by photooxidation [6], chemical oxidation [7] or microwave digestion [8]. Other gen-

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eration systems which have recently been developed involve thermochemical [9] or electrochemical [10,11] processes.

In those cases where a multicomponent analysis is required, different separation techniques and detection systems are used, such as liquid chromatography – mass spectrometry [12], gas chromatography – mass spectrometry [13], capillary zone electrophoresis [14], atomic absorption spectrometry (AAS) [7–10], atomic emission spectrometry (EAS) [14], molecular absorption spectrometry [14,15] and electrochemical methods [16].

The determination of compounds in solution by their conversion to volatile phases is widely used in analytical chemistry. Syty [17] introduced this method in 1973, and Cresser and Isaacson [18] introduced the term gas phase molecular absorption spectrometry (GPMAS). Several inorganic ions have been determined via the generation of NH_3, H_2S, SO_2, Cl_2, Br_2, I_2 and NOCl [19–22].

The introduction of diode-array detection systems allowed the gas phase absorbance spectrum to be recorded over a wide wavelength range. This gives a large amount of information about possible reactions, generation mechanisms and the possibility of simultaneous determination of mixtures of various analytes. For example, using this technique Sb, Se, Ge, As and Bi [23–25] have been determined among others, together with mixtures of As(III) and As(V) [26], Bi and Se or As [27], and Sb and Se [28]. This technique does have some disadvantages; for example its lower sensitivity, which makes necessary the use of preconcentration techniques, and the fact that most inorganic gaseous molecules absorb ultra-violet radiation.

This work proposes a determination system using the generation of dimethylarsine, carried out by continuous addition of the reducing agent and subsequent determination by GPMAS.

2. Experimental

2.1. Apparatus

All measurements were made with a Hewlett–Packard (HP) model 8451 diode-array spectrophotometer equipped with an HP 98155A keyboard, an HP 9121 disk drive for bulk data storage, an HP Thinkjet printer and an HP 7475A graphics plotter. A Hellma 174QS 1 cm quartz flow cell, a Cole Parmer Instrument Co. 7554-20, peristaltic pump, a Agitamatic Heídolph MR 3003 with platinum probe, a Mettler PJ 3600 Delta Range, a Dilvac Dewar flask (2 l) and a Schott ISO 100/250/500/1000/2000 ml generator flask were used. Various generation schemes were studied. The best results were obtained with that shown in Fig. 1, which was used throughout the work. The scheme consists of: I the hydride generator, II the trapping section, III the revolatilizing section and IV, UV detection.

2.2. Reagents

Stock solutions of arsenic compounds were prepared of 1000 $\mu g ml^{-1}$ As as follows: dimethylarsinic acid (DMA), $C_2H_6AsO_2Na$ (Sigma) dissolved in

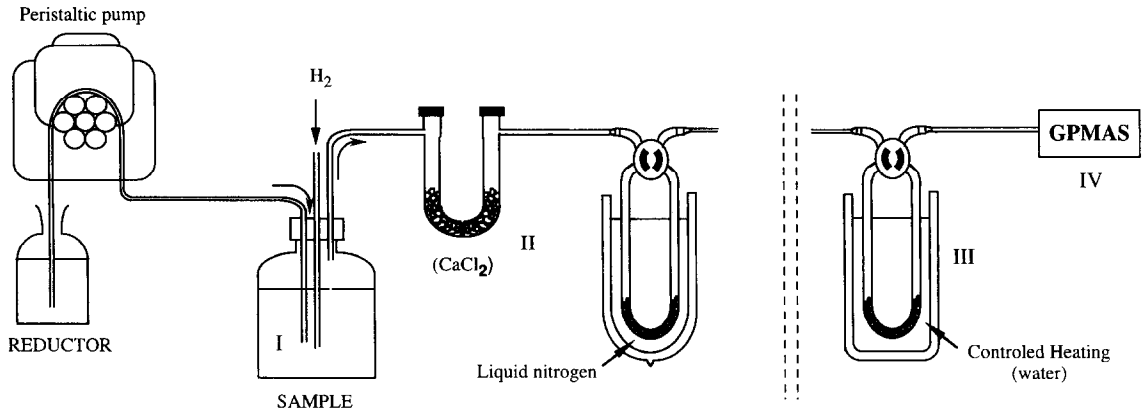

Fig. 1. Schematic diagram of the system.

