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Analysis of Organotin Compounds via a Thermabeam® LC–MS Interface

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Selected organotin compounds, relating to antifouling paints, have been analysed using a particle beam interface system designed for use on liquid chromatography–mass spectrometry (LC–MS) instruments. The resultant mass spectra matched those obtained from conventional electron-impact (EI) techniques, and consistent data over several injections and different elution times were obtained. Data obtained from tributyltin, dibutyltin, monobutyltin, triphenyltin and diphenyltin (each as the chlorides) are presented. This interface has been shown to maintain sample and therefore spectral integrity for these compounds and is of potential use in further investigations relating to organotin environmental pollution.

Keywords: organotin; particle beam; mass spectra; LC–MS

1 INTRODUCTION

Mass spectrometry (MS) is probably the most specific technique for the detection and identification of organic compounds present in samples derived from the environment, especially when contaminants are being investigated. MS can provide not only molecular weight information but also a wealth of structural detail which, when combined, give a unique fingerprint for each analyte. The dynamic combination of gas chromatography (GC) and mass spectrometry has produced the most sensitive and specific method (GC–MS) for the characterization of the volatile components of complex mixtures; but herein lies the weakness of the system, since only volatile analytes can be handled. In the analysis of organotin compounds of environmental significance, the sample must first be derivatized in order to produce the necessary volatility.[1] The techniques utilized include the formation of the hydrides[2] and alkyl derivatives, including the ethyl[3] and pentyl[4] analogues. Derivatization may lead to sample losses and loss of sample authenticity, as well as increasing the total time and cost for each analysis.

High-performance liquid chromatography (HPLC), on the other hand, can separate compounds which are not volatile and therefore it is potentially applicable to a much wider range of analytes than GC. The combination of HPLC with mass spectrometry (LC–MS) should in principle provide the same analytical capability as GC–MS, but for a wider range of compounds.

The interconnection of the two instruments is more complicated than for GC–MS since any successful interface must facilitate the transition of the analyte from solution (in the mobile phase) into the gas phase with either simultaneous or subsequent ionization of the sample molecules. Unwanted solvent molecules must also be removed from the system during this process. There are several interfaces currently being used in MS laboratories, with applications ranging from the determination of pesticides and surfactants in river water to the analysis of antioxidant degradation products from food contact plastics.[5] Lawson *et al.*[1] have investigated the electrospray interface in conjunction with organotin compounds of general formula R_xSnX_{4-x} and reported the formation of both adduct ions and reaction product ions involving the solvent. Similar work using the atmospheric-pressure chemical ionization source (APCI)[7] showed the formation of much larger adduct species, but no reaction products were noted.

An alternative approach, viz. the use of particle–beam (PB) interfaces, should produce mass spectra which are identical to conventional electron-impact (EI) results. The construction and performance of PB interfaces has been reviewed by Creaser and Stygall.[8] Several authors reported some evidence of non-linear response,[9, 10] possibly as a result of particle size cut-off in the interface, although this was not confirmed. The particle-

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beam interface used on the Waters 'Integrity' LC–MS system was employed to investigate a series of organotin compounds and the resultant mass spectra obtained from these compounds, in solution, were compared with data obtained either using conventional probe plus electron-impact techniques or derived from literature references. The reproducibility of the data from the interface was ascertained from a series of multiple injections of the same solutions.

2 BACKGROUND

The particle beam LC–MS interface is mechanically quite simple (see Fig. 1). The LC effluent is passed through a pneumatic nebulizer to form a fine mist of droplets. These droplets pass through a heated desolvation chamber to separate the solvent and the analyte molecules. The solvent molecules are removed from the system by a two-stage momentum separator and are vented to atmosphere. The analyte molecules are transferred into a conventional EI source where they are ionized. There are therefore several advantages to be derived from a particle beam interface.

(a) conventional EI mass spectra should be produced and these should be library-searchable;
(b) there should be little or no constraint on the composition of the solvents which can be used for a particular analysis;
(c) compounds do not have to be readily volatile—compounds of low polarity can be studied.

