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Determination of arsenic compounds by high-pressure liquid chromatography–graphite furnace atomic absorption spectrometry and thermospray mass spectrometry

William R Cullen and Matthew Dodd
Department of Chemistry, University of British Columbia, Vancouver, BC, Canada V6T 1Y6

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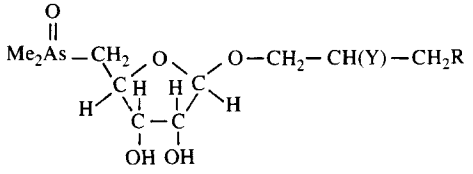
Biologically important arsenic species such as arsenobetaine, arsenocholine iodide, tetramethylarsonium iodide, methylarsonic acid, and dimethylarsinic acid can be separated and quantitated by HPLC. The pH-sensitive separations on a weak anion-exchange column are described, as well as separations on a reverse-phase column with the aid of tetrabutylammonium nitrate or heptanesulfonic acid as ion-pairing agents. The thermospray mass spectra of these arsenicals in addition to those of sodium arsenate and an arsenosugar derivative are described. This technique is suitable for HPLC MS studies.

Keywords: Organoarsenic species, environmental, HPLC, thermospray mass spectra, arsenosugar.

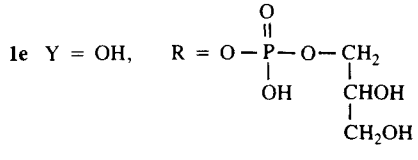
INTRODUCTION

Organoarsenic species such as arsenobetaine $(CH_3)_3As^+CH_2COO^-$ (AB), tetramethylarsonium ion $(CH_3)_4As^+$ (TMA^+), dimethylarsinic acid $(CH_3)_2As(O)OH$ (DMA), methylarsonic acid $(CH_3)AsO(OH)_2$ (MMA), trimethylarsine oxide $(CH_3)_3AsO$ (TMAO), and a range of arsenosugars, **1**, are known to occur in some biological systems and the environment.[1–4] Inorganic arsenic is also found in both III and V oxidation states. These species occur in different concentrations and have very different toxicities.[2,3] In order to estimate effectively any problem associated with the presence of these compounds in a system, the development of improved techniques for their speciation is essential. Examples of the use of a variety of these techniques are as follows: ion-exchange chromatography;[5] ion chromatography,[6] gas chromatography of volatile derivatives such as hydrides,[7,8] and high-pressure liquid chromatography (HPLC).[9–16]

HPLC is potentially the most suitable technique for the separation of nonvolatile arsenic species, especially if it is combined with a graphite furnace atomic absorption (GF AA) spectrometer as the arsenic-specific detector (HPLC-GF AA).[9,10,12] The sampling can be done via a specially designed sampling cup,[12] or fractions can be collected and transferred manually to the spectrometer.[16] The first part of the present work describes the separation of arsenicals on a reverse-phase column by using ion-pair reagents, and then, secondly, separation on a weak anion-exchanger. These techniques were developed for arsenic speciation studies on some marine invertebrates of British



1a Y = OH, R = OSO_3H
1b Y = OH, R = OH
1c Y = OH, R = SO_3H
1d Y = NH_2, R = SO_3H



Columbia. Some results of the speciation studies that employ the methodologies developed in the present paper have previously been published.[17] The third part of this work describes the use of thermospray mass spectrometry (MS) for the detection of arsenic species. This MS technique has the advantage that it can be used on liquid samples, in particular HPLC effluents, without derivitization. In general, little work seems to have been done on the mass spectrometry of environmentally important arsenic species. GC MS of derivatives has been used to identify DMA, MMA, phenylarsonic acid and arsenate.[18–20] Pyrolytic mass spectrometry of AB, and arsenocholine, $(CH_3)_3As^+CH_2CH_2OH$ (AC), has been described.[21,22] Most of the studies on AB and AC have employed fast *atom bombardment* (FAB)[16,21,23,24] and field desorption[22,23] techniques. More recently, atmospheric pressure chemical ionization and electrospray have been used for these species,[25] and an HPLC-ICPMS detection of arsenobetaine has been reported.[26]

EXPERIMENTAL

Apparatus

The HPLC system consisted of Waters M45 and M510 pumps controlled by a Waters Automated Gradient controller. Samples were introduced onto the column via a Waters U6K injector. A Varian Techtron Model AA1275 atomic absorption spectrometer with a Varian GTA-95 graphite furnace atomizer was used as the arsenic-specific detector. Operational details of the HPLC-GF AA system have been described previously.[27] A Waters μ-Bondapak C_{18}, 3.9 mm (i.d.) $\times$ 30 cm steel column and a Waters Protein Pak DEAE 5PW, 7.5 mm (i.d.) $\times$ 7.5 cm steel column were used for separations. Thermospray mass spectra were obtained by using a Vestec Kratos thermospray device interfaced to a Kratos MS 80 RFA mass spectrometer.

