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# Speciation of organotin compounds by tandem mass spectrometry

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**The collision-induced dissociation of a range of organotin compounds has been examined by tandem (MS–MS) mass spectrometry in order to investigate the potential of the technique for speciation without prior chromatographic separation. Tables of parent–daughter ion relationships are prepared for a group of six closely related compounds. The results obtained are sufficiently characteristic to distinguish between the isolated compounds and to identify the individual components of a simple mixture. This procedure has potential applications for less volatile compounds and for quantitative analysis.**

**Keywords: Organotin compounds, speciation, tandem mass spectrometry**

## 1 INTRODUCTION

The analysis and speciation of organotin compounds of environmental importance are usually carried out using a derivatization technique in conjunction with gas-chromatographic separation. Derivatization is used to render the compounds sufficiently volatile and thermally stable for gas-chromatographic separation with subsequent detection by conventional GC detectors, e.g. flame ionization (FID),[1,2] flame photometric (FPD),[2-4] electron capture[1] and mass spectrometry.[5,6] Element-specific detectors have also been used in this application and include both atomic absorption[5] and atomic emission[7] spectrometers. The chromatographic separation, in conjunction with retention-time data derived from authentic compounds or in combination with mass-spectral fragmentation patterns, facilitates the identification of the structure of the original organotin compounds.

Speciation may also be achieved, without the need for derivatization to increase volatility, by the use of high-performance liquid chromatography (HPLC),[8] whilst Mössbauer spectroscopy has also been utilized for the study of a range of triphenyltin compounds.[9]

This work describes the use of tandem mass spectroscopy (MS–MS) methods for the production of speciation data for a range of organotin compounds without the need for prior derivitization and chromatographic separation.

## 2 THEORY

There are several different MS–MS instruments and the range of applications is extensive but the same basic concept is involved throughout: the measurement of the mass-to-charge ratios of ions before and after reaction within the mass spectrometer. The possible reaction types are summarized by Busch *et al.*,[10] who indicate the most common process to be a change in mass as depicted in Eqn [1].

$$m_p^+ \rightarrow m_d^+ + m_n \qquad [1]$$

Generally $m_p^+$ is referred to as the parent ion (not necessarily with the same mass as the molecular ion), $m_d^+$ is the daughter ion and $m_n$ is a neutral species. In MS–MS experiments, therefore, any ion with a significant abundance after the primary ionization process can be used as the parent species.

MS–MS experiments must therefore involve the use of two mass-analyser regions within the same instrument to allow the mass selection of the parent ions in the first stage of analysis, followed by the analysis of any daughter ions, often formed by collision-induced decomposition (CID) processes, in the second stage of mass anlaysis. A typical MS–MS instrument (Fig. 1) will therefore comprise a sample introduction system, an ionizer for the first mass spectrometer (MSI) and a reaction region followed by the second mass spectrometer (MSII), which is used for daughter-ion analyses. The instrument shown in Fig. 1 is a VG TRIO 3 Triple Quadrupole system in which

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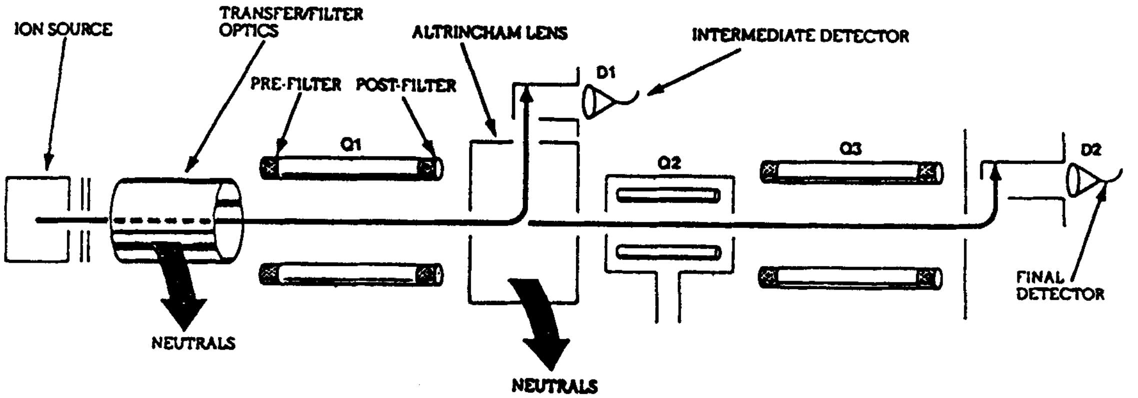


**Figure 1** Schematic diagram of the TRIO 3 triple quadrupole tandem mass spectrometer system.

Q1 and Q3 are the two mass spectrometers and Q2 is the non-mass-selective reaction/decomposition region.

The most frequently encountered experiments in MS–MS analyses involve the identification of the daughter ions resulting from selected parent ions. Q1 is used to select the parent ion (mass M1) and Q3 is scanned repeatedly to monitor all the ions produced by the reaction/decomposition of M1 within Q2. Once the data for M1 have been collected Q1 can be re-set and the experiment repeated for a different parent ion. The general experimental approach is shown schematically in Fig. 2 and the extent of reaction/decomposition in Q2 is determined by both the nature and pressure of the collision gas introduced into this region. For most experiments the collision gas is usually air, argon or xenon.