The configuration of the particle beam interface with respect to the mass spectrometer on the 'Integrity' system is shown in Fig. 2. The initial region of the nebulizer/expansion volume is maintained typically at 150 °C but the two momentum separator regions, where the pressure is reduced in stages from atmospheric to near-normal mass-spectrometer vacuum conditions, are at lower temperatures (50–65 °C). Typical pressures which occur in this interface are shown on the diagram. It is not readily evident from this diagram, but the entire interface assembly is easily demountable for maintenance and cleaning.

3 EXPERIMENTAL

These experiments were carried out in order to test:

(a) whether a particle-beam system produced comparable EI mass spectra for organotin compounds;
(b) whether the sample and results retained the expected authenticity during the analysis; and

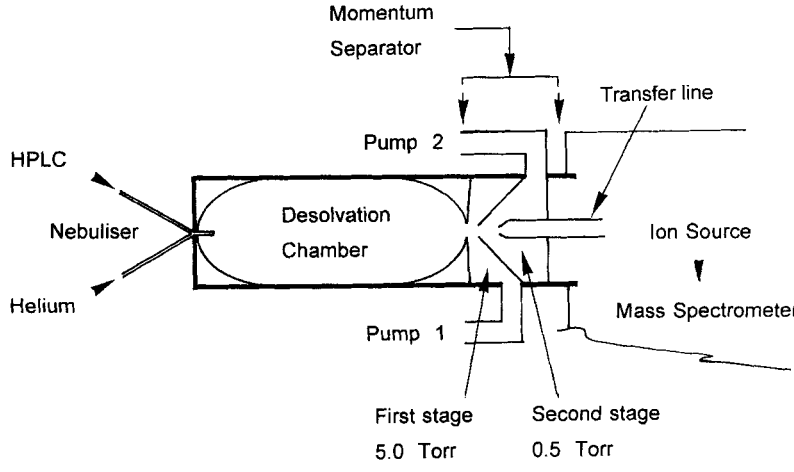

Figure 1 Schematic diagram of a particle beam interface, showing the nebulizer, desolvation chamber and momentum separator The ion source itself is not shown.

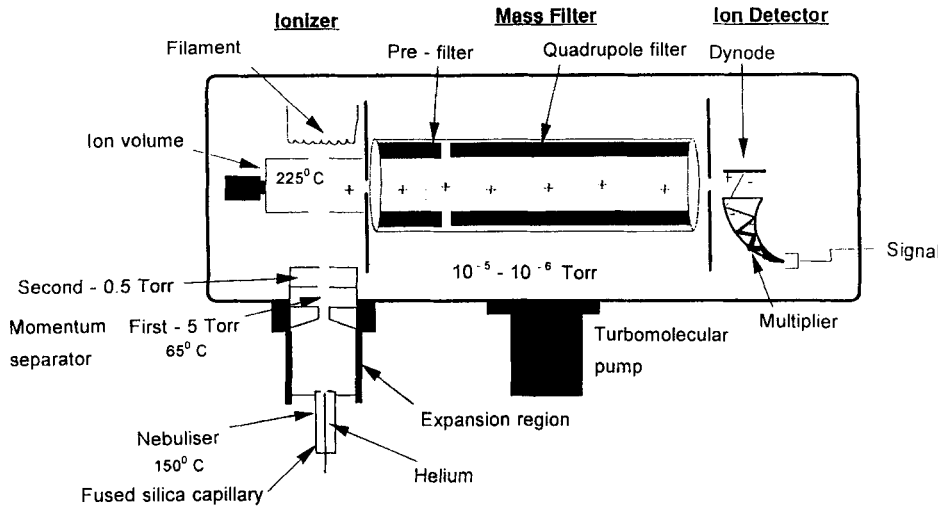

Figure 2 Schematic diagram of the 'Thermabeam interface' showing the relationship of the interface to the mass spectrometer ion source and detailing the system operating parameters.

(c) whether there was any evidence of 'carry-over' between one sample and the next.

In this study, based on the 'Thermabeam® interface' used in the Waters LC–MS system, no actual LC separations were carried out. Solutions of the authentic organotin compounds in either acetonitrile/water or methanol/water, simulating the column effluent, were injected directly into the interface.

