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Electrospray Mass Spectrometry: An Alternative Method for the Identification of Organotin Compounds

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The limitations of conventional gas chromatography–mass spectrometry (GC–MS) analyses for alkyl- and aryl-tin compounds are discussed, particularly the excessive fragmentation from electron impact (EI) ionization. Negative EI methods exhibit low ionization capabilities and are restricted to compounds with an electronegative centre, and are thus not suitable for general routine analysis. Liquid chromatography–MS (LC–MS) interfaces offer potential advantages in terms of reduced sample work-up since no derivatization is required. Electrospray techniques give reproducible mass spectra for each compound studied under fixed instrumental parameters. Changes in the cone/repeller voltages can radically alter the observed mass spectra. High-mass species were observed for each compound studied and tentative structures for these species are proposed.

Keywords: organotin compounds; electrospray; mass spectra; clusters

1 INTRODUCTION

The approaches used for the determination of organic contaminants in the environment are usually relatively long and involved because the target analyte is often present at low levels in a complex matrix and frequently there are interfering species present at higher concentrations. Confirmation of the chemical nature of organometallic compounds extracted from environmental samples usually requires the combination of a separation method, either chromatographic or differential volatility, coupled on-line to either an atomic absorption spectrometer (AA) or a mass spectrometer (MS).[1–2] In inductively coupled plasma—MS (ICP-MS)[3] systems the nature of the organic substituents can only be inferred from retention time data based on known calibration samples. Where derivatization has been used to produce volatile compounds, the nature of the organic groups can be determined from retention times (GC) or from the electron impact (EI) mass spectra produced for each component of the mixture (GC–MS).[4] Single ion monitoring can also be used in conjunction with GC–MS methods but a suitable characteristic ion must be selected.[4] An increase in sensitivity of at least two orders of magnitude can be achieved by this approach. In all of these approaches there is a time delay while the analytes elute from the separation stage.

A possible alternative approach is to use a tandem mass spectrometer to provide the equivalent of both the prior separation stage and the confirmatory analyses, by use of the first and second mass spectrometers respectively.[5] Thus delays in the GC–MS analysis can be eliminated by MS–MS methods where the complete sample is evolved from the heated probe and the target analyte ions are sequentially identified at millisecond intervals. This approach has been trialled for both simple combinations of compounds[5] and complex environmentally derived[6] materials; under both sets of conditions, reproducible and characteristic results were obtained and confirmed by alternative, more conventional, methods. Whilst the MS–MS approach can reduce time, there are some organometallic compounds which have EI mass spectra which contain only limited evidence for the presence of the tin atom (see Fig. 1). For such compounds the MS–MS system, under EI conditions, has little to offer.

This paper presents some alternative mass spectrometer methods which might alleviate some or all of the problems cited above. The different types of mass spectrometer which may be used for the analytes in question are summarized in Figure 2. The magnetic sector, quadrupole and ion trap are all commonly used as GC detectors. The magnetic sector, double quadrupoles and ion