Reagents

Arsenobetaine[28] and arsenocholine iodide[29] were prepared by literature methods. Tetramethylarsonium iodide was prepared by condensing 1.7 g of trimethylarsine into 1.0 g of methyl iodide dissolved in 10 cm^3 of diethyl ether. The Carius tube was sealed and the mixture was left overnight at room temperature. The white precipitate was isolated, recrystallized from acetone–ethanol, 4:1 v/v, and dried under vacuum. The compound was characterized by NMR spectroscopy (singlet at δ 1.8) and electron impact mass spectrometry, *m/z* 135, 120, 105.

All solvents used were of HPLC grade and were filtered through Millipore 0.45 μm membrane filters. Deionized water (Aquanetic Aqua Media System) was distilled in glass apparatus and filtered through Millipore 0.45 μm filters before use.

Procedures

HPLC

Water–methanol mixtures, 5 mmol dm^{-3} with respect to tetrabutylammonium nitrate, sulfate or phosphate, were used as the mobile phase at a flow rate of 1 cm^3 min^{-1} for separations on the reverse-phase column. The working pH range was kept between 4 and 7. Fractions of the effluent were collected at 30 s intervals and analyzed by GF AA.[27]

For separations on the Protein Pak Column, 5 mmol dm^{-3} ammonium acetate was used as the mobile phase. The pH of which was adjusted with acetic acid or ammonium hydroxide to a working range of 4–10. The flow rate was maintained at 1 cm^3 min^{-1} and fractions were collected at 30 s intervals and analyzed by GF AA.[27]

Standard arsenical solutions were injected (20 μl) into the HPLC to establish retention times, calibration curves, limits of detection and reproducibility. Purified extracts of marine organisms (details of the extraction and purification procedures are available[17]) were dissolved in 1 cm^3 of water and passed through a 0.45 μm Durapore membrane filter (Millex HV, Millipore Corporation) and 20 μl aliquots were injected into the HPLC.

Thermospray MS

Aqueous ammonium acetate (concentration 1 mol dm^{-3}) was used as the mobile phase. The eluent from a HPLC system was introduced into the interface at a flow rate of 1 cm^3 min^{-1}. Samples were introduced into the interface via a U6K injector. The conditions for the operation of the interface and mass spectrometer were optimized for each arsenical and are given for each spectrum in the Results and Discussion section.

RESULTS AND DISCUSSION

Separations on ion-exchange columns

Various strong ion-exchange resins[9,10,17] have been used for the separation and determination of the arsenicals AB, AC, TMA^+, As(III), As(V), DMA, and MMA. The separation of these species on a weak anion-exchange column was investigated in this work. The Protein Pak packing is a fully porous hydrophilic polymeric resin onto which is bonded diethylaminoethyl functional groups. This packing can be used over a wide pH range from 2 to 12, which allows considerable flexibility in optimizing separations; however, the column does have a low exchange capacity. The following aqueous eluting solutions were used: 5 mmol dm^{-3} sodium acetate, adjusted to pH 4 with acetic acid; 5 mmol dm^{-3} ammonium acetate, pH 6.65; and 5 mmol dm^{-3} ammonium acetate adjusted to pH 10 with ammonium hydroxide.

A typical chromatogram obtained for a mixture of arsenicals is shown in Fig. 1A. At pH 4, AB, As(III) and DMA elute close together immediately after the solvent front. MMA and As(V) are well resolved; however, As(V) has a long retention time of 40 min. In order to separate the three species eluting together, the pH of the eluent is increased to 6.65 by using 5 mmol dm^{-3} ammonium acetate. The chromatogram obtained is shown in Fig. 1B. DMA is resolved from the other two. The retention time of MMA is increased to over 60 min and arsenate is not eluted from the column even after 80 min. On changing the eluent to 5 mmol dm^{-3} ammonium acetate, pH 10, further separation is achieved (Fig. 1C). As(V) and MMA are not eluted from the column before 60 min. Thus by varying the pH of the eluent, the separation of the five species is achieved. For practical purposes the column is run at pH 4 for the detection of As(V) and MMA and then at pH 10 for work involving the other three compounds.

In the eluent at pH 4, arsenate will be mainly present as the $H_2AsO_4^-$ ion;[30] this interacts less with the anion exchanger than the ions present at pH 10, which will be predominantly $HAsO_4^{2-}$. The retention of As(V) at pH 10 is such that it is not eluted from the column even after 80 min. The retention of the other arsenicals shows similarly the effect of pH; however, the retention of AB, a zwitterion $(CH_3)_3As^+CH_2CO_2^-$, is not greatly affected by change of pH.