The samples used in this work were tributyltin chloride (TBT), dibutyltin dichloride (DBT), monobutyltin trichloride (MBT), diphenyltin dichloride (DPT) and triphenyltin chloride (TPT). These were prepared as stock solutions at 10 mg cm^{-3} and subsequently diluted to around 100 μg cm^{-3} prior to investigation. All the samples were obtained from Aldrich Chemical Co.

The other experimental parameters for the particle beam interface were:

Injection volume	20 μl
Sample flow rate	0.8 ml min^{-1}
Mass spectrometer scan	70–400 amu s^{-1}
Ion source temperature	225 °C
Source potential	8.0 V (initial)
Interface temperature	Nebulizer 150 °C (see Fig. 2)
	Separator 65 °C

The parameters for the probe samples were as follows:

Mass spectrometer	VG TRIO 3 quadrupole
Ion source temperature	200 °C
Mass spectrometer scan	40–700 amu s^{-1}
Probe	No auxiliary heating

4 RESULTS

Repeat injections were carried out to investigate the reproducibilty of both the mass spectrum and the total ion signal for each compound. Averaged mass spectra for individual compounds were then compared with the mass spectrum obtained from the probe mass-spectral analysis of each compound. Finally the mass spectra were examined for any traces of carry-over between one sample and the next, i.e. whether there were any peaks present in the mass spectrum of the second compound which belonged to the mass spectrum of the first.

4.1 Data reproducibility

The reproducibility of the data was assessed using the 'Spectrum Index' software which allows similar spectra from different injections to be compared in a graphical format. Figure 3 shows the data obtained from repeat injections of TPT. In this Figure the total detector signal is shown at the bottom and the individual mass spectra are recorded at the top. Comparison of these mass spectra show a remarkable degree of reproducibility; the same reproducibility is not

