ELSEVIER

Journal of Chromatography A, 683 (1994) 223–231

JOURNAL OF CHROMATOGRAPHY A

Determination of organotin compounds by capillary supercritical fluid chromatography with inductively coupled plasma mass spectrometric detection

Earl Blake[a], Mark W. Raynor[a,*], David Cornell[b]

[a]*Department of Chemistry and Applied Chemistry, University of Natal, King George V Avenue, Durban 4001, South Africa*
[b]*Department of Geology, University of Natal, King George V Avenue, Durban 4001, South Africa*

Abstract

Supercritical fluid chromatography with inductively coupled plasma mass spectrometric detection is a new technique being developed for the analysis of organometallic compounds. A new interface has been developed for coupling the two instruments and this has been evaluated in terms of the restrictor temperature. The effect of concentration of analyte on peak intensity has been evaluated and reasons for the observed behaviour have been proposed.

1. Introduction

Organotin compounds are used extensively as biocides and in marine anti-fouling paints and as these compounds are continuously released into the marine environment they accumulate in sediments, marine organisms and water [1,2]. Many of these compounds are toxic to aquatic life such as shell fish and can accumulate through the food chain to cause damage to other species as well. The compounds most important in this respect are the short-chain organotin compounds such as methyl-, ethyl-, propyl- and butyltin compounds and more specifically the tetra- and trialkyltin compounds [3]. These compounds are also capable of forming breakdown products which may or may not be toxic to aquatic life [1]. In the case of butyltin compounds tetrabutyltin will decay in the presence of small amounts of ultraviolet light to form tributyltin chloride which in turn decays to dibutyltin dichloride and eventually butyltin trichloride before decaying completely to inorganic tin. A characteristic of this decay is that toxicity generally increases with the number of alkyl chains with greatest toxicity being from tributyltin chloride [1].

There has recently been much interest in the analysis of organotin species in the environment and the methods employed have included GC with atomic absorption spectrometry (AAS) and atomic emission spectrometry (AES) as detectors and HPLC with mass spectrometric (MS) detection [4–10]. Later work has concentrated on linking GC with plasma MS detectors such as microwave-induced plasma (MIP) MS [11] and inductively coupled plasma (ICP) MS [12]. Within the past two years a method that has been shown to be amenable to the analysis of these organotin compounds is supercritical fluid chromatography (SFC) with ICP-MS detection. This

* Corresponding author.

0021-9673/94/$07.00
SSDI 0021-9673(94)00479-S

method has been shown to allow speciation of organotin compounds using SFC and detection of these compounds at very low detection limits using ICP-MS [13,14]. The main advantage of this method is its ability to analyse involatile and thermally labile compounds thus eliminating the need for derivatisation to compounds more suitable for GC. Moreover, the use of high-pressure programmes can reduce the analysis time to less than 5 min. If a modifier is added to the mobile phase then it is possible to analyse many polar compounds that could not be analysed using pure CO_2 mobile phase. Compounds that are amenable to SFC should also be amenable to supercritical fluid extraction (SFE) assuming that matrix effects are not too great. This eliminates the need for extraction using potentially harmful organic solvents and possible loss or contamination of analyte during extraction. Thus, it should be possible to develop an on-line method for extraction and analysis of organometallics using SFE–SFC–ICP-MS.

The method used for linking the SFC with ICP-MS has involved a heated transfer line from the SFC and a series of Swagelok unions to connect the restrictor to the torch. A copper tube housing the restrictor was inserted into the ICP torch and the restrictor was connected to the butt connector through a three-way Swagelok. Through the third arm of the union heated argon was added as make-up gas. The principle of this interface is to heat the entire interface and the argon make-up gas and thus keep the restrictor heated at the same time. The transfer line is enclosed in heating tape and heated to the same temperature as the oven thus ensuring a constant temperature along the column [13]. The principles of this interface are good but it would appear that this interface is bulky and difficult to assemble. Moreover, once SFC has been linked to ICP-MS the only work that can be carried out is that using SFC–ICP-MS and if either instrument must be used individually it would be necessary to dismantle the interface before continuing. In addition, the work so far has made use of frit restrictors which are costly to replace if blocked or damaged and which have been shown by Pinkston and Hentschel [15] to perform inadequately at high elution pressures.