The separation described above can be quantitated. For example, arsenobetaine elutes between fractions 5 and 7, and when the sum of all individual peak areas (from GF AA measurements) is plotted against the amount of arsenical injected (20 μL of a standard

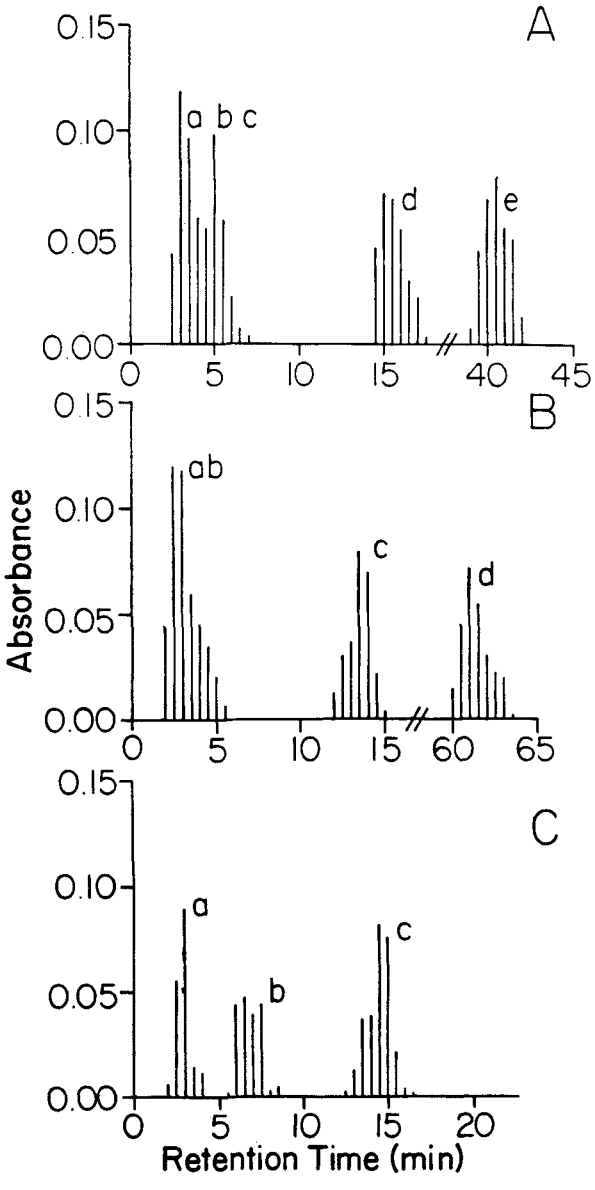


Figure 1 Separation by HPLC of: a, arsenobetaine; b, arsenite; c, dimethylarsinate; d, methylarsonate; e, arsenate. Waters Protein Pak DEAE column; 20 μL samples containing 500 ng arsenic of each arsenical were used. Fractions were collected every 30 s and 20 μL of each fraction was subsequently injected into the graphite tube for arsenic analysis. A, Mobile phase sodium acetate adjusted to pH 4 with acetic acid; B, mobile phase ammonium acetate; C, mobile phase ammonium acetate adjusted to pH 10 with ammonia. Flow rate 1 cm^3 min^{-1}.

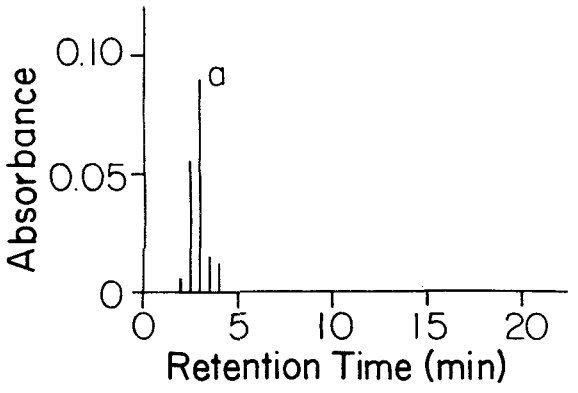


Figure 2 HPLC-GF AA chromatogam of 20 μL of purified Manila clam extracts. Conditions were the same as described in Fig. 1A; 'a' corresponds to arsenobetaine.

solution), a good linear correlation is obtained over the concentration range 100–600 ng. The limit of detection, defined as the analytical concentration giving a signal equal to the blank plus three standard deviations of the blank, is 20 ng. Similar calibration curves for the other species are easily obtained.

As mentioned above, when the Protein Pak column is being used for the analysis of extracts of marine organisms, the column is first run at pH 4 to detect any MMA and As(V) and then at pH 10 to detect other arsenicals. In many samples only arsenobetaine is present. The chromatogram for purified Manila clam (*Venerupis japonica*)[17] extract is shown in Fig. 2 as an example.