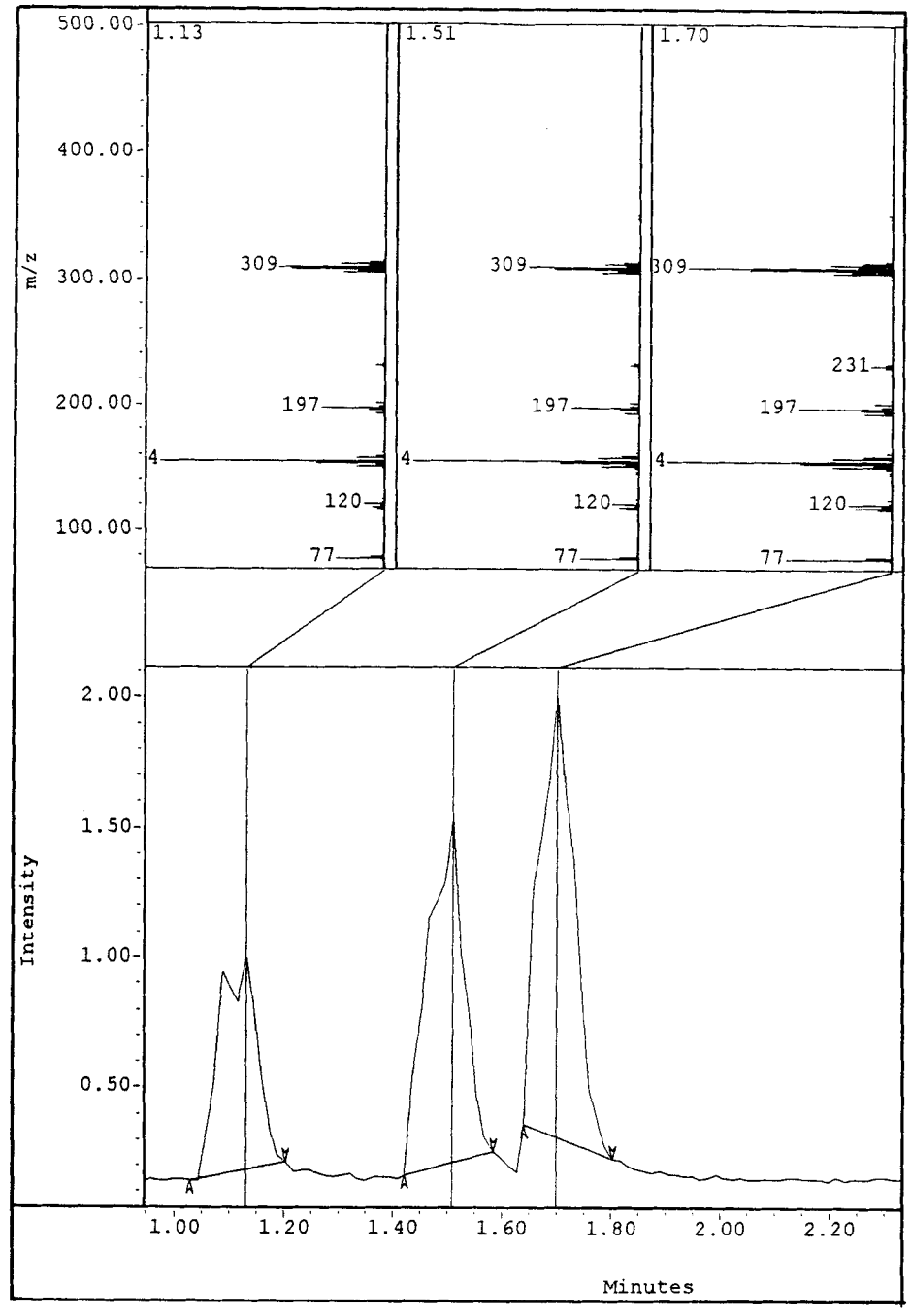

Figure 3 Mass spectra and total ion current signals from repeat injections of TPT.

shown by the signal for the total ion current, where a variation of almost a factor of two is apparent. Figure 4 shows the same data for DPT: in this case there is a somewhat lower level of reproducibility in the mass spectral data, with some more obvious differences in the relative abundance of the *m/z* 230 and 232 peaks. The lower signals for these peaks in two of the traces may result from losses due to collision-induced dissociation in the presence of elevated volumes of sample in the nebulizer, as evidenced by the larger total ion current peaks.