water, methylarsine dibromide, CH_3AsBr_2 (Alfa) dissolved in water. Working standards were prepared, immediately before use, by serial dilution of the stock solutions with water. Aqueous solutions of sodium tetrahydroborate(III), $NaBH_4$ (Sigma) were prepared immediately prior to use. Hydrochloric acid (37%, 1.186 g ml^{-1}), nitric acid (65%, 1.400 g ml^{-1}) and sulphuric acid (96%, 1.835 g ml^{-1}) were RPE grade from Carlo Erba. Working solutions were prepared daily by diluting the concentrated solutions with water. All water used was double-distilled, the Calcium chloride was dried granular RE grade from Carlo Erba. The carrier gases were nitrogen and hydrogen (C-50 Carburos Metálicos).

2.3. Procedure

A volume of 750 ml of a previously acidified dimethylarsinate standard solution (0.2 M HCl) was put into the generator (1 l). A peristaltic pump was used to introduce the reducing agent, 50 ml of $NaBH_4$ solution, at a flow rate of 20 ml min^{-1}; a hydrogen flow (550 ml min^{-1}) was simultaneously introduced through the solution. Once the reducing agent was consumed, the hydrogen flow was maintained for 2 min more. Hydride generation was carried out at a controlled temperature (40°C). The generated volatiles were swept through the $CaCl_2$ trap to remove water and were condensed in the U-tube immersed in liquid nitrogen.

The U-tube was removed from the liquid nitrogen and left for 3 min at room temperature. Volatilization of the hydrides was achieved by heating the trap at 95°C. After 1 min, the hydrides were transported to the detector with a nitrogen flow (2000 ml min^{-1}), through PTFE tubing. The arsenic species were detected using the BASIC program as given in the experimental procedure; arsine absorbance spectra from 190 to 280 nm were obtained every 0.2 s for 7 s (enough time for the absorbance to fall to zero). The program allows the storage of the molecular absorption spectra.

3. Effects of experimental parameters

It is known that the detection of volatile phases using molecular absorption spectrometry does not have a high sensitivity. This fact, together with the low concentration in the environment of the species to be analyzed, makes a preconcentration step necessary for the volatiles generated; this is carried out by retention in a cryogenic bath. A wide range of temperatures were studied, with the best results being those obtained from the liquid nitrogen bath at −196°C. This is significant because, given that dimethylarsine's boiling point is 36°C, it would have been expected that the retention could have been possible at higher temperature. The results obtained indicate that a very low temperature is needed to liquefy the gases, probably due to their speed of passage through the cold trap.

A particularly relevant parameter for this method is the type and flow rate of carrier gas used for the volatiles once the reaction has been carried out. The effect is to be seen not only in response increase at high flow rates but also in a notable change in the forms of the spectra. While increasing the gas carrier flow, a new band appeared in the spectra; this phenomenon could be explained if we consider that the compound that produces this signal has a high molecular weight and a higher flow is necessary to remove it from the solution. The gas carrier had particular importance for these changes; hydrogen offered the best analytical results.

The relation between the capacity of the generator used and the volume of sample which it contained must also be considered. With the aim of obtaining the lowest possible proportion of dead volume and the most efficient volume, various generators (from 100 to 2000 ml) were studied by varying the sample volume (from 50 to 750 ml) and maintaining the amount of analyte unchanged in all cases. Best results were obtained with a 1000 ml generator and a sample volume of 750 ml.

Three inorganic acids were used for the arsine generation: hydrochloric, nitric and sulphuric acids at concentrations ranging from 0.05 to 0.8 M. No formation of nitrogen, sulphur or chlorine volatile oxides was observed during the arsine generation. No significant differences were seen in the results obtained from each of the acidic media; the best results were obtained when 0.2 M acid was used.