Separations on a reverse-phase column

Reverse-phase chromatography involves the use of a nonpolar stationary phase and a polar immiscible mobile phase. Compounds are separated by their relative hydrophobicity, i.e. the most polar compounds are eluted first; thus many arsenicals elute together immediately after the solvent front (water/methanol, 80:20 v/v). The separation of ionic species on a reverse-phase column can be improved by the addition of a suitable lipophilic counterion to produce a hydrophobic ion-pair that is retained more strongly by the stationary phase. The tetrabutylammonium ion (TBA) is used as the ion-pairing reagent in this study. The separation of As(III), As(V), MMA, and DMA is shown in Fig. 3. This separation employed a water/methanol (95:5 v/v) mobile phase adjusted to pH 6.8 with ammonium hydroxide and made 5 mmol dm^{-3} in tetrabutylammonium nitrate (TBAN). The retention of these species is related to their pK_a values. Arsenite, pK_a 9.23,[30] elutes first because it is undissociated under these conditions, and does not pair up with the tetrabutylammonium cation. DMA, pK_a 6.19,[31] is present as the pair $(CH_3)_2AsO_2^-$/$(CH_3)_2AsO_2H$, whereas MMA, pK_{a_1} 4.58 and pK_{a_2} 7.82,[31] is probably present as the pair $CH_3AsO_3^{2-}$/$CH_3AsO_3H^-$. MMA is therefore more likely to form ion-pairs resulting in its longer retention. As(V), the most acidic species among the four with pK_{a_1} 2.25, pK_{a_2} 6.67, and pK_{a_3} 11.60, is retained longest, probably as the ion-pair $[TBA^+]_2HAsO_4^{2-}$.

Brinckman *et al.*[10] described the use of the ion-pair reagents tetrabutylammonium phosphate (TBAP) and tetraheptylammonium nitrate (THAN) for the separation of As(III), As(V), MMA and DMA on a C_{18} column. All four compounds are satisfactorily separated by using water/methanol (75:25 v/v) at pH 7.6, saturated with THAN, as mobile phase. However, they report a retention time of approximately ~36 min for As(V) compared with the approximately ~15 min observed in this study.

The separation shown in Fig. 3 compares well with

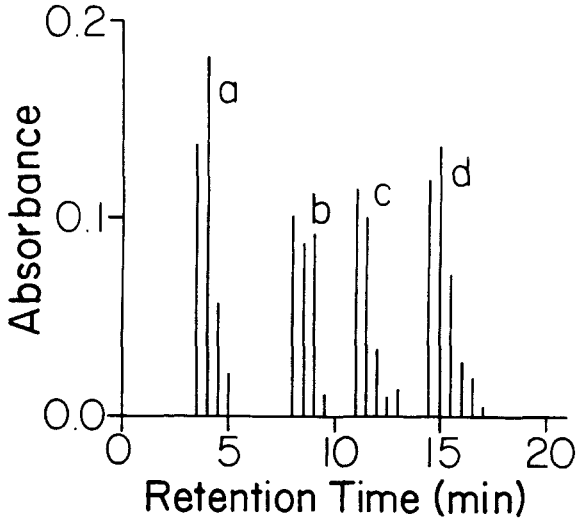


Figure 3 HPLC-GF AA chromatogram of: a, arsenite; b, dimethylarsinate; c, methylarsonate; d, arsenate. Water μ-Bondapak C_{18} column; 20 μL of a sample containing 500 ng arsenic of each arsenical was placed on the column. Mobile phase, water/methanol (95:5 v/v), 5 mmol dm^{-3} in tetrabutylammonium nitrate, adjusted to pH 6.8 with ammonium hydroxide. Flow rate, 1 cm^3 min^{-1}. Fractions were collected every 30 s; 20 μL of each fraction was injected for arsenic analysis by GF AA.

that obtained by Irgolic and co-workers[32] on a reverse-phase column by using two different mobile phases: first 0.002 mol dm^{-3} hexadecyltrimethylammonium bromide (HTAB) at pH 9.6 followed by water/acetic acid (99:1 v/v). These solvent systems are not suitable for use on the Waters C_{18} column, which is unstable above pH 7.6.

The concentration of ion-pair reagent and the composition of the single mobile phase is critical to achieve separation. Thus a change of the water/methanol composition from 95:5 to 90:10 v/v results in faster elution of the compounds; however, MMA and As(V) are not well resolved. If the mobile phase is saturated with TBAN, no separation is obtained. All the compounds elute close to the solvent front.

Others report similar results,[11] prompting a study of the effect of the tetrabutylammonium counterion on the separation of arsenicals when water/methanol (90:10 v/v) is used as mobile phase.

No useful separations are obtained with the eluent saturated with tetrabutylammonium nitrate (TBAN), tetrabutylammonium sulfate (TBAS) and tetrabutylammonium phosphate (TBAP). The four arsenicals all elute close to the solvent front. Moreover, severe interference is obtained in the GF AA analysis of the fractions due to the large excess of the ion-pair reagents, leading to poor reproducibility. Much better separations are obtained when a 5 mmol dm^{-3} concentration of the ion-pair reagent is used. The best separation is obtained with TBAN, Fig. 3: with 5 mmol dm^{-3} TBAP, As(III) is separated from As(V), but MMA and DMA co-elute; with 5 mmol dm^{-3} TBAS, only As(III) is separated.

