HIGH-RESOLUTION GAS AND LIQUID CHROMATOGRAPHY OF ORGANOARSENIC COMPOUNDS

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SUMMARY

High-resolution gas chromatography and high-performance liquid chromatography (HPLC) of organoarsenic compounds is reported. Thermogravimetric analysis indicates that analyte decomposition may occur in injection and detection interfaces, thus careful temperature control is needed. Specific element detection for arsenic and carbon was by microwave induced plasma spectroscopy. HPLC was optimized on phenylbonded silica with hexane–dichloromethane mobile phase. Eluate integrity was confirmed by d.c. argon plasma emission.

INTRODUCTION

High-resolution inorganic chromatography provides many challenges since chemical reactivity, stability, solution behavior and volatility may all affect quantitative elution. Among neutral inorganic compounds, metal chelates and carbon-bonded organometallics have received most attention in gas chromatography (GC)[1] and high-performance liquid chromatography (HPLC)[2]. Relatively few studies have examined the comparative merits of high-resolution gas chromatography (HRGC) and HPLC for compounds of an element which contain both sigma bonded organometallic and "chelated" moieties. Further, organometalloids with these characteristics have been largely neglected. This paper presents some preliminary results for a group of analytically significant organoarsenic compounds.

"Speciation" of inorganic or organometallic analytes, *i.e.,* the qualitative and quantitative determination of specific chemical species in addition to "total inorganic element analysis", is of particular importance for arsenic compounds whose environmental hazards vary widely with molecular form.

Until the early 1970s the analysis of arsenic generally involved digestion and determination of the total arsenic concentration as arsine, AsH_3, without regard to its origin. A method to distinguish As(III), As(V) and organo-arsenic compounds was developed by Yasui *et al.*[3], involving extraction of As(III), reduction of As(V)

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to As(III) and re-extraction of arsenic followed by digestion and generation of arsines with atomic absorption detection. Howard[4] varied the pH of a solution to control selective reduction and sequential evolution of arsines. From As(III), As(V), mono-methylarsonic acid (MMAA) and dimethylarsinic acid (DMAA). Atomic absorption was used in the detection.

The development of graphite furnace atomic absorption (GFAA) coupled, as an element specific detector, to a high-performance liquid chromatograph, allowed separation and identification of a number of arsenic species. Brinckman *et al.*[5,6] used reversed-phase HPLC with GFAA detection to determine arsenite (AsO_2^-), arsenate (AsO_4^{3-}), MMAA and DMAA. Woolson and Aharonson[7] developed a similar method. A number of researchers[8-11] employed ion chromatography with GFAA detection for the determination of the same species. An analytical gas chromatographic approach was that of Schwedt and Russel[12]; it involved complexation and extraction of arsenic from solution followed by a Grignard reaction for conversion of arsenic to triphenylarsine, gas chromatography and flame ionization detection. Total arsenic only was determined. A gas chromatographic separation of eight arsines was described by Gudzinowicz and Martin[13], using an argon ionization detector. A method for the determination of As(III), As(V), MMAA, DMAA and several alkyl arsines was developed by Talmi and Bostick[14,15]. It involved digestion and conversion of arsenic compounds to the corresponding arsines followed by either cold trapping or extraction into an organic solvent. Subsequent analysis used a microwave inudced plasma (MIP) for specific element detection.

In 1982, Brinckmann and Jewitt[16] separated arsonate (AsO_4^{3-}), monomethyl-arsonic acid (MMAA) and phenylarsonic acid (PAA) using an HPLC–GFAA system with simultaneous UV detection. In a subsequent paper, Weiss *et al.*[17] utilized HPLC–GFAA to resolve these species in a methanol extract of Green River Oil Shale. Derivatization of MMAA and PAA with 3-methylcatechol gave compounds which were analyzed by GC–MS to provide further positive identification[18].

Work performed concurrently in this laboratory was aimed at the development of instrumental methods for the identification of organoarsenicals directly without sample modification such as derivatization.

EXPERIMENTAL

Instrumentation

Gas chromatography with microwave plasma spectral detection. A Varian 2440 gas chromatograph equipped with a glass-lined injection port was used. A 30 m × 0.25 mm I.D. thin film DB-1 bonded phase fused-silica capillary column was fed through a transfer line and interface oven to the microwave plasma detector, which consisted of a "Beenakker" copper cavity mounted on the end of the interface oven. A quartz tube (6.2 mm O.D. × 0.5.–1.0 mm I.D.) extended from the interface oven into the cavity to allow the end of the column to be threaded to within 3–4 mm of the plasma, thus eliminating contact of the sample with anything except for the column before reaching the detector. A detailed description of the gas chromatograph–microwave emission detector used is given by Quimby[19]. The plasma was operated at 30 W forward power and approximately 0.5 W reverse power; it was monitored on the 228.8-nm arsenic line and the 247.9 nm carbon line. The plasma

flow was 46 ml/min helium and the column flow was 1.5 ml/min. Injections were split 30:1.