After generation and trapping of the volatile hydride, the trap was removed from the liquid nitrogen and left for 3 min before starting the revolatilization in

Table 1
Final conditions for the determination of DMA

Parameter			
T^a generation	40°C	Time of revolatilizing T^a amb.	3 min
T^a revolatilizing	95°C	Time of revolatilizing 95°C	1 min
T^a measurement	20°C	Reductor concentration	30 g l^{-1}
Flow generation (H_2)	550 ml min^{-1}	Reductor flow	20 ml min^{-1}
Flow rate (N_2)	2200 ml min^{-1}	Reductor volume	50 ml
HCl concentration	0.2 M	Sample volume	750 ml

hot water. This avoided any sudden temperature changes: it was seen that this period at room temperature favored the later revolatilization.

Revolatilization of the hydrides took place simultaneously with the submerging of the trap in the temperature-controlled hot water bath: the best results were obtained with a bath temperature of 95°C.

The best conditions obtained for DMA determination are shown in Table 1.

4. Results and discussion

4.1. Spectrum change

During our study of the operating conditions, spectra were observed (see Fig. 2) which were not assignable purely to the dimethylarsine, supposedly the only product of the reaction. These observations led us to an in-depth study of the mechanisms influencing the

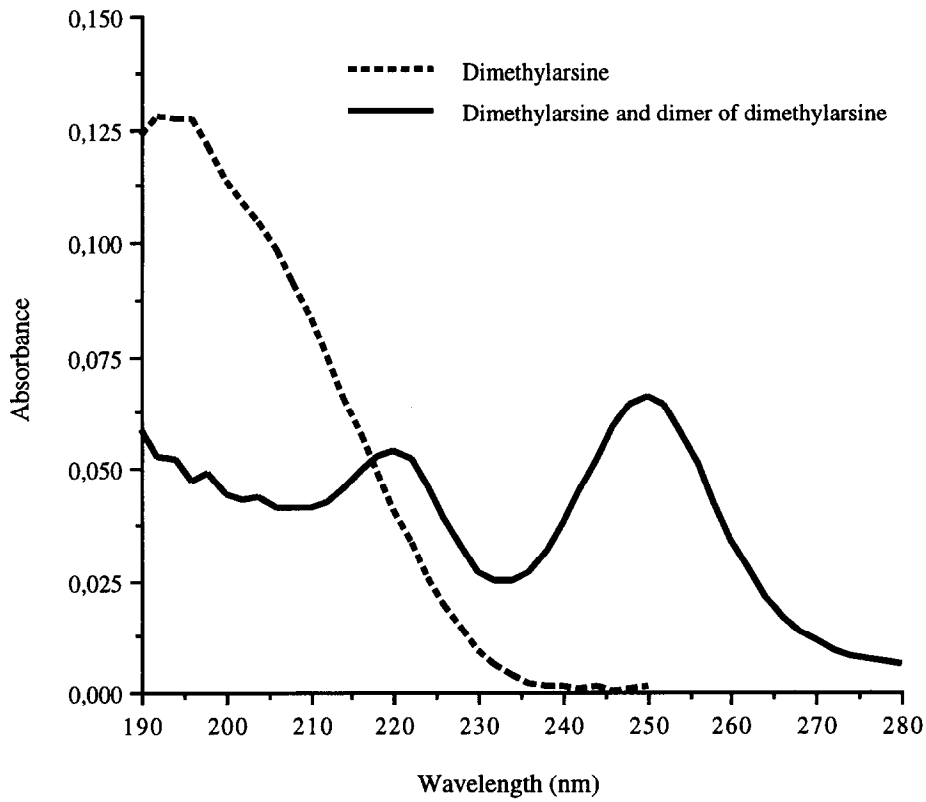

Fig. 2. Spectra of dimethylarsine under different conditions (see text).

generation, retention and revolatilization of the volatiles.

Two large bands were observed in the spectra obtained. One of these, between 190 and 230 nm, could be assigned to the dimethylarsine: the second, at wavelengths above 250 nm, was present as a function of the operating conditions. The appearance of this band in a longer wavelength zone of the spectrum implied a greater complexity in its structure.

Keeping this fact in mind and considering the characteristics of the compound generated, this signal can be assigned to the $Me_2AsAsMe_2$ ($Me{=}CH_3$) the dimer of dimethylarsine. This would be produced, in a similar way to the dimer of inorganic arsine, by the reaction:

$$2Me_2AsO_2^- + BH_4^- + 3H^+ \rightarrow Me_4As_2 + B(OH)_3 + H_2O + H_2$$

with the difference that it shows a greater stability than the arsine dimer, principally due to the methyl groups present in its structure.