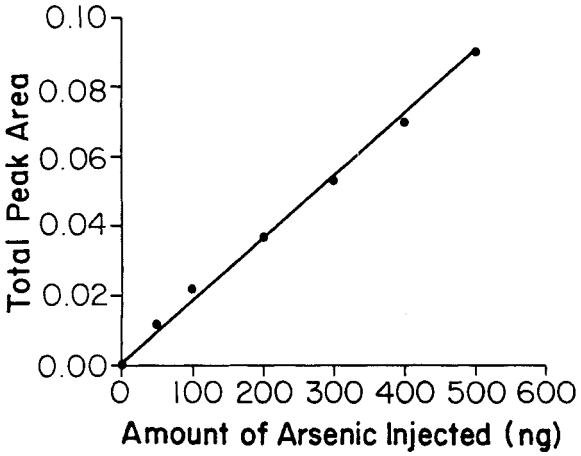


Figure 4 Typical calibration curve for the HPLC-GF AA determination of arsenite under the conditions described for Fig. 3.

Separations on the C_{18} column can also be quantitated and a typical calibration curve for As(III) is shown in Fig. 4. The curve is linear for the concentration range 0–500 ng arsenic and has a linear correlation coefficient of 0.98. The limit of detection, defined earlier, is determined to be 40 ng. The calibration curves for the other arsenicals follow a similar trend, with the limits of detection being 30 ng for As(V), 40 ng for MMA, and 50 ng for DMA. These detection limits are comparable with those reported elsewhere.[10]

Application of ion-pair chromatography to extracts of marine organisms

The chromatogram of a sample of purified Manila clam extract shows an arsenic-containing fraction that elutes earlier than the four compounds studied. As described above, the presence of AB in the Manila clam extract is established by using the Protein Pak column. To confirm this, AB was chromatographed on the C_{18} column; AB elutes close to the solvent front and has a retention time similar to the arsenical in the extract; in fact, they co-elute from mixtures.

Separation of AB, AC and TMA^+ on a C_{18} column

These arsenicals all elute close to the solvent front when TBAN is used as the ion-pair reagent on the C_{18} column. This is not surprising since these compounds exist in solution mostly as cations under the conditions used and are therefore not capable of forming ion-pairs with the tetrabutylammonium ion. Heptanesulfonic acid or dodecylbenzenesulfonic acid, however, are capable of forming ion-pairs with these arsenicals, and Stockton and Irgolic[12] used these reagents to accomplish the separation of AB, AC, As(III) and As(V) on a C_{18} column. We find that their solvent system, water/acetonitrile/acetic acid (95:5:6 by vol.) 5 mmol dm^{-3} in heptanesulfonic acid, also can be used for the separation of tetramethylarsonium ion (TMA^+), which elutes close to, but distinguishable from, AC (Fig. 5A). A chromatogram run under similar conditions of an extract of the leg muscle of the crab *Chionoecestes baidii* is shown in Fig. 5B. Four fractions are obtained. Fraction 'a' is probably AB, they coelute; however, the identity of the others remains uncertain.

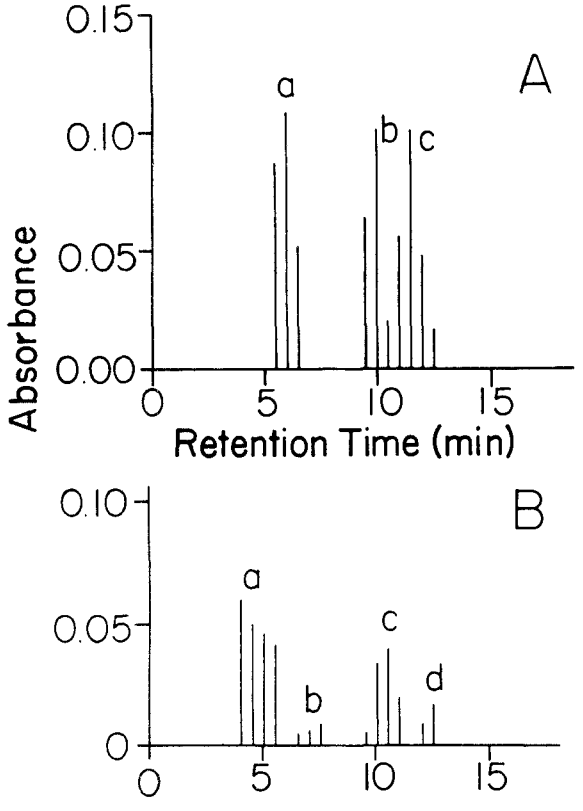


Figure 5 A, HPLC-GF AA chromatogram of: a, arsenobetaine; b, arsenocholine; c, tetramethylarsonium iodide. μ-Bondabak C_{18} column; 20 μL of a sample containing 500 ng arsenic of each arsenical placed on the column. Mobile phase, water/acetonitrite/acetic acid (95:5:6 by vol.), 5 mmol dm^{-3} in heptanesulfonic acid. Flow rate 1 cm^3 min^{-1}. Fractions were collected every 30 s; 20 μL of each fraction was injected for GF AA analysis. B, HPLC-GF AA chromatogram of crab leg muscle extract, as in A.