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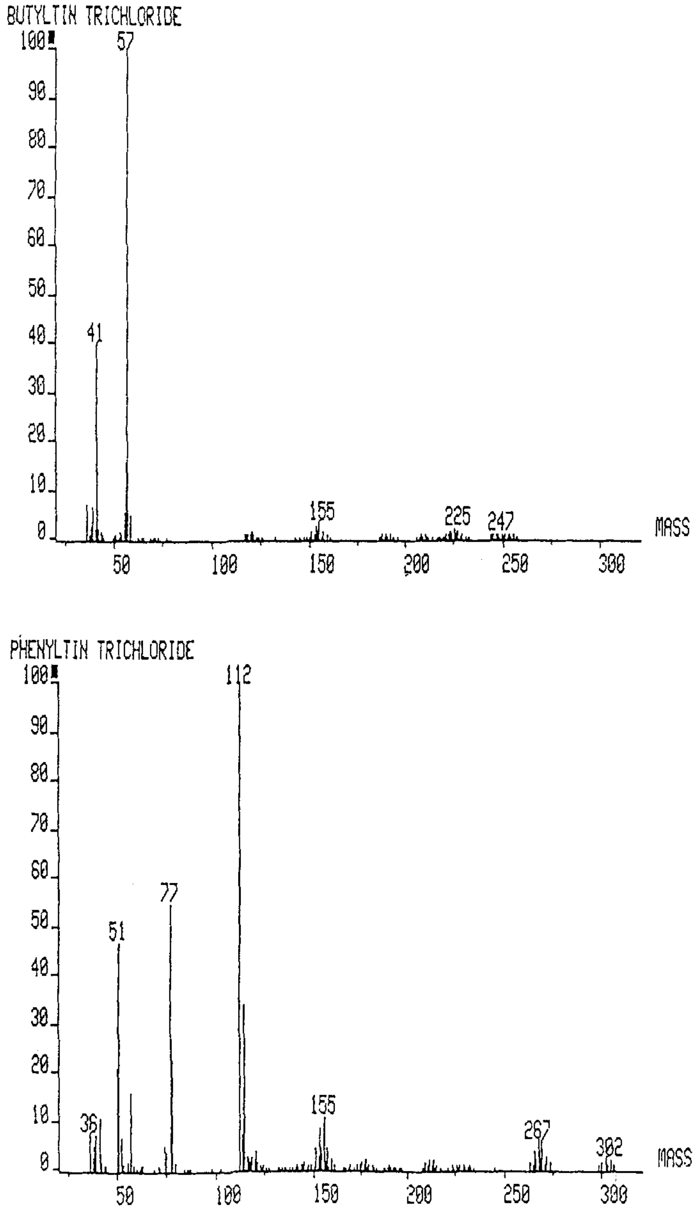

Figure 1 Electron-impact mass spectra of butyltin trichloride and phenyltin trichloride demonstrating the absence of significant structural data in these non-derivatized multihalogen species using this technique.

trap are frequently used as tandem instruments, and in some instances a combination of the sector and either time of flight or a quadrupole performs this function. ICP systems usually incorporate quadrupoles for the mass analysis since they can accommodate a poorer control over the range of incident ion energies. From the above it can be seen there is no fundamentally new mass analysis technique which can be used, and alternative methods based on either new ionization methods or new sample introduction techniques were investigated.

One relatively simple change which has been investigated[7] is the use of negative-ion electron impact ionization (NIEI). Under these conditions there should be reduced fragmentation with

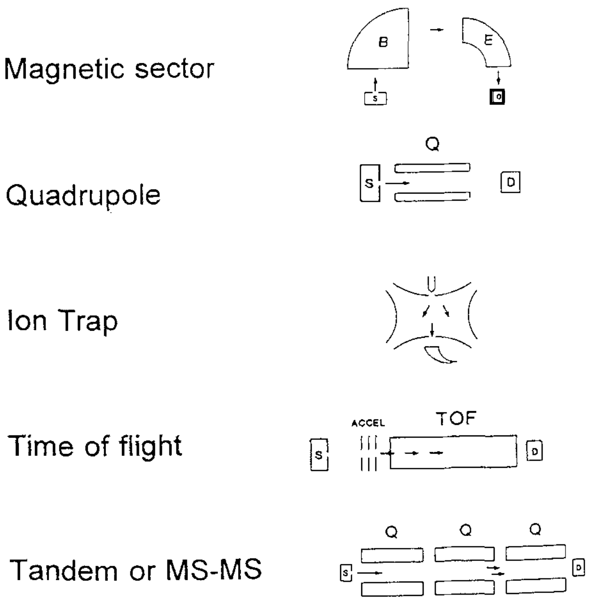

Figure 2 Summary of the types of mass spectrometers.

consequently more structural data evident in the mass spectrum. This was the case for compounds which contained an electronegative centre, but other compounds, e.g. the tetra-alkyltins, were virtually non-detectable under NIEI conditions. A further problem is the virtual absence of any significant database of negative-ion mass spectra.