4.2. Separation of the compounds

The different boiling points of dimethylarsine and the dimer of the dimethylarsine, at 36°C and 78°C respectively, are due to their structural differences. Because of this difference it was possible to separate and individualize both spectra in the gas phase. The system used in this study was the same as discussed above, with variations in the operating conditions for each compound. The tests showed that revolatilization was obtained with high carrier gas flows for both species; the temperature, however, had a differentiating effect. The monomer was revolatilized at room temperature while the dimer needed higher temperatures.

The following method was used to separate the compounds:

1. Starting with a dimethylarsine solution of 1 $\mu g\ ml^{-1}$ As, the volatiles were generated and trapped in the liquid nitrogen cold trap.
2. Using a nitrogen flow at room temperature, the volatiles were carried through the continuous flow cell, making measurements from 190 to 280 nm. The spectrum found is shown as the dotted line of Fig. 2.
3. Once the disappearance of the dimethylarsine spectrum had been observed, the trap was placed in a hot water bath at 80°C for 1 min in order to revolatilize the second compound.
4. Using a nitrogen flow at 80°C, the volatiles were carried to the flow cell to obtain their spectrum, shown as a continuous line in Fig. 2.

4.3. Identification of the compounds

The compounds were retained separately, as explained previously, in several solvents of different polarities (water, methanol, chloroform, dichloromethane and hexane). The retention system is shown in Fig. 3. This system allowed the gas spectra of the volatile generated to be measured prior to its retention in the liquid phase.

The tests were carried out in the presence and absence of dimethylarsinate, which allowed possible bands produced by other species present in the system, such as the solvents, to be excluded. The spectra obtained in the liquid phase are shown in Figs. 4 and 5. A large difference can be seen in the species retained in methanol and hexane. Two different bands can be seen clearly in these solvents, one at room temperature (short wavelengths) corresponding to the dimethylarsine and other at 80°C (longer wavelengths) which corresponds to the dimer of dimethylarsine. These bands agree with those observed for the gas phase.

Keeping this fact in mind, the retentions were carried out again, using deuterated chloroform as the retention solvent; the ^1H NMR spectra of the retained species were then obtained. By comparing the results with the literature [29,30], it was possible to

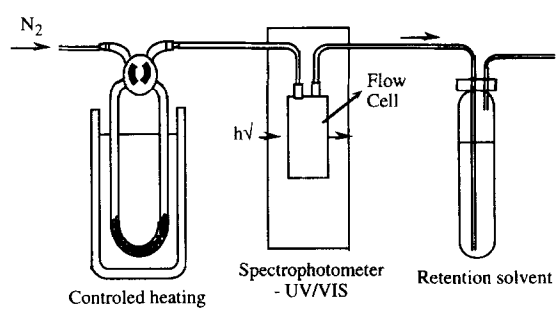

Fig. 3. Absorption system used for the retention of compounds in different solvents.