Thermospray mass spectrometry of arsenic species

The mass spectra are obtained in the positive ion mode. The spectrum of arsenobetaine is shown in Fig. 6A. The base peak is at *m/z* 329. This is due to $[2AB + NH_4 - COOH]^+$. Other peaks occur at 178 $[AB]^+$, 193 $[AB + CH_3]^+$, and 214 $[AB + H_2O + NH_4]^+$. It is difficult to account for the peak at *m/z* 305; possibly it is $[AB + I]^+$, but the source of iodine (I) is not obvious. This spectrum is obtained with the vaporizer at 201 °C, probe 128 °C, block 156 °C, jet 251 °C, and water/methanol 1 molar in ammonium acetate as eluent. If higher temperatures are used (vaporizer 214 °C, probe 131 °C, block 206 °C, jet 284 °C), the spectrum obtained, Fig. 6B, shows a base peak at *m/z* 135 $[(CH_3)_4As]^+$ due to fragmentation of the arsenical. Other peaks occur at *m/z* 305, 329, and 397; the parent peak at *m/z* 178 is not observed. The spectrum of tetramethylarsonium iodide, Fig. 7A, shows some resemblance to that of the higher temperature AB spectrum (Fig. 6B). Both show a base peak at *m/z* 135 due to $[(CH_3)_4As]^+$; however, the peak at *m/z* 329 distinguishes AB from the arsonium compound. The thermospray mass spectrum of arsenocholine iodide, AC, is shown in Fig. 7B, with peaks at *m/z* 135 $[(CH_3)_4As]^+$, 147 $[AC\text{-}H_2O]^+$, 165 $[AC]^+$, 439 $[2AC + I - H_2O]^+$, 457 $[2AC + I]^+$, and 421 $[2AC + I - 2H_2O]^+$.

The spectrum of sodium arsenate (Na_2HAsO_4) is shown in Fig. 8. The base peak is seen at *m/z* 187 $[Na_2HAsO_4 + H]^+$, and other peaks at 168 $[186 - H_2O]^+$, 201 $[186 + CH_3]^+$ and 217 $[186 + OCH_3]^+$. Figure 8 also shows the spectrum of DMA. The base peak is at *m/z* 139 $(DMA + H)^+$, with other peaks at 277 $[2DMA + H]^+$ and 153 $[DMA + CH_3]^+$. This last peak is also present in the electrospray spectrum of DMA,[25] and was attributed to $[DMA + H - H_2O + CH_3OH]^+$ (effectively $[DMA + CH_3]^+$) by these workers.

Finally, the thermospray mass spectrum of a sample of an arsenosugar derivative, **1b**, is shown in Fig. 9. The base peak is at *m/z* 329 with other peaks at *m/z* 177, 221, and 311. Possible assignments for some of these peaks are given as follows:

329 $[P + H]^+$, 311 $(P + H - H_2O]$,

221 $[(CH_3)_2AsCH_2\overline{CHCHOHCHOHC}^+O]$,

177 $[(CH_3)_2\ AsCH_2CH(OH)C\overset{+}{=}O]$.

The spectra described above are reproducible and can be used for the identification of fractions from HPLC columns as outlined in an earlier publication.[17] The quantitative aspects of these thermospray spectra are being investigated. Preliminary studies indicate that matrix effects may be severe.

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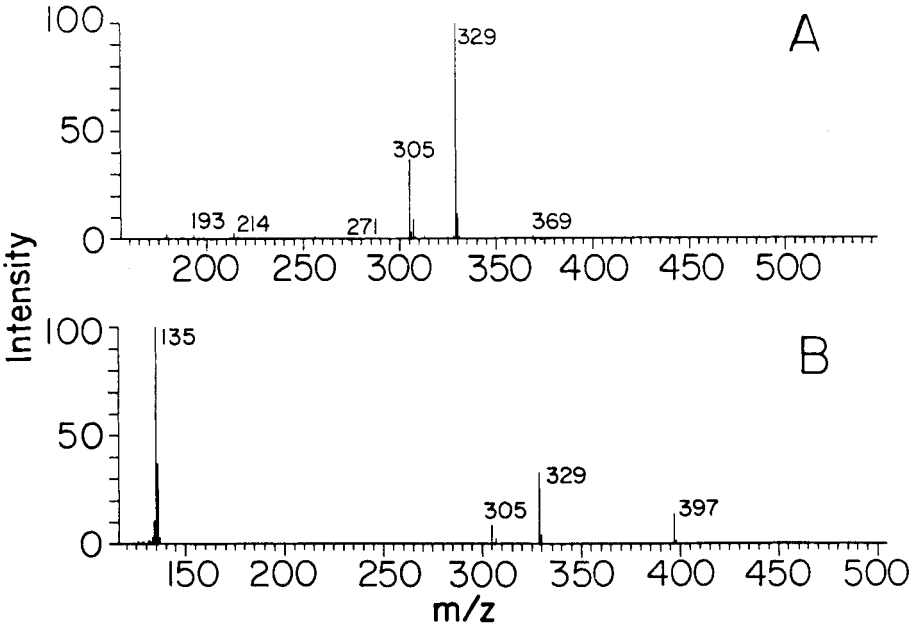