An alternative approach is to consider the use of liquid chromatography (LC) to separate the non-volatile compounds and thus eliminate the need for any derivatization. LC separation methods can be used in conjunction with particle beam (PB), electrospray (ES), atmospheric pressure (APCI) and fast atom bombardment (FAB) interfaces to allow direct coupling to an MS to provide the confirmatory data. ES, APCI and FAB techniques are all regarded as 'gentle' methods for the production of ionic species in the gas phase and the production of mass spectra exhibiting little or no fragmentation would be expected; indeed, for the organotin compounds the formation of solvent addition ions has been reported.[8,9] A particle beam interface, on the other hand, is really a conventional EI source mounted after a desolvation system, and as such should produce mass spectra very similar to EI systems, which should show wide fragmentation and also be database-searchable. An investigation of the Waters 'Integrity' system reported elsewhere[10] confirms the applicability of such systems to the identification and quantification of organotin compounds.

The investigation reported here concentrates on the determination of the mass-spectral data from selected alkyl- and aryl-tin compounds under different conditions in an electrospray (ES) interface.

2 ELECTROSPRAY INTERFACE

In the electrospray interface (Fig. 3) desolvation and charge separation occur at the same time. For tributyltin chloride, for example, Bu_3Sn^+ and Cl^- would be the ions anticipated to be present in solution, with the degree of solvation being dependent on the nature of the solvent or mobile phase. Electrochemical oxidation or reduction reactions have also been reported as leading to the formation of ions in ES systems.[11] In all cases the solution is dispersed into an aerosol of charged droplets which decrease in size as the solvent evaporates. The observed degree of solvation and/or fragmentation depends on the conditions in the interface region; for example, a high repeller/cone potential would lead to lower levels of solvation and an increased degree of fragmentation resulting from collision-induced dissociation (CID) reactions. Lower potential differences should lead to the observation of ions with a greater degree of solvation, for example $[Bu_3Sn(MeOH)_n]^+$ where $n = 2$ or 3. Under these various conditions different mass spectra for the same compound may be observed and it is important to ensure that the instrumental conditions remain fixed during a particular investigation.

3 EXPERIMENTAL

3.1 Sample preparation

The organotin compounds, obtained from Aldrich Chemical Co. (better than 98% pure) were each prepared as received at concentrations of around 10 ng^{-1} µl in methanol/water (90:10) and were further diluted to around 10 pg^{-1} µl immediately prior to analysis. For this initial series of analyses samples were injected directly into the mass spectrometer interface, by direct-loop injection and/or continuous-flow injection