Preparation of organoarsenicals

Samples of 2-phenyl-2,2'-spirobi(1,3,2-benzoxarsole) (As-CAT), 2-phenyl-2,2'-(3H,3'H)-spirobi(1,3,2-benzoxazarsole) (As-NH) and 2-phenyl-2,2'-spirobi-(1,3,2-ethylenedioxarsole) (As-EG) were obtained from Dr. Arjun Sau and from Dr. Robert Holmes (University of Massachusetts). Additional quantities were synthesized according to published procedures[20]. Triethylarsine and tripropylarsine were synthesized by literature methods[21,22] with the following modifications. Ethyl bromide (0.3 moles) or propyl iodide was added to tetrahydrofuran (50 ml) in a 250-ml round-bottomed flask equipped with a condenser. The solution was cooled, magnesium turnings (0.3 moles) were added and the the mixture was maintained at a reflux until most of the magnesium had reacted. After 4 h solid As_2O_3 was added slowly and the solution was stirred and refluxed overnight. After cooling, it was added to a 5% solution of hydrochloric acid containing ice, to hydrolyze any unreacted Grignard reagent. Aliquots (50 ml) of the solution were extracted twice with 75-ml portions of eithyl ether, which were rotoevaporated, leaving a dark brown solution from which triethylarsine was distilled at approximately 138°C. The product was characterized by NMR. A vacuum distillation was needed to obtain the tripropylarsine although difficulties were encountered in isolating a pure product. Tripropylarsine was confirmed by mass spectral analysis. Triphenylarsine was obtained from Chemical Dynamics, S. Plainfield, NJ, U.S.A.

Thermogravimetic analysis

Thermogravimetric analysis was performed on As-CAT, As-NH, and As-EG on a DuPont 950 thermogravimetric analyzer and a DuPont 900 thermal analyzer (DuPont Instruments, Wilmington, DE, U.S.A.). The system was purged with nitrogen and samples were heated at 15°C/min from 50°C to 600°C.

Liquid chromatographic separations with UV detection

Triphenylarsine, As-CAT and As-NH were dissolved in dichloromethane and analyzed on an LC/9533 liquid chromatograph (IBM Instruments, Danbury, CT, U.S.A.). Separation was obtained on an IBM 5 μm phenyl bonded phase column (25 cm × 4.5 mm I.D.). HPLC grade hexane and dichloromethane were used (Fisher Scientific, Fair Lawn, NJ, U.S.A.). UV detection was at 254 nm.

Gas chromatography

Typical requirements for the gas chromatography of metallic or metalloid compounds necessitate that the compounds be coordinatively saturated, monomeric, low in molecular weight, neutral, thermally stable, volatile and that there be organic shielding of the metal atom. The five representative compounds investigated include As(III) and As(V) derivatives. The former, tripropylarsine and triphenylarsine, are monomeric and of low molecular weight, are neutral, reasonably thermally stable and have organic shielding of the arsenic atom without coordinative saturation. Tripropylarsine is considerably more volatile than triphenylarsine. The As(V) derivatives, As-CAT, As-NH and As-EG, are depicted in Fig. 1. They are coordinatively
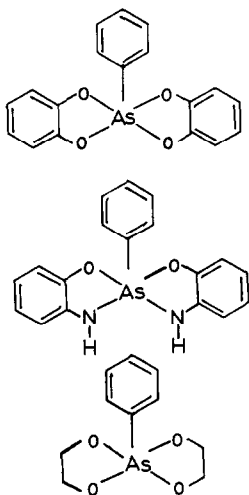
Fig. 1. Structures of arsenic (V) compounds. Top: As-CAT, 2-phenyl-2,2'-spirobi(1,3,2-benzoxarsole). Center: As-NH, 2-phenyl-2,2'(3H,3'H)-spirobi(1,3,2-benzoxazarsole). Bottom: As-EG, 2-phenyl-2,2'-spi-robi(1,3,2-ethylenedioxarsole).
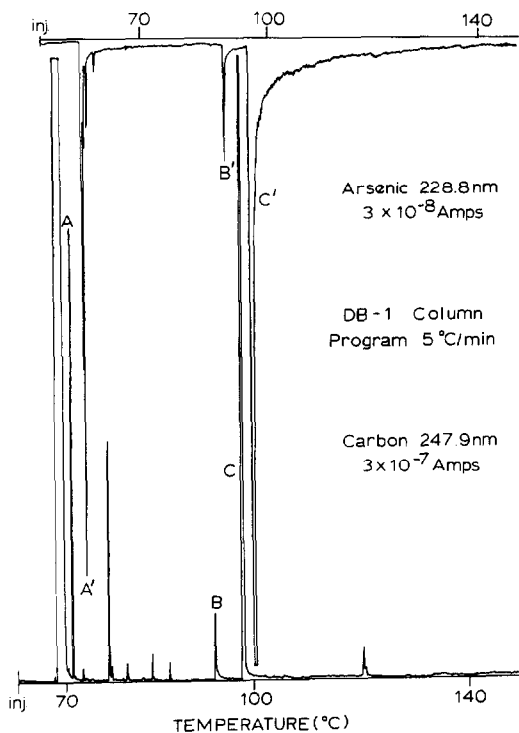