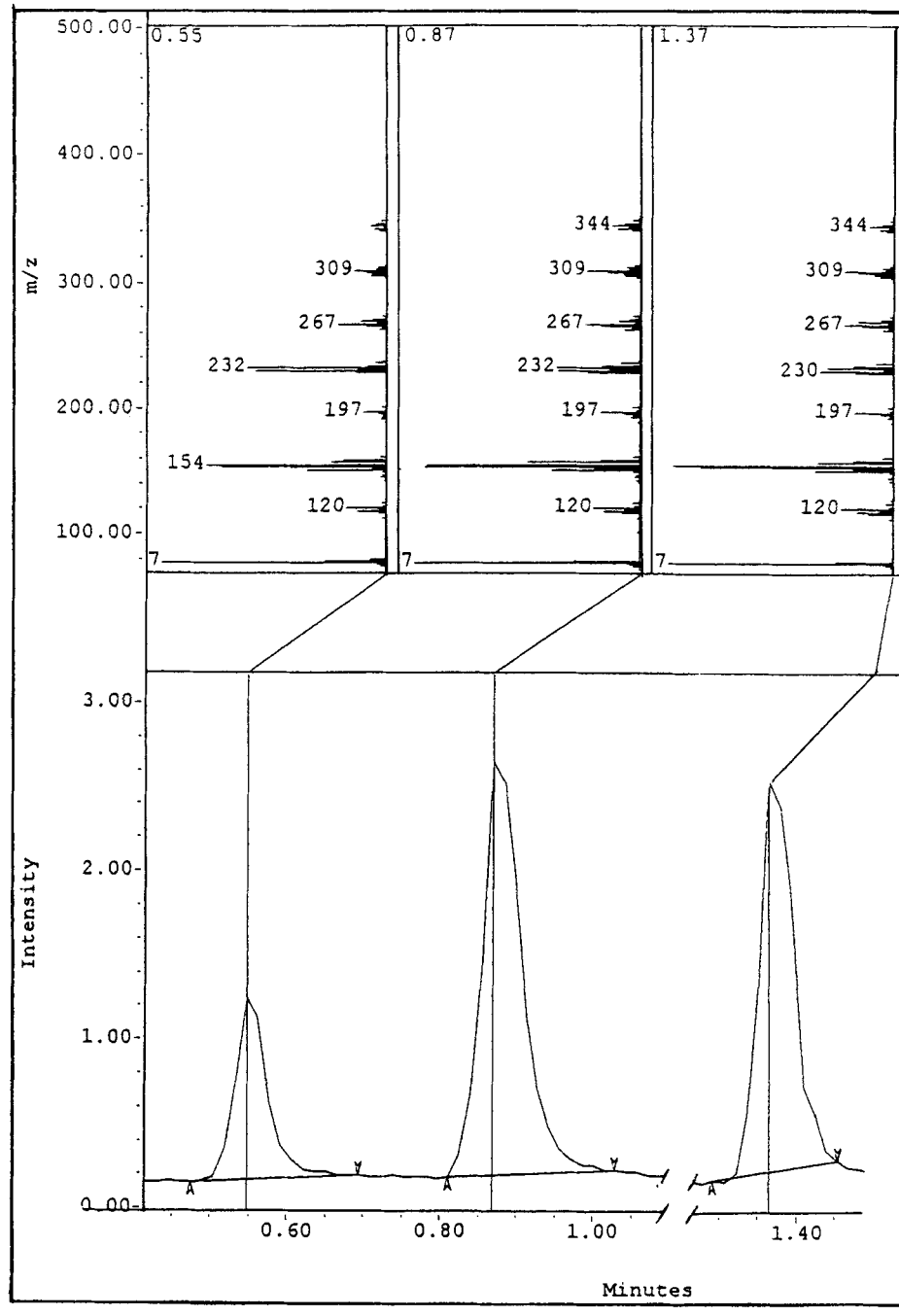

Figure 4 Mass spectra and total ion current signals from repeat injections of DPT.

These compounds might be expected to give similar mass spectra since they both contain the same groups, but the results in Figs 3 and 4 show a consistent group of different mass spectra for each compound. The data for DBT (Fig. 5) show the reverse trend, with the total ion current signal being more reproducible than the individual mass spectra. The averaged data for the latter are comparable with the probe results, however.