In this study a new interface has been developed and evaluated using environmentally relevant organotin compounds and a different type of restrictor has been used. The effects of the restrictor temperature and changes in the concentration have been studied. Changes in the plasma due to the mobile phase pressure program have also been studied. The ICP-MS conditions have been optimised by focusing and tuning the instrument on the element of interest. The results obtained have allowed the evaluation of ICP-MS as a detection method for SFC.

2. Experimental

2.1. Supercritical fluid chromatography

The chromatograph consisted of a Lee Scientific Series 600 GC/SFC oven, a Lee Scientific Series 600 syringe pump and a Lee Scientific Series 600 controller (Lee Scientific, Salt Lake City, USA). The pump and injection valve were cooled to approximately 7°C using a Neslab Endocal RTE 110 cooler. The mobile phase was SFC-grade CO_2 (Air Products, Allentown, USA). The capillary column was a 2 m SB-Biphenyl-30 capillary column with a 0.25-μm film thickness and the tapered restrictor was made in the laboratory from 50 μm I.D. capillary tubing (Lee Scientific) [16]. The tapered end of the restrictor was protected by a sleeve of 320-μm I.D. capillary tubing (SGE, Australia) bonded to the restrictor with polyimide resin. The gaseous restrictor flow at 15.2 MPa was measured using a bubble flow meter to be 1.5 ml/min. Injection onto the column was through a AC14UWP Valco injector with a 200-nl sample loop and a polyether ether ketone (PEEK) splitless adapter and activated using helium gas. Time-split injection was used with a 100 ms injection time.

2.2. Mass spectrometry

The ICP-MS instrument was a VG PlasmaQuad (VG Elemental, Cheshire, UK) controlled by an IBM personal computer. All acquisitions were obtained using single-ion monitoring

Table 1
Typical ICP operating conditions and MS settings

Incident power (kW)	1.35
Reflected power (W)	<5
Coolant gas flow (l/min)	14
Auxillary gas flow (l/min)	0.5
Make-up gas flow (l/min)	0.8
Intermediate pump (mbar)	$2.0 \cdot 10^{-4}$
Expansion pump (mbar)	2.4
Analyser pump (mbar)	$4.2 \cdot 10^{-6}$

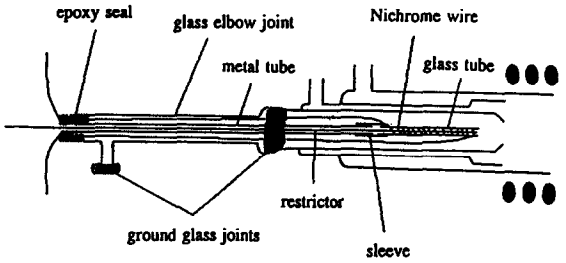

Fig. 2. Schematic diagram of the capillary SFC–ICP-MS interface design.

with 2048 channels. The dwell time per channel was altered according to the total analysis time on SFC. The operating and tuning parameters are shown in Table 1.

2.3. SFC–ICP-MS interface

The SFC–ICP-MS system is shown in Fig. 1 and details of the interface are shown in Fig. 2. The glass elbow between the nebuliser and the torch was modified to include a third arm so that the elbow resembled a T-join. A 1/16 in. (1 in. = 2.54 cm) I.D. stainless-steel tube with a fitting housing a ferrule to secure the fused-silica transfer line leading to the restrictor was placed in the end opposite the ground glass joint. A melting point tube was fitted with a heater consisting of tightly wound Nichrome wire (GM Heating, Durban, South Africa) which was bonded to the melting point tube and insulated using polyimide resin. The ends of the wire were coated with shrinksleeve to provide adequate insulation. The melting point tube was connected to the stainless-steel tube using a glass sleeve and polyimide resin. The wires from the heater were brought through the modified glass elbow to emerge where the stainless-steel tube entered the elbow. The stainless-steel tube and wires were then fixed in place using 372 epoxy which also formed a gas-tight seal. Care was taken during assembly to ensure that the stainless-steel tube and the melting point tube were kept level and straight thus ensuring that when the interface was fitted to the torch the maximum amount of sample would enter the plasma and no condensation or crystallisation would occur in the torch. The restrictor was inserted in the tubing so that the restrictor end was flush with the end of the melting point tube. The restrictor was held in place using an SGE nut and graphitised vespal ferrule on the stainless-steel tube. The restrictor was connected to the column using an SGE butt connector. The oven was placed as close as possible to the ICP to minimise the loss of chromatographic efficiency and the column was brought out of the side of the oven and con-