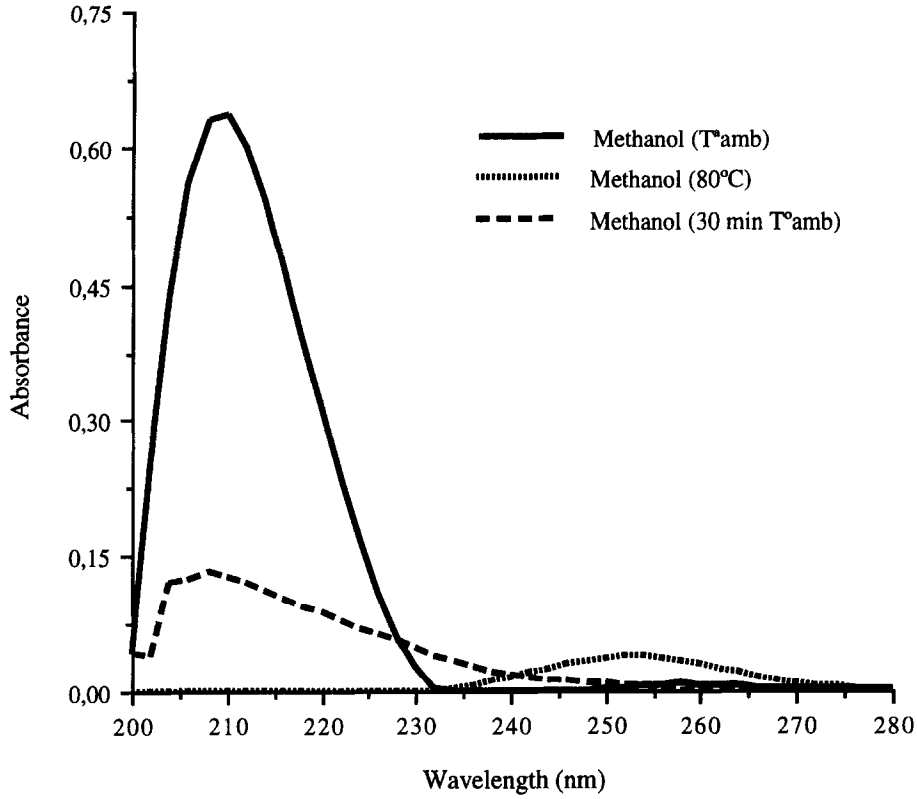

Fig. 4. Absorption spectra of dimethylarsine in methanol under different condition.

distinguish the different compounds. In the low temperature retention, the signals were as follows: for dimethylarsine, 1.02 (Me_2As; d), 2.41 (AsH, s) and monomethylarsine, which is formed by the demethylation of the dimethylarsine, 1.25 (MeAs, t), 4.1 (AsH_2q, q); and in the high temperature retention, the dimer of the dimethylarsine: 1.9 (Me_2As, s); all ppm vs. tetramethylsilane.

Starting from these solutions, we investigated the changes in the retained compounds over time. To do this, the solutions were left at room temperature for 30 min and their spectra were obtained again. It was seen that the spectra obtained after this period from the 80°C gas phase solutions were different from those obtained initially: there was a displacement in the bands towards shorter wavelengths, that is, towards the monomer band.

These data demonstrate that the band at longer wavelength corresponds to the dimer of the dimethylarsine which is formed during the reduction, while the band located at short wavelengths relates to dimethylarsine. A relationship between these two species is therefore produced during the generation which can be represented as follows:

$$2Me_2AsH \rightleftarrows Me_2AsAsMe_2 + H_2.$$

This equilibrium is very interesting from the analytical point of view. The signal can increase considerably depending on the dominant species, as the relation between the decrease in the dimer signal and the conserved increase in the monomer signal is nearly from 1 to 10. The method's sensitivity depends on the direction in which the equilibrium moves.

To test whether this same behavior can be observed in the gas phase, a study was carried out on the generation, retention and revolatilization conditions, varying both temperature and time in each case. The most important result was observed when changing the carrier gas used during generation from nitrogen to hydrogen; it agreed with the proposed equilibrium, in that a greater supply of hydrogen moved the balance further towards the disappearance of the dimer thus