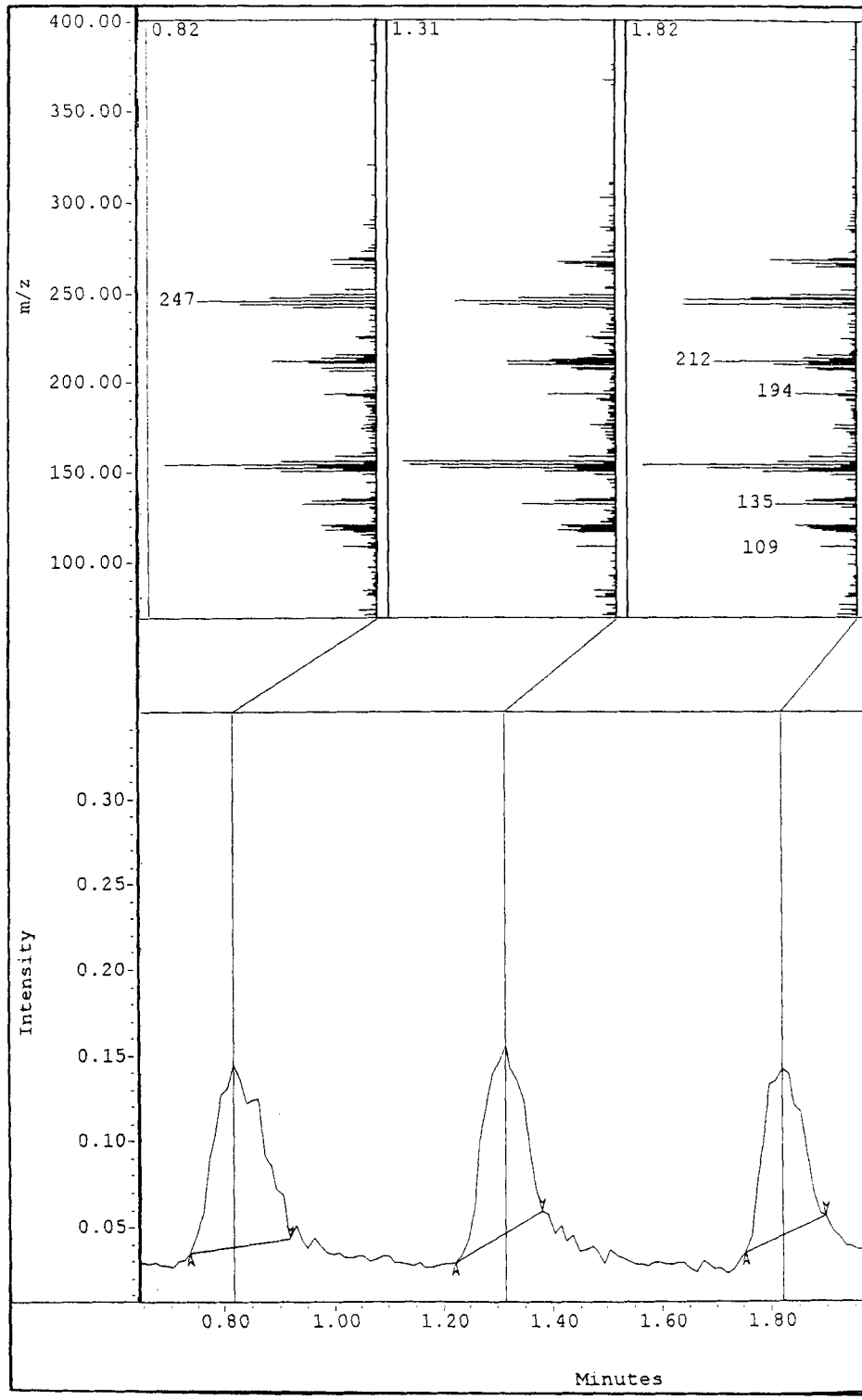

Figure 5 Mass spectra and total ion current signals from repeat injections of DBT.

Table 1 Comparison of mass-spectral data from conventional EI systems versus the particle-beam interface

TBT									
m/z	155	269	153	177	213	211	267		
RA[a]									
Probe	(100)	(70)	(65)	(65)	(59)	(55)	(35)		
LC–MS	(100)	(60)	(56)	(40)	(50)	(44)	(36)		
DBT									
m/z	155	153	247	212	210	245	151	157	269
RA									
Probe	(100)	(65)	(56)	(54)	(40)	(38)	(37)	(37)	(35)
LC–MS	(100)	(65)	(75)	(70)	(38)	(45)	(30)	(37)	(25)
MBT									
m/z	155	153	225	227	157	223	151	159	
RA									
Probe	(100)	(78)	(65)	(60)	(48)	(46)	(46)	(25)	
LC–MS	(100)	(76)	(72)	(66)	(59)	(47)	(28)	(46)	
TPT									
m/z	154	155	309	307	153	305	197	77	
RA									
Probe	(100)	(60)	(50)	(40)	(35)	(30)	(30)	(30)	
LC–MS	(100)	(60)	(60)	(40)	(35)	(20)	(37)	(32)	
DPT									
m/z	154	155	153	232	151	157	77	309	267
RA									
Probe	(100)	(95)	(75)	(31)	(30)	(30)	(25)	(24)	(20)
LC–MS	(100)	(95)	(90)	(50)	(50)	(52)	(95)	(24)	(30)

[a] RA values (in parentheses) are percentages of the principal *m/z* peak.