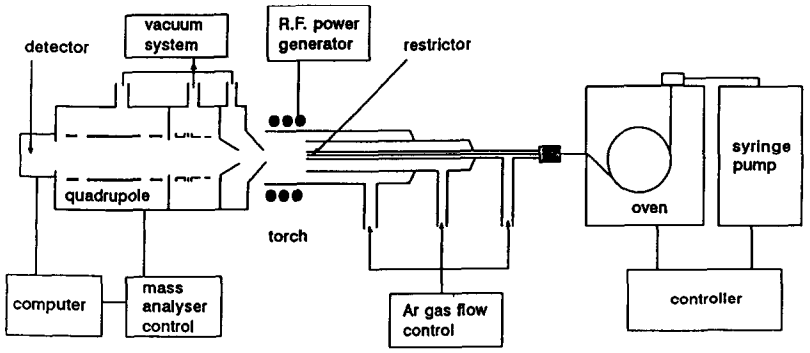

Fig. 1. Schematic diagram of the SFC–ICP-MS system. R.F. = Radio frequency.

nected to the restrictor without any heating. The length of column outside the oven was about 30 cm. As the interface was a modification of the glass elbow between the nebuliser and the torch, it could be fitted to the torch and nebuliser in the normal way. The interface was heated by connecting the wires to a GP 30-5 d.c. power supply. The temperature of the interface was varied by controlling the voltage applied to the wires.

2.4. Reagents

Tetrabutyltin (TBT) was obtained from Aldrich (Milwaukee, USA). Tributyltin chloride (TBTCl) and tetraphenyltin (TPT) were obtained from Janssen Chimica (Geel, Belgium) and triphenyltin chloride (TPTCl) was obtained from Merck (Darmstadt, Germany). The purities of the analytes were 98, 90, 97 and 98%, respectively. The solvent used for preparing solutions was dichloromethane (Holpro Lovasz, Midrand, South Africa). All solutions were prepared from stock solutions of 1000 μg/ml in each analyte.

3. Results and discussion

3.1. Interface use and assembly

The interface is relatively easy to assemble from commonly available materials and can be used with a minimum of disruption to either the SFC system or the ICP-MS instrument. As it is a modification of the elbow joint between the nebuliser and the ICP torch it can be inserted into the torch in less than a minute. Moreover, because it is attached to the nebuliser there is no need to use elaborate methods for the introduction of the heated argon make-up gas as the argon can be heated internally in the ICP-MS instrument and then follow its normal path to the torch through the nebuliser. A further advantage of this interface is that only the restrictor is heated directly and the temperature of the restrictor can be controlled rather than keeping the whole interface at high temperatures. The remainder of the transfer line was heated to 60°C by the heated argon.

The temperature of the restrictor is controlled by the voltage applied to the Nichrome wire. Although this is simple to do using a d.c. power supply with variable voltage and current, it is more difficult to measure the temperature. To obtain an idea of the temperature the interface was placed together with a thermocouple in a torch on the bench top. The voltage was then increased from 0 V in one volt increments and the temperature inside the torch next to the restrictor was noted. A period of 30 min was left between each reading to allow the temperature to equilibrate. It was found that a voltage range of 6 to 10 V gave a temperature range of about 200 to about 320°C. Although these results give a general idea of the voltage/temperature dependence, it should not be assumed that the same relationship will apply under operating conditions. Due to the difficulty of measuring the temperature of the restrictor under operating conditions it is not possible to propose a "true" voltage/temperature relationship. However, as the argon make-up gas is heated and flows over the glass tube rather than over the restrictor it is reasonable to assume that the parameters to be used under operating conditions will be similar to those used in the bench-top experiment. There are difficulties in testing this assumption as a low voltage will allow condensation of some analytes and the restrictor will block up and a high voltage could cause the glass tubing and the polyimide to melt or decompose and this in turn could seriously damage the ICP-MS instrument. However, in this study an operating range of 6 to 10 V was found to be adequate.