Figure 6 Thermospray mass spectrum of arsenobetaine: A, vaporizer at 201 °C, probe at 128 °C, block at 156 °C, and jet at 251 °C; B, vaporizer at 214 °C, probe at 131 °C, block at 206 °C, and jet at 284 °C.

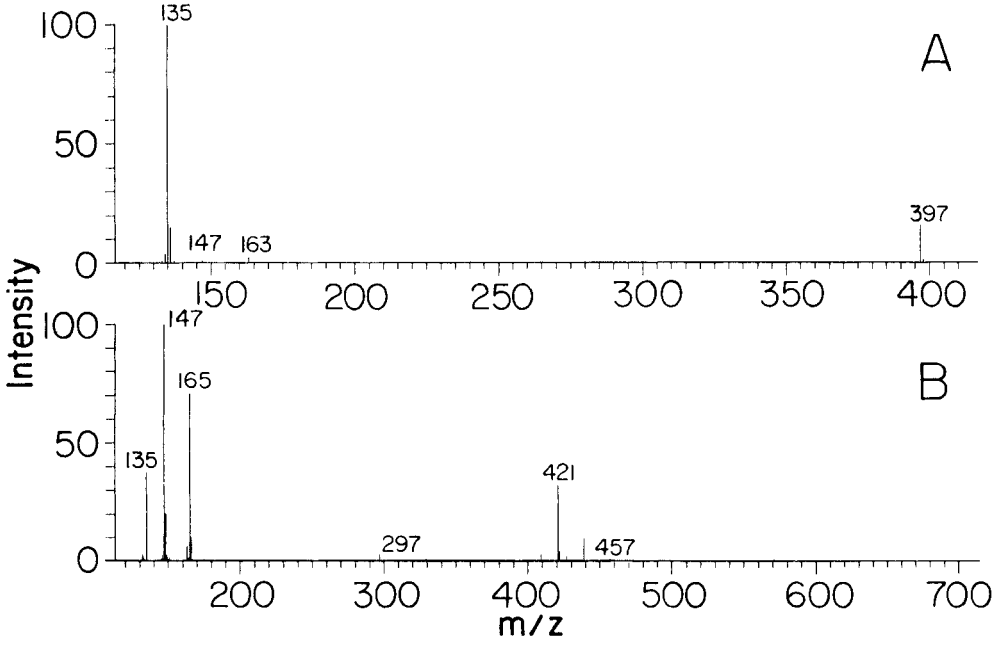

Figure 7 Thermospray mass spectrum of: A, $(CH_3)_4AsI$; B, $(CH_3)_3As^+CH_2CH_2OH$; vaporizer at 212 °C, probe at 133 °C, block at 171 °C, and jet at 234 °C; 20 μL of solution (1 mg dm^{-3}) was injected.