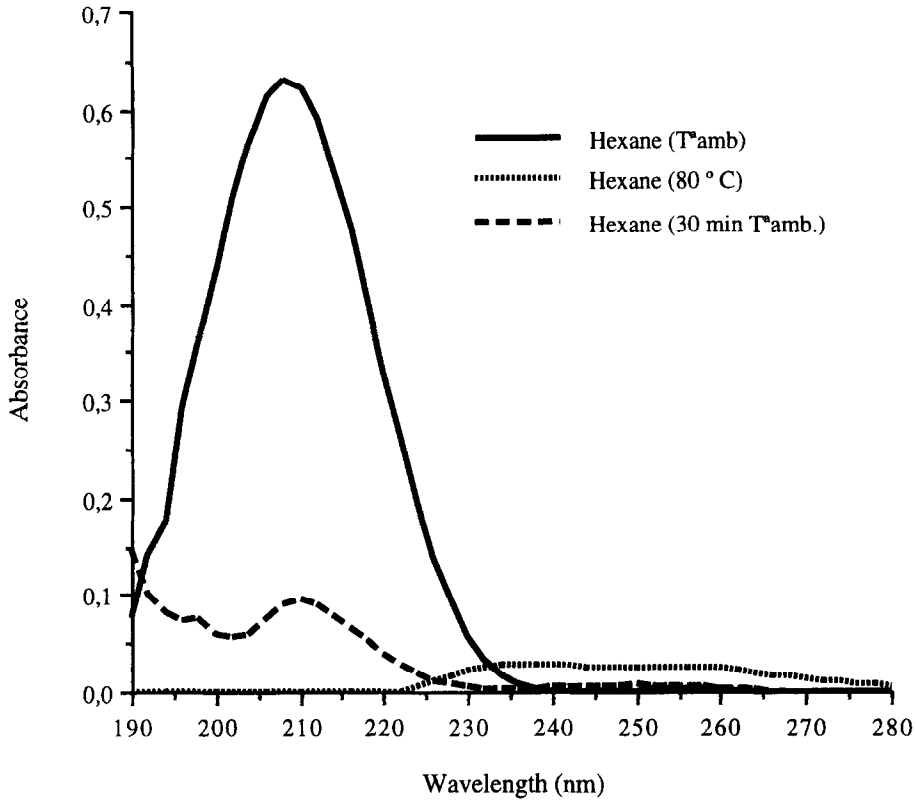

Fig. 5. Absorption spectra of dimethylarsine in hexane under different condition.

giving a considerable signal increase. Another way to increase the amount of hydrogen present during the reaction is to increase the concentration of reducing agent.

The variations in temperature and time led us to the conclusion that once the compounds are formed in the reaction, they can interreact as a function of the conditions: the monomer is favored by short waiting times and high temperatures. An increase in the compound's contact time favors the equilibrium situation, increasing the dimer concentration and reducing the analytical signal.

4.4. Application to other arsenic species

Using the system described above, the determination of methylarsine dibromide was carried out through generation and subsequent measurement of monomethylarsine. From the results shown above, appearance of the dimer of monomethylarsine could have been expected; however, the spectra obtained did not show more than one band, at short wavelength (190 nm) corresponding to monomethylarsine.

As with the DMA, the various experimental conditions were altered; in this case, no large differences were seen at any point in the study. The final conditions for the determination of this substance are similar to those found for DMA, making possible a simultaneous determination for both under optimum conditions.

4.5. Analytical characteristics

Under the instrumental and chemical conditions outlined in the experimental section, individual calibration studies were made for each compound, using the wavelengths of maximum absorbance for dimethylarsinic acid (194 nm). The slopes, intercepts, correla-

Table 2
Calibration parameters for organoarsenic compounds

	Intercept	RSD (%)	Slope	RSD (%)	r^2	RSD (%)
DMA	0.013	14.3	0.0053	1.04	0.999	0.447
Methylarsine bromide	0.013	12.7	0.0028	0.63	0.998	0.052

n=5.

Table 3
Detection limits, precision and accuracy values obtained for organoarsenic compounds

	Detection limit (ng ml^{-1})	RSD [a] (%)	Accuracy [b] (%)
DMA	1.1	8.46	98
Methylarsine bromide	2.8	8.04	97

[a] n=20.
[b] Recovery for 20 determinations at 10 times detection limit.

tion coefficients and their relative standard deviations (RSDs) are shown in Table 2. The detection limits (Table 3) were calculated according to IUPAC (K_d: 6), the values reported are the mean of five replicates. RSD values, calculated from 20 determinations obtained from different days, together with accuracy values obtained from a solution containing 10 times the corresponding detection limit, are given in Table 3.

5. Conclusions

The hydride generation gas phase molecular absorption spectrometry system provides good results for the determination of monomethyl and dimethylarsine, the introduction of a preconcentration step giving results which are comparable to other, more sensitive techniques. The use of a diode-array molecular absorption spectrometer as the detector allows spectra of the generated volatiles to be obtained over a wide wavelength range, making possible observations of the different reactions taking place in the dimethylarsine generation by continuous addition of sodium tetrahydroborate. It was observed that, during this generation, different related compounds are formed, which has a significant effect on the analytical signal. The spectral study allows us to assess not only the compounds formed during the different steps of the process (generation, retention, revolatilization), but also the relation between the species present and the experimental parameters.