The interface can be considered as a modification of the ICP sample introduction system and so causes minimum disruption to this instrument. If necessary, the interface can be easily removed and replaced with the normal elbow joint to allow the ICP-MS instrument to be used individually or, for minor tests on sensitivity and other minor experiments, the interface can be left in and ICP-MS standards can be introduced with the SFC connected. This saves time and

minimises the possibility of equipment damage during disassembly.

3.2. Effect of the pressure program on the plasma

When using ICP-MS as a detection method for SFC it is necessary to monitor changes in the argon plasma as any changes may give an indication of possible interferences and the effect of the mobile phase on the plasma. To monitor the plasma the instrument was tuned on the ion at $m/z = 80$ which corresponds to the argon dimer cation. Fig. 3 shows the change in the plasma with no mobile phase flowing and with a solvent injection of dichloromethane under normal analysis conditions. With no mobile phase flowing there is no change to the plasma and only a slight negative baseline drift is observed. When mobile phase flows at the normal pressure program it can be seen that there is a distinct drop in the baseline approximately half way through the analysis. This corresponds to a pressure of about 27 MPa and is contrary to results obtained using the other interface which found a drop in the baseline at the onset of a much higher pressure ramp [14]. As the pressure ramp in this study is fairly low it can be assumed that at lower pressures the plasma will not be affected by the mobile phase but at higher pressures the mobile phase causes a damping effect on the formation of argon dimer as other side reactions occur within the plasma. The combined results indicate that as the pressure ramp increases the greater this damping effect will be. This is due to the greater flow of mobile phase at higher ramp rates. If dichloromethane solvent is injected there is a distinct negative peak in the baseline. This is the result of a side reaction in the plasma as argon reacts with the chlorine in the solvent to preferentially form ArCl and prevent argon dimer formation. After the solvent peak has been eluted and there is again a lack of chlorine the formation of dimer resumes.

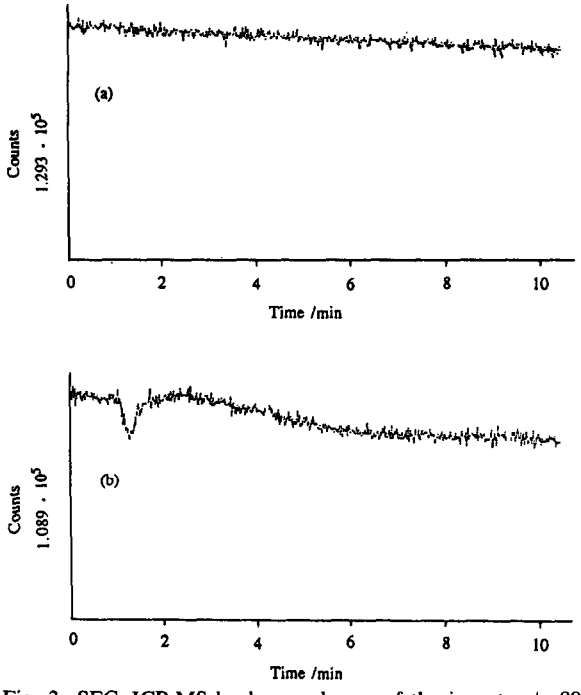

Fig. 3. SFC–ICP-MS background scan of the ion at m/z 80 with no mobile phase flowing (a) and with a dichloromethane solvent injection under normal analysis conditions (b). CO_2 programmed at 3.04 MPa/min from 12.2 MPa (hold for 30 s) to 40.5 MPa (hold for 1 min) and an isocratic temperature of 75°C.

Fig. 4 shows the effect of the mobile phase program on ArC^+ at $m/z = 52$. There is no significant change in the plasma at this charge-to-mass ratio despite a small increase in the flow of mobile phase with increased pressure from 1.5 to 3.5 ml/min. This can be ascribed to a constant increase in supply of carbon into the plasma with a constant rate of ArC^+ formation. This would

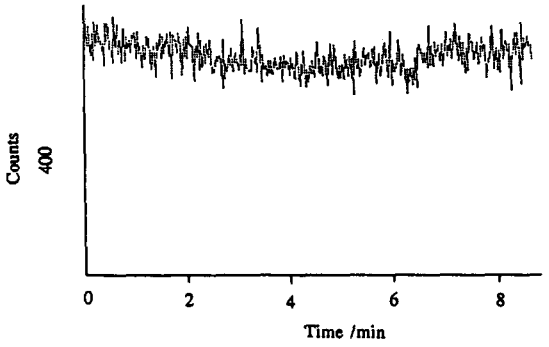

Fig. 4. The effect of mobile phase on ArC^+ at m/z 52. Mobile phase programmed from 12.2 MPa (hold for 30 s) to 40.5 MPa (hold for 1 min) at 3.04 MPa/min and an isocratic temperature of 75°C.