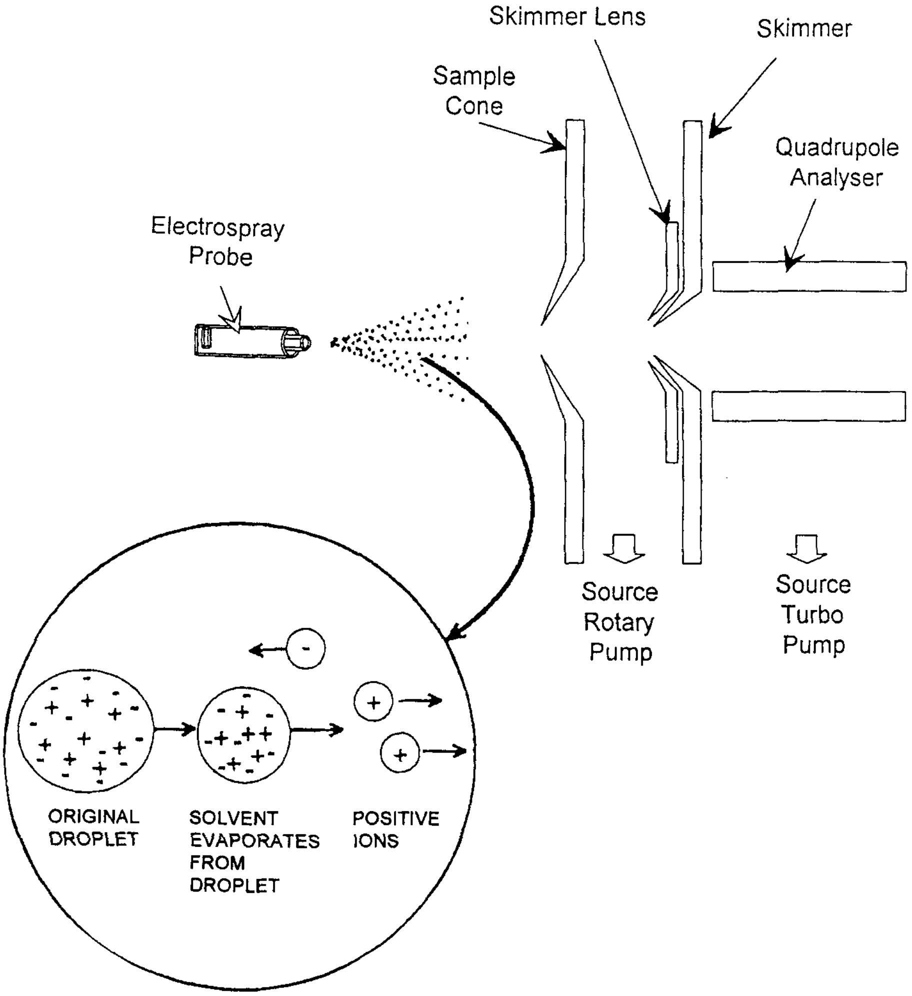

Figure 3 Schematic diagram of a simplified electrospray interface.

using a Harvard syringe pump, without prior chromatographic separation. After calibration data had been obtained from the individual standard compounds, two mixtures were analysed to investigate whether any cross reaction had taken place.

3.2 Instrumental parameters

The ES experiments were carried out using a Fisons Instruments VG Quattro equipped for either 200 µl min^{-1} or 1.0 ml^{-1} min sampling rates, using continuous-flow sample injection of the individual components in order to obtain characteristic spectra for a 3 kV needle voltage, and different operating conditions of the cone/repeller voltage: 18 V, 64 V and 80 V respectively. The recorded data were signal-averaged using the MAX-ENT software routine.

4 RESULTS

Tin has ten isotopes; in order to simplify the discussion, only the ^{120}Sn isotope will be considered, except for the high-mass cluster compounds containing more than one tin atom in which case the ^{118}Sn isotope produces the more abundant signals.

4.1 Spectra recorded at low cone/repeller voltage

On the VG Quattro, for this series of experiments, cone potentials of between 18 and 21 V were used. The results obtained showed similar reactions occurring to those reported by Jones and Betowski[9] using a Vestec 201 system but the overall mass-spectral details were different. Jones and Betowski used methanol with acetic acid and the major ions formed, i.e. the acetate addition ions, would not be duplicated in the current investigation. Furthermore, it is possible that the operating parameters of the two different instruments may have led to some significant differences in the observed mass spectra. For example, the Vestec 201 system appears to produce a relatively greater degree of fragmentation for a given