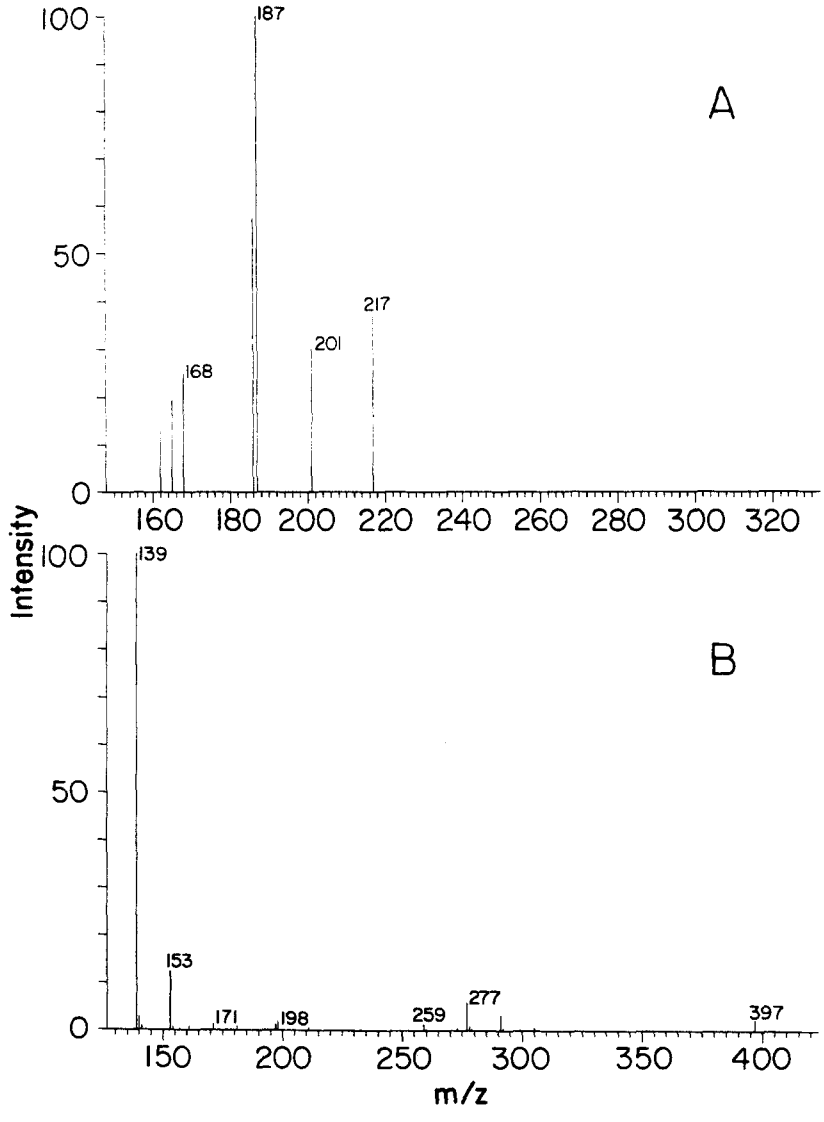

Figure 8 Thermospray mass spectrum of: A, Na_2HAsO_4; B, $(CH_3)_2AsO(OH)$; same conditions as for Fig. 7.

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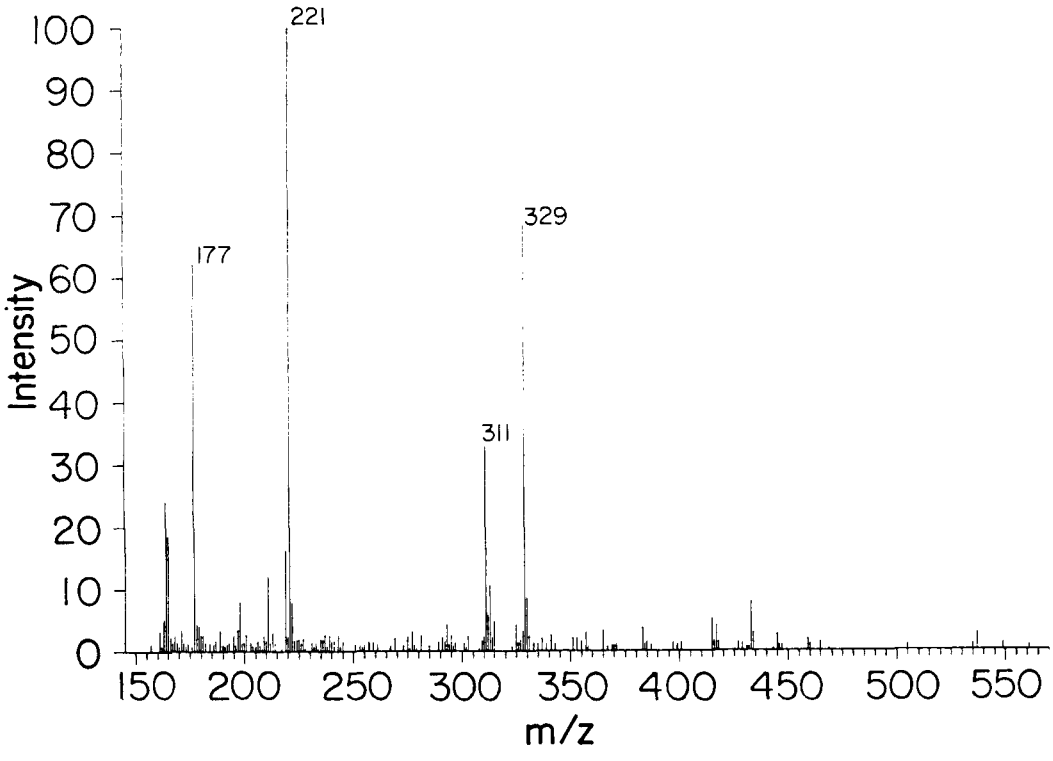

Figure 9 Thermospray mass spectrum of **1b** vaporizer at 201 °C; probe at 131 °C, block at 156 °C, and jet at 251 °C; 20 μL of solution (1 mg dm^{-3}) was injected.

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