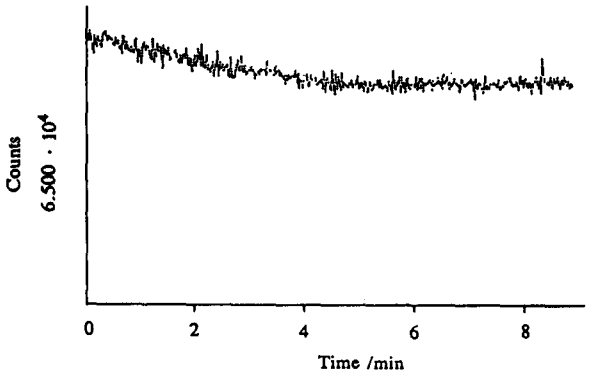

Fig. 5. The effect of mobile phase on ArO at m/z 56. Mobile phase programmed from 12.2 MPa (hold for 30 s) to 40.5 MPa (hold for 1 min) at 3.04 MPa/min and an isocratic temperature of 75°C.

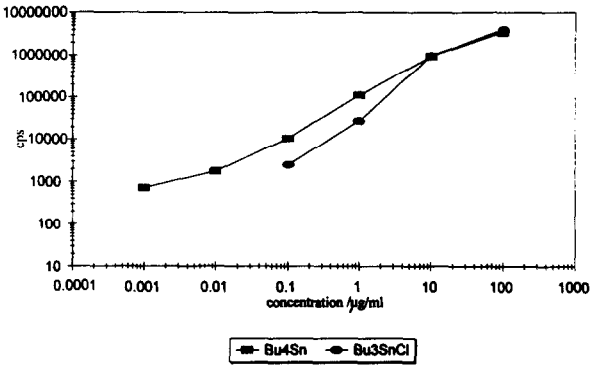

Fig. 6. A comparison of the effects of concentration on peak intensity for Bu_4Sn and Bu_3SnCl.

account for the fairly high background of this ion and should not cause any interference with the analysis. Fig. 5 shows the effect of the oxygen on the plasma by monitoring ArO. There is no significant change in the ArO present and even a slightly negative drift is observed. However, the background level is quite high compared to that of ArC^+ and this is expected as there is significantly more oxygen in the mobile phase than carbon. Moreover, as the plasma is exposed to the atmosphere there must also be some reaction with atmospheric oxygen.

3.3. *Effect of the analyte concentration*

The analytes initially considered were tetrabutyltin, tributyltin chloride, tetraphenyltin and triphenyltin chloride. However, it was found that triphenyltin chloride had a significant memory effect within the injector and thus interfered with the analysis at low concentrations. Thus, it was decided to limit the study of concentration dependence to tetrabutyltin and tributyltin chloride. Solutions of tetrabutyltin and tributyltin chloride ranging through 0.001, 0.01, 0.1, 1, 10 to 100 μg/ml were prepared from a stock solution of 1000 μg/ml. Each solution was analysed in triplicate and a plot of concentration versus peak intensity was made.

From the graph in Fig. 6 it can be seen that for tetrabutyltin there is a slight increase in intensity below concentrations of 0.01 μg/ml and thereafter a sharp increase in peak intensity between 0.01 and 10 μg/ml. Beyond 10 μg/ml the increase in peak intensity again begins to level off. This trend corresponds to the detector's ability to "see" the compound of interest. Below 0.01 μg/ml, although the detector can detect the Sn ion, any increase in concentration will give only marginal increase in the detector sensitivity. However, above 0.01 μg/ml each increment increase in concentration will be significantly easier for the detector to detect. Above 10 μg/ml any increase in concentration will more or less "flood" the detector and any increase in sensitivity will be marginal. Thus, it is reasonable to assume that above concentrations of about 1000 μg/ml very little increase in sensitivity will be obtained and at such high concentrations there may even be damage to the detector due to overload of the ion of interest.