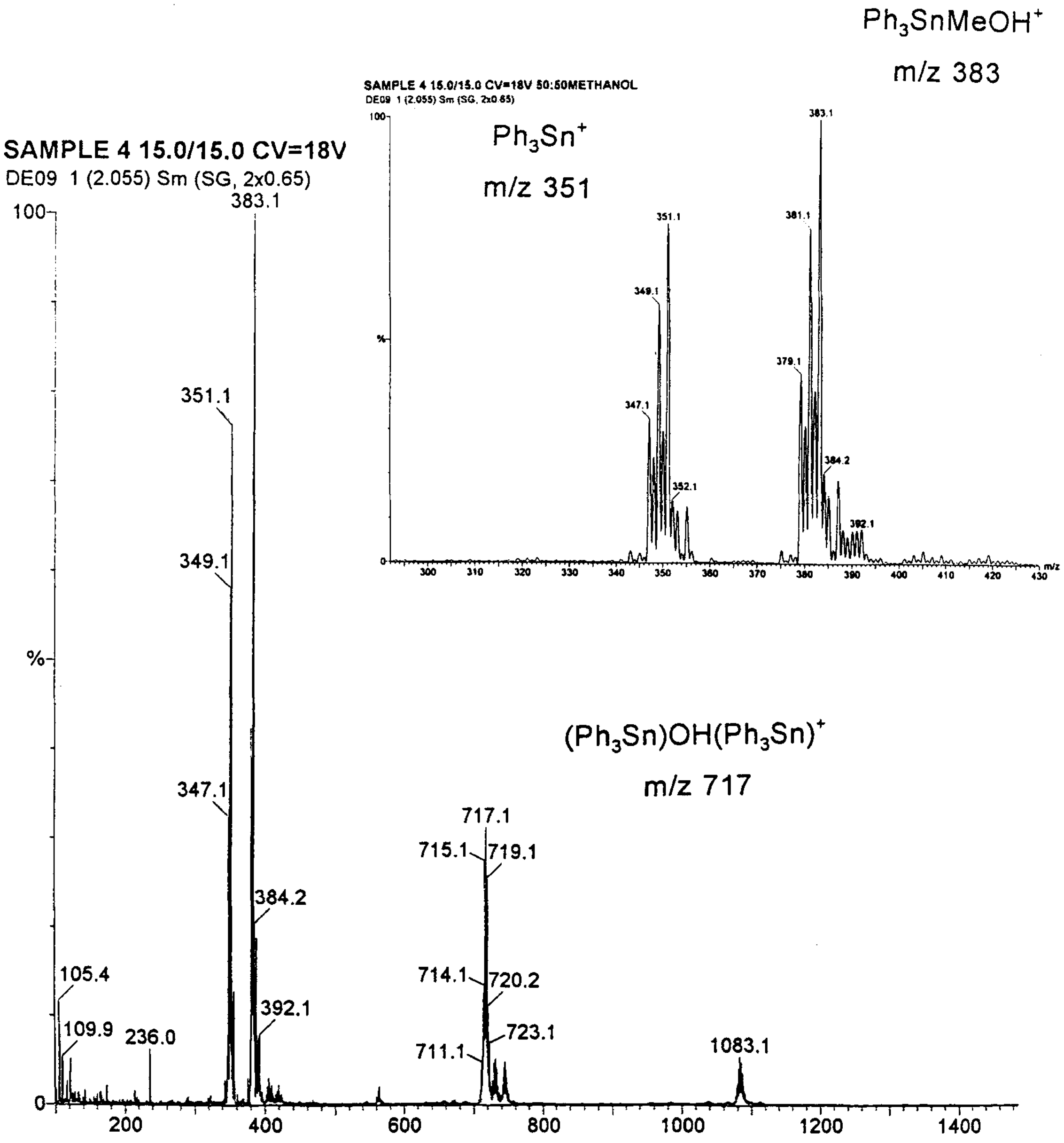

Figure 4 ES–MS data for triphenyltin chloride (Inset shows details of the *m/z* 351 ansd 383 isotope cluster peaks).