Fig. 2. Carbon and arsenic GC–MED profiles of tripropylarsine solution.

saturated, monomeric, of low to moderate molecular weight, and have shielding of the central arsenic atom both by chelation and by organometallic sigma bonded phenyl groups. The thermal stability and volatility of these compounds had not previously been investigated.

Although mass spectral confirmation of tripropylarsine as the major product of preparation had been obtained, its complete purification had proved difficult; the specific element capillary GC traces shown in Fig. 2 emphasize the usefulness of this technique. GC–MIP responses are shown for carbon emission (lower chromatogram) and arsenic emission (Upper chromatogram) (the traces are offset for clarity). The carbon channel shows a solvent peak (diethyl ether) and a number of other peaks including those labeled A, B, and C, which also contain arsenic (upper trace, A', B', and C'). These three components, particularly the largest (C', identified independently as tripropylsilane), all show tailing in the arsenic specific profile. Some tailing is seen for peaks B and C in the carbon prifile, attributable to on-column berhavior. The more extensive tailing in the arsenic profile, particularly for peak C', is probably due to a plasma tube "wall hold-up" effect for released elemental arsenic similar to that noted for boron[23].

It was noteworthy that while the tripropylarsine eluted at a retention temperature of approximately 96°C, triethylarsine (b.p. *ca.* 140°C) eluted with solvent in the "dead volume" of the column even at a column temperature of 50°C.

Initial attempts at chromatography of the As(V) derivatives resulted in irreproducible peaks with severe tailing. This indicated the possibility of decomposition so thermal stability was investigated by thermogravimetric analysis. Fig. 3 depicts the thermogravimetric traces. Major weight loss corresponding to volatilization accompanied by decomposition of the As-CAT and As-NH occurs at approximately 260°C. Weight loss occured at approximately 210°C for As-EG with less decomposition in view of the small residue. The results indicated that decomposition of the compounds was certainly occuring at the temperature of the injection port (260°C),
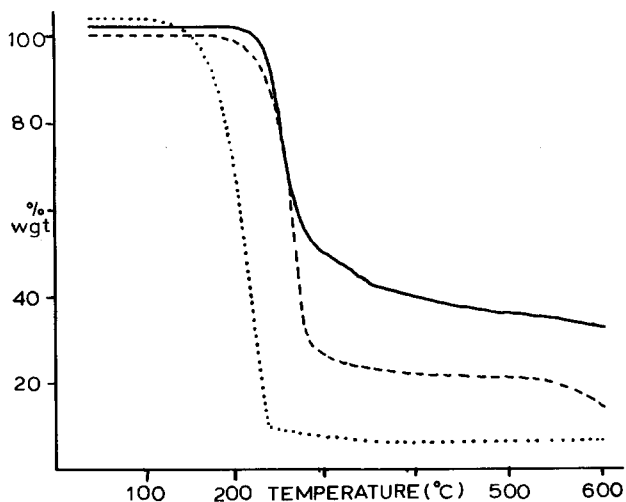

Fig. 3. Thermogravimetric profiles of As-CAT (– – –), As-NH (———) and As-EG (...........). Atmosphere, nitrogen; heating rate, 15°C/min.

transfer line and interface oven (275°C) initially used. Careful variation of these tem-
peratures indicated that there was a very narrow region of thermal stability and
adequate volatility for these compounds. The As-NH compound could not be gas
chromatographed regardless of the temperatures employed. This was explicable in
view of the extensive decomposition seen in the thermogram.