Fig. 6 also shows the trend for change in peak intensity with concentration for tributyltin chloride. This is significantly different from tetrabutyltin in that the lowest concentration that can be detected is 0.1 μg/ml. The reason for this is the compounds greater polarity than tetrabutyltin. Tributyltin chloride will tend to adsorb more strongly onto any active sites in the column resulting in a certain amount of peak tailing as shown in Fig. 7. At lower concentrations the same adsorption interactions will occur as at high concentrations but as there is less analyte at the low concentration tailing becomes more relevant

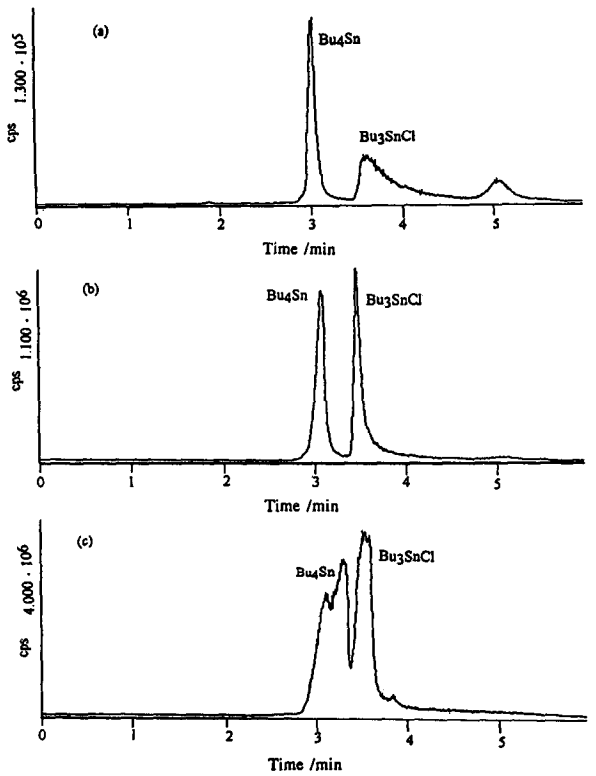

Fig. 7. Single-ion scan chromatograms of ^{120}Sn with Bu_4Sn and Bu_3SnCl concentrations of (a) 1 μg/ml, (b) 10 μg/ml and (c) 100 μg/ml. SFC Conditions: 2 m × 50 μm SB-Biphenyl-30 column, CO_2 mobile phase programmed from 12.2 MPa (hold for 30 s) to 24.3 MPa (hold for 1 min) at 3.04 MPa/min and constant temperature of 75°C. Time split injection of 100 ms and an applied voltage on the interface of 8.0 V.

resulting in a decrease in the detection limit. However, at high concentrations, although the same interactions occur and the same amount of sample adsorbs to the column, in relation to the large amount of analyte present this tailing will be less significant in relation to the peak intensity.

The comparison of the two analytes in Fig. 6 shows that below 10 μg/ml the intensity of tetrabutyltin is significantly greater than tributyltin chloride but at 10 μg/ml the two analytes converge. Above 10 μg/ml there is a slight trend for tributyltin chloride peak intensity to be greater than tetrabutyltin. In Fig. 7c it is evident that there is a change in the peak shape of tetrabutyltin as the peak broadens and begins to split. This is due to overloading of the column and interface or the ICP-MS detector. The linearity of tetrabutyltin and tributyltin chloride is over three orders of magnitude from 0.1 to 10 μg/ml. The slope of the linear range (log–log) for tetrabutyltin is 0.970 and for tributyltin chloride is 1.29.

3.4. Effect of interface temperature

To monitor the effect of the interface temperature the 10 μg/ml solution was chosen as this gave the best peak shape under the initial conditions. As stated earlier the exact temperature under operating conditions is difficult to measure and hence all results are given as a function of the applied voltage rather than temperature. At low voltage (and low temperatures of about 200°C) there is a small increase in intensity for tributyltin chloride as the applied voltage is increased but above 7 V (at about 230°C) there is a significant increase in peak intensity as applied voltage is increased. For tetrabutyltin greater increase in peak intensity occurs above 7.5 V. A comparison of these trends is made in Fig. 8 where it can be seen that the increase in peak intensity is greater for tributyltin chloride than for tetrabutyltin.