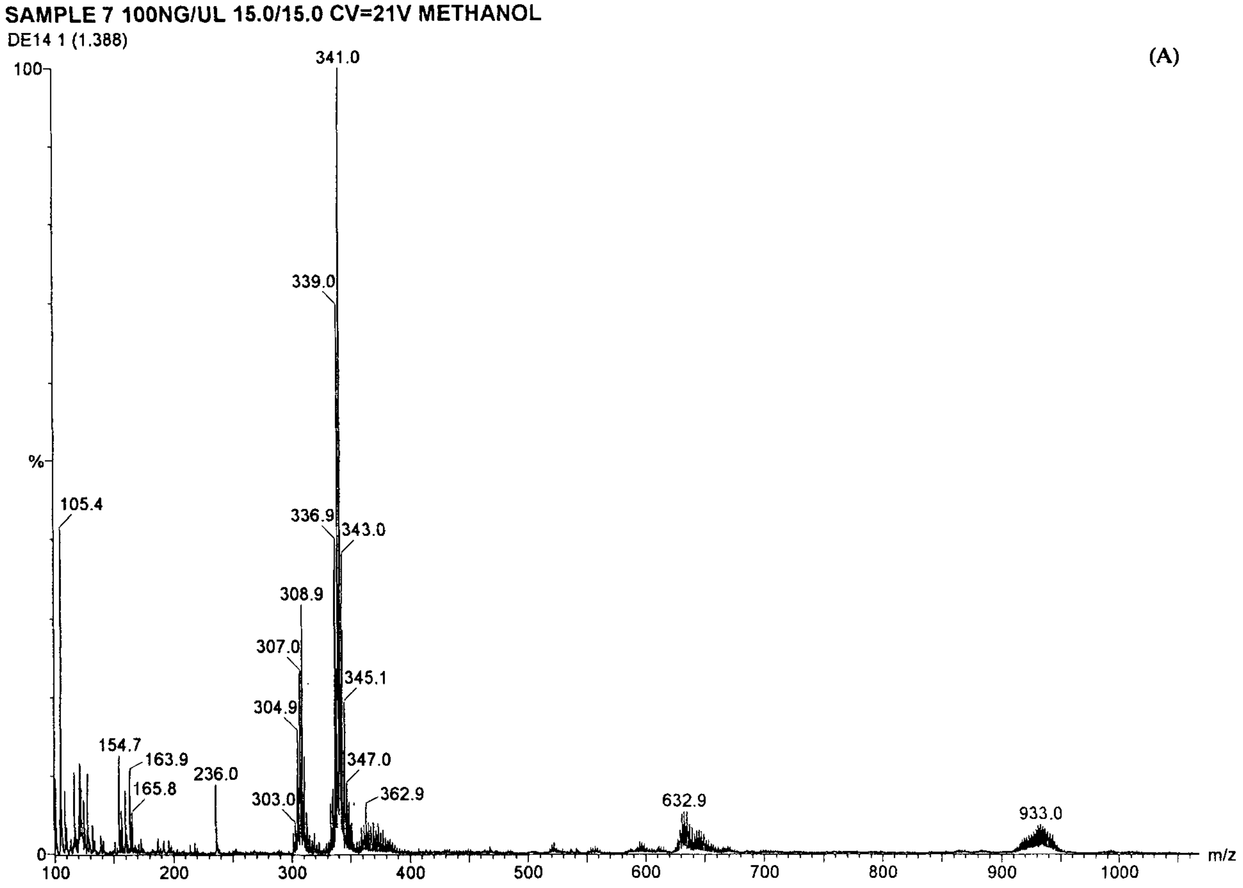

Figure 5a ES–MS for diphenyltin dichloride for 21 V cone voltages.

applied potential than does the Quattro. Both investigations noted the production of groups of high-mass cluster ions all exhibiting isotope patterns consistent with the presence of multiple tin atoms. In several instances these high-mass clusters were present at significant relative abundances (RA), for example *m/z* 597 (80% RA) in tributyltin chloride (TBT, M_r, 326) and *m/z* 717 (35% RA) in triphenyltin chloride (TPT, M_r 386); see Table 1.

The ES mass spectrum of TPT, which is typical of the results produced in this phase of the investigation, is shown in Fig. 4 and the data obtained from all the compounds studied are summarized in Table 1. Under these experimental conditions the aryltin compounds favoured formation of methanol addition ions, after the loss of a chlorine atom, to produce the base peak. The alkyltin compounds produced $[M - Cl]^+$ as the base peak, with an almost equal yield of the methanol addition ion $[M - Cl + MeOH]^+$. There was no evidence of fragmentation leading to ions equivalent to *m/z* 179, the acetate addition ion postulated by Jones and Betowski.[9] Sequential loss of the three butyl groups from TBT was also reported by Jones and other workers,[8, 9] whereas in this investigation the loss of only one butyl group to give *m/z* 235 and the formation of the methanol addition ion $[M - Cl + MeOH]^+$ (*m/z* 267) were the only fragmentations observed. The RA of the *m/z* 235 ion was only 15% in this work, compared with 100% reported by Jones and Betowski.