The As-EG could be chromatographed at temperatures between 180°C and
200°C but reproducibility of peak shape and response was poor. With the tempera-
ture of the injection port, transfer line and interface oven maintained at 245°C peak
integrity was obtained for the As-CAT compound. The peak shown in Fig. 4 rep-
resents the arsenic specific response of the MED to 2.4 ng of arsenic as the As-CAT
compound. The small amount of baseline noise at $t_R = 1$ min corresponds to the
elution of the solvent peak, showing the excellent selectivity contained over carbon
at 228.8 nm[24]. The response to the compound on the carbon line was similar, except
that slight overlap with the solvent occured. The peak efficiency for the As-CAT
compound is not great and some tailing is evident as was seen for tripropyl arsine.
The compound however contains four polarizable donor oxygens and is basic in
nature, thus, high peak symmetry even on a fused silica column might not be pre-
dicted. The "basic" column interaction of As-CAT was seen further in comparison
of the results obtained on two different fused-silica columns. The DB-1 bonded phase
columns remain slightly acidic from the deactivation process whereas coated SP-2100
silicone columns are left slightly basic on preparation. Less tailing was obtained on
a SP-2100 column for As-CAT. The compound eluted very rapidly despite its high
molecular weight and relatively high boiling point, and was clearly poorly retained
by the methyl silicone bonded phase. It is likely that in view of the aromatic content
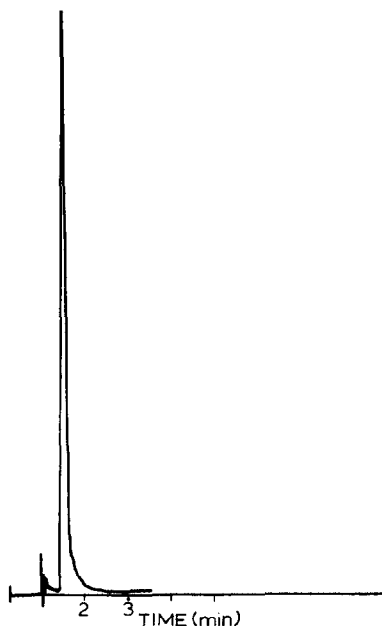

Fig. 4. Arsenic MED response to As-CAT (2.4 ng arsenic). Column, DB-1 fused-silica (30 m × 25 mm
I.D.); arsenic 228.8 line; 10 × 10^{-8} A.

of the molecule, elution behavior might be superior on a bonded phase incorporating some phenyl groups while still maintaining "inert" character.

Liquid chromatography

As was noted earlier, HPLC methods for organoarsenic compounds have focused mainly on ion exchange and ion pairing separations of anionic species such as the alkyl substituted arsenic acid anions[5,6,16,17]. The separation of the chelated As(V) compounds has not been reported. In view of their solubility and tendency to hydrolyze, it appeared unlikely that reverse phase polar solvent systems would be suited for analysis and this was found to be so. Also initial experiments with normal phase adsorption on silica and partition on cyano-bonded phases showed no peak integrity on elution.

A suitable compromise column material appeared to be phenyl-bonded silica utilized with a relatively non-polar *n*-hexane–dichloromethane (1:1) mobile phase. A secondary but perhaps important interaction may be between the aromatic portions of the molecules and the phenyl substrate. Fig. 5 depicts a separation of three organoarsenic compounds having phenyl or phenyl-derived substitution, triphenylar-
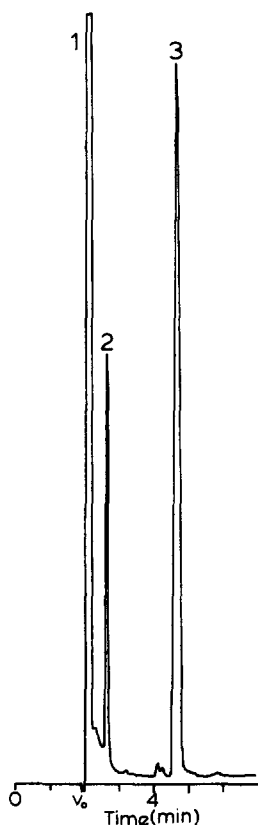

Fig. 5. HPLC separation of triphenylarsine (1), As-CAT (2) and As-NH (3). Column, 5-μm phenyl (25 m × 4.6 mm I.D.); mobile phase, hexane–dichloromethane (50:50); flow-rate, 15 ml/min.

sine, As-CAT and As-NH. Peaks are symmetrical and efficiencies for the two chelated compounds are around 5000 theoretical plates.

It is noteworthy that the phenyl substitution of triphenylarsine did not cause its retention past the column void volume and thus simple aromatic–aromatic interaction is less of a factor in retention than the specific interaction of the chelated rings. A similar conclusion could also be drawn for GC retention on bonded methyl silicone.

The integrity of elution of these compounds was also confirmed by eluent monitoring with d.c. argon plasma emission[25] and the potential of HPLC for quantitative separation of such compounds is excellent. These results also serve to indicate that GC on phenyl bonded-phase capillary columns should prove viable.

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