It is possible to carry out the separation and identification of the two generated volatiles, dimethylarsine and the dimer of the dimethylarsine, by their revolatilization at different temperatures and obtaining their ^{1}H NMR spectra. The comparison between the molecular spectra obtained in the gas and liquid phases led us to the conclusion that different bands for different chromophoric groups are to be found in the spectra. The first related to the As–H bond, to be found in the 190 nm range and which can be observed only in the dimethylarsine spectrum. The second is the band from 210 to 230 nm, which can be seen in the spectra of both dimethylarsine and dimer of the dimethylarsine, and relate, to the As–C bond. A third band, in the 250 nm range, can be seen only in the dimer of the dimethylarsine spectra; this is assigned to the As–As bond.

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References

[1] H. Hasegawa, Y. Shorin, M. Matsui, M. Hojo and M. Kawashima, Anal. Chem., 66 (1994) 3247.
[2] R.S. Braman and C.C. Foreback, Science, 182 (1973) 1247.
[3] Y. Talmi and D.T. Bostick, Anal. Chem., 47 (1975) 2145.
[4] M.O. Andreae, Anal. Chem., 49 (1977).
[5] J.R. Ashby and P.J. Craig, Sci. Total Environ., 78 (1989) 219.
[6] R. Rubio, A. Padró, J. Albertí and G. Rauret, Anal. Chim. Acta, 283 (1993) 160.
[7] B. Zhu and M.A. Tabatai, J. Environ. Qual., 24 (1995) 622.
[8] X.C. Le, W.R. Cullen and K.J. Reimer, Appl. Organomet. Chem., 6 (1992) 161.
[9] J.S. Blais, G.M. Momplaisir and W.D. Marshall, Anal. Chem., 62 (1990) 1161.
[10] Y. Lin, X. Wang, D. Yuan, P. Yang and B. Huang, J. Anal. Atom. Spectrom., 7 (1992) 287.
[11] A. Brockmann, C. Nonn and A. Golloch, J. Anal. Atom. Spectrom., 8 (1993) 397.
[12] S. Branch, L. Ebdon and P. Oneill, J. Anal. Atom. Spectrom., 9 (1994) 33.
[13] Y. Ionue, K. Kawabata, H. Takashashi and G. Endo, J. Chromatogr. A., 675 (1994) 149.
[14] M.B. Amran, A. Hagège, F. Lagarde and M. Leroy, Chem. Anal., 40 (1995) 309.
[15] P. Morin, M.B. Amran, S. Favier, R. Heimburger and M. Leroy, Fresenius' Z. Anal. Chem., 342 (1992) 357.
[16] H. Greschonig and K.J. Irgolic, Appl. Organomet. Chem., 6 (1992) 565.
[17] A. Syty, Anal. Chem., 45 (1973) 1744.
[18] M.S. Cresser and P. Isaacson, Talanta, 23 (1976) 885.
[19] K. Dittrich, CRC Crit. Rev. Anal. Chem., 16 (1986) 223.
[20] K. Dittrich, Prog. Anal. At. Spectrosc., 3 (1980) 209.
[21] W.Y. Wen and R.M. Noyes, J. Phys. Chem., 76 (1972) 1017.
[22] K. Koga, T. Hadeishi and R. Takeyama, Anal. Chem., 57 (1985) 1265.
[23] J. Sanz, F. Gallarta, J. Galban and J.R. Castillo, Fresenius' Z. Anal. Chem., 330 (1988) 510.
[24] J. Sanz, F. Gallarta, J. Galban and J.R. Castillo, Analyst, 113 (1988) 510.
[25] J. Sanz, L. Ortega, J. Galban and J.R. Castillo, Microchem. J., 41 (1990) 29.
[26] J. Sanz and F. Gallarta, Anal. Chim. Acta, 255 (1991) 113.
[27] J. Sanz, S. de Marcos, J. Galban and F. Gallarta, Analusis, 21 (1993) 27.
[28] J. Sanz, S. Cabredo and J. Galbán, Anal. Chim. Acta, 300 (1995) 321.
[29] N.N. Greenwood and A. Earnshaw, Chemistry of the Elements, Pergamon Press, Oxford, 1984.
[30] D.K. Srivastava, L.K. Krannich and C.L. Watkins, Inorg. Chem., 30 (1991) 2441.