Similar results were observed from dibutyltin dichloride DBT (M_r 304) with the formation of *m/z* 269 $[M - Cl]^+$ (100% RA) and *m/z* 301 $[M - Cl + MeOH]^+$ (90% RA). Butyltin trichloride MBT (M_r 282) reverses this trend with the

Table 1 Ions observed in the ES mass spectra of organotin compounds

Compound	*m/z* of principal ions (RA) Proposed structure[a]				
Triphenyltin chloride	383 (100)	351 (75)	717 (35)	1083 (12)	
	$[M - Cl + MeOH]^+$	$[M - Cl]^+$	$[(Ph_3Sn)_2OH]^+$	?[b]	
Diphenyltin dichloride	341 (100)	309 (35)	155 (14)	633 (10)	651 (5)
	$[M - Cl + MeOH]^+$	$[M - Cl]^+$	$[SnCl]^+$	$[(M - Cl)_2OH]^+$	$[(M - Cl)_2O + H_2O + H]^+$
Tributyltin chloride	291 (100)	323 (95)	597 (80)	625 (10)	
	$[M - Cl]^+$	$[M - Cl + MeOH]^+$	$[(M - Cl)_2OH]^+$	$[(M - Cl)_2O + H_2O + H]^+$	
Dibutyltin dichloride	269 (100)	301 (90)	No data	No data	
	$[M - Cl]^+$	$[M - Cl + MeOH]^+$			
Butyltin trichloride	279 (100)	247 (15)	521 (12)		
	$[M - Cl + MeOH]^+$	$[M - Cl]^+$	?[b]		

[a] Based on ^{120}Sn and ^{35}Cl.

[b] Possibly a three- or four-membered tin cluster.