The trend in Fig. 8 can be explained in terms of the volatility of the two compounds. Tetrabutyltin is more volatile than tributyltin chloride

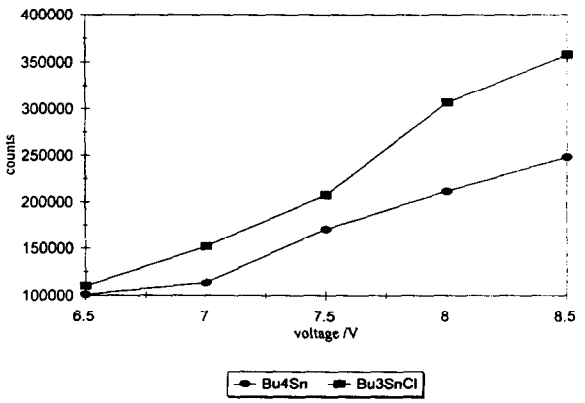

Fig. 8. A comparison of the effects of interface applied voltage on the peak intensities of Bu_3SnCl and Bu_4Sn.

and is thus less likely to condense in the restrictor than tributyltin chloride. At lower temperatures there may be some condensation of the less volatile tributyltin chloride within the restrictor due to adiabatic expansion of the mobile phase. As the temperature of the restrictor is increased both compounds will show an increase in peak intensity as the Joule–Thompson effect is more efficiently counteracted. However, as the temperature of the restrictor is increased any tributyltin chloride which may have condensed in the restrictor at low temperatures is now volatilised and the resulting increase in the amount of analyte which is transferred into the plasma accounts for the increase in peak intensity.

It was noted with reference to Fig. 8 that a plateau region (where peak intensity reaches a maximum with increasing restrictor temperature, or applied voltage) has not yet been reached for tetrabutyltin and tributyltin chloride, which indicates that detector sensitivity can still be improved. This may be achieved by changing the insulating material from polyimide to some other material capable of withstanding temperatures greater than 400°C, or by supplementing the filament heater by introducing a hot make-up flow of argon around the restrictor. This would also reduce the possibility of analyte condensation in the torch.

3.5. Detection limits and reproducibility

Triplicate 10 μg/ml mixtures of tetrabutyltin and tributyltin chloride were injected with the interface at an applied voltage of 8.5 V. The detection limits were calculated according to three times the standard deviation of the background for the triplicate injections. From previous experiments it was estimated that a time-split injection of 0.100 s corresponds to an injection of approximately 67 nl and thus a 10 μg/ml solution injected for 0.100 s will be an injection of 670 pg. The standard deviation is 27 and the sensitivity for tributyltin chloride is 3284 cps/pg. Thus, the theoretical absolute detection limit is 0.025 pg. For tetrabutyltin the sensitivity is 2287 cps/pg and the theoretical absolute detection limit is 0.035 pg. These results compare well with those obtained by Shen et al. [13] and for tributyltin chloride these results show a significant improvement. This can be seen in Fig. 6 which shows practical detection limits of 0.07 pg for tetrabutyltin and 6.7 pg for tributyltin chloride. Although tetrabutyltin was only investigated at concentrations above 0.001 μg/ml this was not the limit of detectability and hence the practical and calculated detection limits are approximately the same. However, as previously discussed, there is significant tailing on tributyltin chloride and it is doubtful that the calculated detection limit could be obtained unless a modifier was added to the mobile phase or a very well deactivated column was used. Thus, the detection limit calculated for tributyltin chloride for a 10 μg/ml solution is a statistical indication of the detection limit under ideal conditions and assuming that the peak shape would be similar to that of tetrabutyltin at all concentrations.