4.2 Comparison of mass-spectral data (probe versus particle beam)

This comparison is based on selecting the major peaks from the conventional EI spectra and recording the *m/z* values and relative abundance (RA) in decreasing order. The RAs for the same *m/z* values obtained from the interface system are added as the third row of values for each compound. These data are summarized in Table 1; whilst it is evident that there are no variations in the principal (i.e. characteristic) *m/z* values, there are some differences in the observed relative abundances. These differences are however commensurate with the differences which can be found in mass-spectral databases when different mass spectra for the same compound are compared. These results clearly show that comparable data were obtained from each compound and, more importantly, that in the particle–beam interface data there appears to be no detectable contribution from the solvent systems. Whilst some variations in the relative abundance were noted, the general overall agreement can best be illustrated by reference to the two mass spectra for dibutyltin dichloride (DBT), recorded by conventional EI probe methods and via the particle-beam interface (Fig. 6).

4.3 Mass-spectral integrity

Kim *et al.*[11] reported the appearance of mass-spectral peaks in one compound resulting from the previous eluent; this was termed 'carry-over', and was thought to be due to particles condensing inside the interface and then being revolatilized by subsequent collision with another particle. In this investigation the mass spectra recorded after a different analyte was injected for the first time were scrutinized for the presence of any peaks

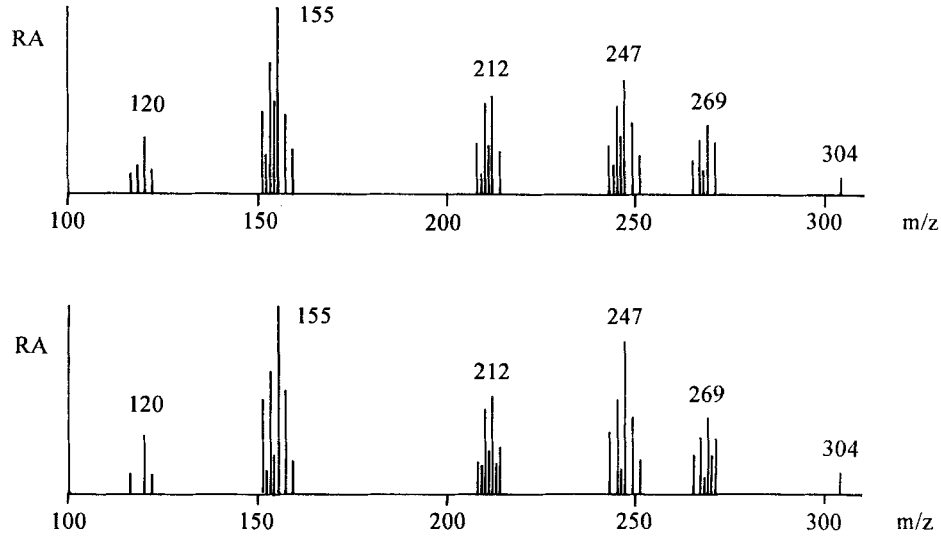

Figure 6 Comparison of the mass spectra obtained from dibutyltin dichloride (DBT) using conventional EI probe techniques (above) and the particle beam system (below).

which were a 'carry-over' from the previous sample. Where there was no chromatographic separation it was not really possible to simulate closely eluting peaks which would magnify the effects of 'carry-over', and no evidence of this phenomenon was observed.

4.4 Detection limits

In the total ion mode the range of compounds studied exhibited approximately the same signal output (within a factor of two) and it was therefore possible to calculate the mean detection limit for this group of compounds. However, no attempt was made in this investigation to determine an absolute minimum detection level, for example by using the maximum multiplier voltage on the mass spectrometer.

Under the experimental conditions used in these investigations the detection limit was between 2 and 4 ng injected into the system.

5 DISCUSSION

The mass-spectral results obtained from the Thermabeam® interface are comparable with those from conventional EI systems and would therefore be database-searchable.

Data have been obtained for compounds which are usually derivatized prior to analysis, and thus the potential for direct analysis by LC–MS has been demonstrated. Whilst this investigation did not directly address the problem of minimum detection levels appropriate for environmental analyses, it has demonstrated that LC–MS analyses could lead to significant savings in both time and expense.

Reproducible mass spectra have been obtained from this interface and its use would therefore enable the identification of previously unsuspected contaminants by reference to database material. Improved precision with respect to the total ion current signal would be desired for quantitative applications and the particle–beam interface is therefore worthy of further investigation with organometallic samples derived from areas of environmental importance.

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