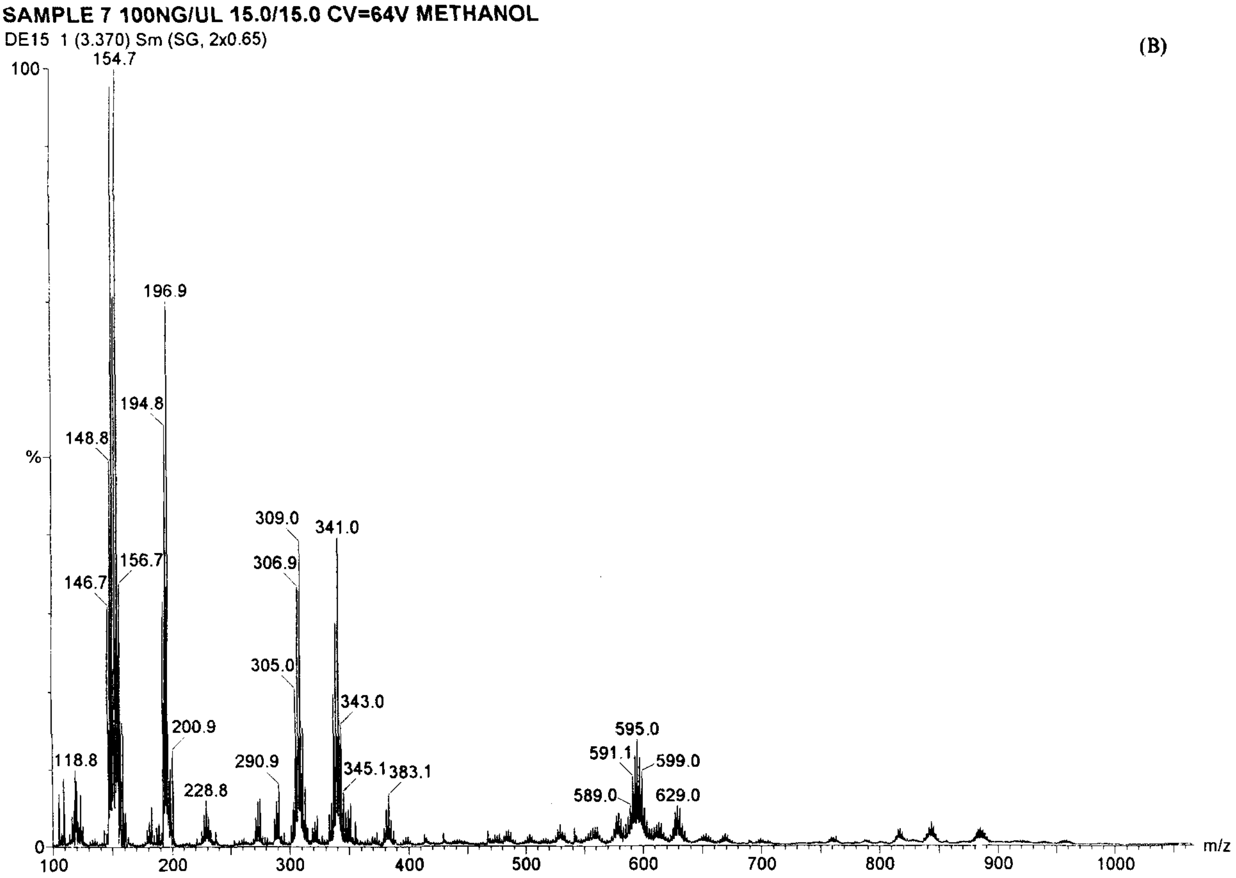

Figure 5b. ES–MS for diphenyltin dichloride for 64 V cone voltage showing increased fragmentation at higher cone voltage.

$[M - Cl]^+$ ion, *m/z* 247, having an RA of only 15%, whilst the solvated species at *m/z* 279 was the base peak.

The ions observed at high *m/z* values (717, 633 and 597), derived from solutions of TPT, DPT and TBT respectively in methanol/water mixtures, cannot be explained in terms of increasing levels of solvation. Furthermore, the tin isotope distribution pattern is the same as that calculated for a compound containing two tin atoms in which the most intense peak corresponds to $2 \times {}^{118}$Sn (i.e. at *m/z* 236 plus the other substituents). The only structures which can be proposed which correspond to these *m/z* values appear to be:

There are several other high-mass groups of peaks for which structures have yet to be postulated, although there is evidence for the hydrated ions derived from those shown above for DPT and TBT, i.e. at *m/z* 651 and 625 respectively. The mechanism for the formation of these species is as yet unclear although the presence of water in the solvent does seem to be necessary. It is interesting to speculate whether these compounds were originally present in solution or are formed during the electrospray process in a manner similar to the reactions seen in a tandem mass spectrometer at low (order of 2–5 eV lab frame) collision energies.[12]

$[Ph_3Sn{-}O{-}SnPh_3]H^+$	for *m/z* 717 from TPT
$[Ph_2ClSn{-}O{-}SnClPh_2]H^+$	for *m/z* 633 from DPT
$[Bu_3Sn{-}O{-}SnBu_3]H^+$	for *m/z* 597 from TBT
$[Cl_2BuSn{-}O{-}SnBuCl_2]Me^+$	for *m/z* 521 from MBT

4.2 Mass spectra recorded at high cone/repeller voltage

At higher cone voltages a greater degree of fragmentation was observed, as shown in the mass spectrum (Fig. 5) recorded for diphenyltin dichloride (DPT; M_r 344) where the base peak changes from m/z 341 to m/z 155 $[SnCl]^+$ for 64 V applied to the skimmer cone. Other major peaks in the spectrum include $[PhSn]^+$, m/z 197 (75% RA); $[M-Cl]^+$ at m/z 309 (45% RA); and m/z 341 $[M-Cl+MeOH]^+$ (45% RA). There was very little apparent change to the high-mass ion clusters when the increased cone voltage was applied.

Similar results were obtained from TPT when a cone bias of 80 V was used. Fragmentation to the tin ion was observed, with m/z 120 being the base peak, m/z 197 $[SnPh]^+$ at 90% RA and the previously more dominant peaks m/z 351 and 383 both reduced to less than 35% RA. Thus it can be seen that significant collision-induced fragmentation can be produced by the use of comparatively high cone/repeller bias voltages.

5 CONCLUSIONS

The mass spectra recorded by ES techniques showed a significant dependence on the repeller/cone voltage potential. High cone voltages produced much-enhanced fragmentation processes, which led to a complete change in the mass-spectral traces. For the compounds studied, the base peak was either the $[M-Cl]^+$ ion or the solvated species $[M-Cl+MeOH]^+$. All the compounds studied showed the presence of groups of ions at high mass, and some proposals for the structure of these species based on substituted Sn — O — Sn groups and their solvated derivatives have been given. The LC/ES–MS combination shows potential for the analysis of organometallic compounds but, if this method is to be used, care must be taken when comparing information from different instrumental systems.

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