Optimisation of the conditions for SFC are not presented as these are not specific to the detector and will be specific for analyses of different compounds. The conditions for optimising the chromatography include pressure and density programmes and the temperature of the oven as well as the initial and final hold times and the injection time. These will all affect peak shape, resolution, selectivity and retention time but these conditions can be optimised using any suitable detector and a suitable analyte concentration. Thus, the chromatographic conditions were optimised using flame ionization detection by varying conditions of pressure and temperature and all analyses on SFC–ICP-MS were performed using these conditions. It was found that a constant temperature of 75°C was suitable for thermally labile and involatile analytes while a pressure program of 3.04 MPa/min gave the best compromise between peak shape and resolution.

4. Conclusions

The interface developed in this study is easy to assemble and use and causes minimum disrup-

tion of either SFC or ICP-MS. Analysis of the peak intensity of tetrabutyltin and tributyltin chloride with concentration shows linearity over three orders of magnitude and detection limits comparable to and even lower than those previously reported. Moreover, the design of the interface is important as it is this factor which will optimise the restrictor heating and so minimise the Joule–Thompson effect. Although the mobile phase cause changes in the plasma these do not interfere with the analysis. The low detection limits offer potential for environmental analysis and the opportunity exists to link this method with supercritical extraction and hence provide on-line extraction and analysis of environmental samples at ultra-trace levels. Poole et al. [17] have recently reported the SFC–FID analysis of a mixture of 12 organotin compounds including some polar compounds such as dibutyltin dichloride and diphenyltin dichloride using packed columns and formic acid modified carbon dioxide. As the addition of small amounts of modifier such as formic acid are unlikely to interfere with ICP-MS, this would further broaden the scope of this method. SFC with ICP-MS detection offers a fast method for analysing organometallic compounds that have not previously been amenable to chromatographic analysis. In addition low detection limits provide ultra-trace analysis of potentially harmful compounds.

Acknowledgements

The authors thank the Foundation for Research and Development, Pretoria, South Africa and the University Research Fund, University of Natal, Durban, South Africa for the financial support for this project and Stefan Nicolescu for his help with the ICP-MS work.

References

[1] J.R. Ashby and P.J. Craig, in R.M. Harrison (Editor), *Pollution: Causes, Effects and Control*, Royal Society of Chemistry, London, 2nd ed., 1990, Ch. 16.
[2] R.J. Maguire, *Environ. Sci. Technol.*, 18 (1984) 291.
[3] N.P. Vela and J.A. Caruso, *J. Anal. At. Spectom.*, 7 (1992) 971.
[4] Y.K. Chau, P.T.S. Wong and G.A. Bengert, *Anal. Chem.*, 54 (1982) 246.
[5] K.L. Jewett and F.E. Brinckmann, *J. Chromatogr. Sci.*, 19 (1981) 583.
[6] R.M. Harrison and C.N. Hewitt, *Int. J. Environ. Anal. Chem.*, 21 (1985) 89.
[7] R.C. Forster and A.G. Howard, *Anal. Proc.*, 26 (1989) 34-36.
[8] H.A. Meinema, T. Burger-Wiersma, G. Versluis-de Haan and E. Ch. Gevers, *Environ. Sci. Technol.*, 12 (1978) 288.
[9] K. Robards, P. Starr and E. Patsalides, *Analyst*, 116 (1991) 1247.
[10] O. Evans, B.J. Jacobs and A.I. Cohen, *Analyst*, 116 (1991) 15.
[11] J.M. Carey, F.A. Byrdy and J.A. Caruso, *J. Chromatogr. Sci*, 31 (1993) 332.
[12] A. Kim, S. Hill, L. Ebdon and S. Rowland, *J. High Resolut. Chromatogr.*, 15 (1992) 665.
[13] W.-L. Shen, N.P. Vela, B.S. Sheppard and J.A. Caruso, *Anal. Chem.*, 63 (1991) 1491.
[14] N.P. Vela and J.A. Caruso, *J. Anal. At. Spectrom.*, 7 (1992) 971.
[15] J.D. Pinkston and R.T. Hentschel, *J. High Resolut. Chromatogr.*, 16 (1993) 269.
[16] M.W. Raynor, K.D. Bartle, I.L. Davies, A.A. Clifford and A. Williams, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 11 (1988) 289.
[17] C.F. Poole, J.W. Oudsema and K.G. Miller, presented at the *5th Int. Symp. on Supercritical Fluid Chromatography and Extraction, Baltimore, MD, 11–14 January, 1994*, Abstracts, p. 18.