The basic information available from this type of experiment is shown in Fig. 3, where the specific decomposition pathways for preselected ions are determined. For the analysis of environmental samples it is necessary to determine the parent and daughter ion relationship from authentic 'pure' compounds initially. Consider the example given in Fig. 4 where there are two suitable parent ions $M_1^+$ and $M_2^+$ produced by MSI from the primary ionization. If it is assumed that some of each individual parent ion dissociates into the related daughter ion $m_1^+$ and $m_2^+$, then for any measurement the ion detector will 'see' both parent and daughter ions in a fixed ratio dependent upon the reaction conditions. Under fixed instrumental operating conditions, therefore, the identification of the correct daughter ions resulting from several preselected parent ions can be used to identify and quantify those compounds of interest provided that suitable data are available.

In an environmental sample many different compounds may produce $M_1^+$ under the primary ionization conditions, all of which will contribute to the species leaving Q1 (MSI) but only the species of direct interest will produce ions $m_1^+$ in the required relative intensity and thus the signals for $m_1^+$ are recorded. These data in conjunction with similar evidence for $M_2^+$ and $M_3^+$ via $m_2^+$ and $m_3^+$ are indicative of the presence of the compounds of interest in the environmental sample.

This approach has been successfully used for the study of dioxins in samples obtained from

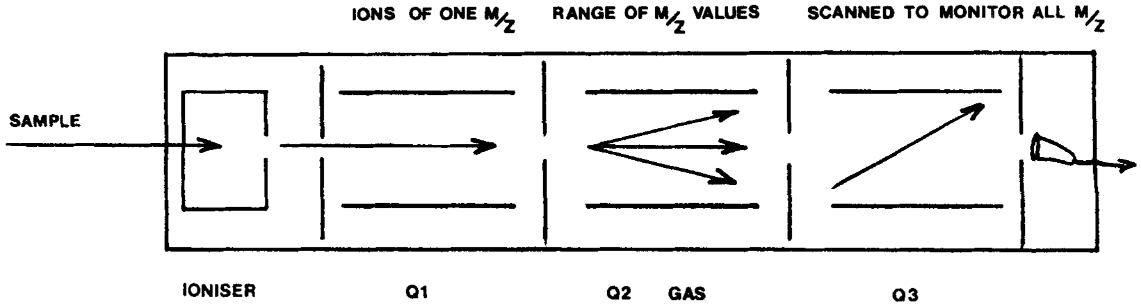


**Figure 2** Triple quadrupole system used in daughter ion monitoring. Q3 is used to determine the decomposition products of the ion selected by Q1 after collision with argon in Q2.

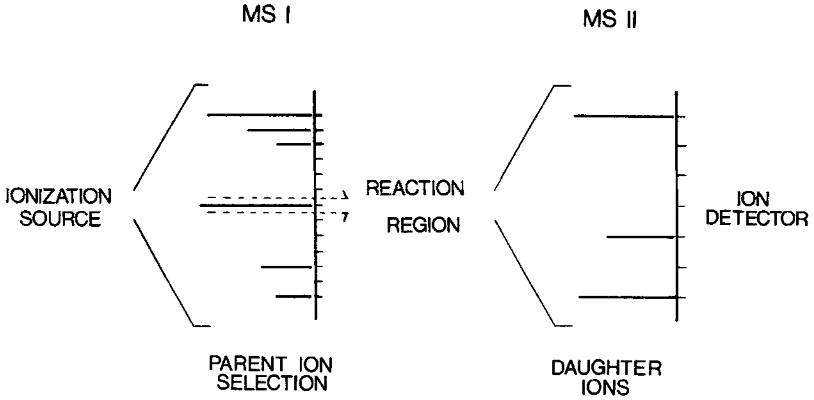


**Figure 3** Schematic representation of an MS–MS experiment showing the selection of the parent ion from the conventional mass spectrum and the resultant daughter ions from the CID process. MS I and MS II are equivalent to Q1 and Q3 respectively.

landfill sites[11] and air filters.[12] Chess and Gross[11] reported the use of the transition $320^+ \rightarrow 257^+$ and $322^+ \rightarrow 259^+$ to monitor tetrachlorodibenzodioxin with a detection level equivalent to 5 ppt in the soil sample. Similar analyses were carried out by Harvan *et al.*[12] on the extract from air filters and a linear response over the range investigated was demonstrated.

Sin *et al.*,[13] who studied organotin compounds using tandem MS with atmospheric pressure ionization (API) techniques, reported difficulty in identifying the organotin compounds in mixtures. API methods are not yet as well understood and controlled as the standard electron impact method of ionization used by Chess, Harvan *et al.* and in the work reported here, and some differences in conclusions might therefore be expected.

This approach to the use of MS–MS instrumentation is in many ways analogous to experiments carried out in GC MS in instruments (see Fig. 4). In GC MS the initial separation of a complex mixture into its individual molecules occurs in the gas chromatograph whereas in MS–MS a separation into individual ions occurs in the first mass spectrometer. The reaction/decomposition region of the MS–MS system has the same function as the ion source in the GC MS system, i.e. the production of the diagnostic ions for compound identification. These ionic species are not the same in the different systems, since in the GC MS application the monitored ions are derived from conventional primary electron impact ionization whereas in the MS–MS approach it is the daughter ions derived from the primary ions which are monitored (cf. Fig. 4).

In GC MS the separation of each component

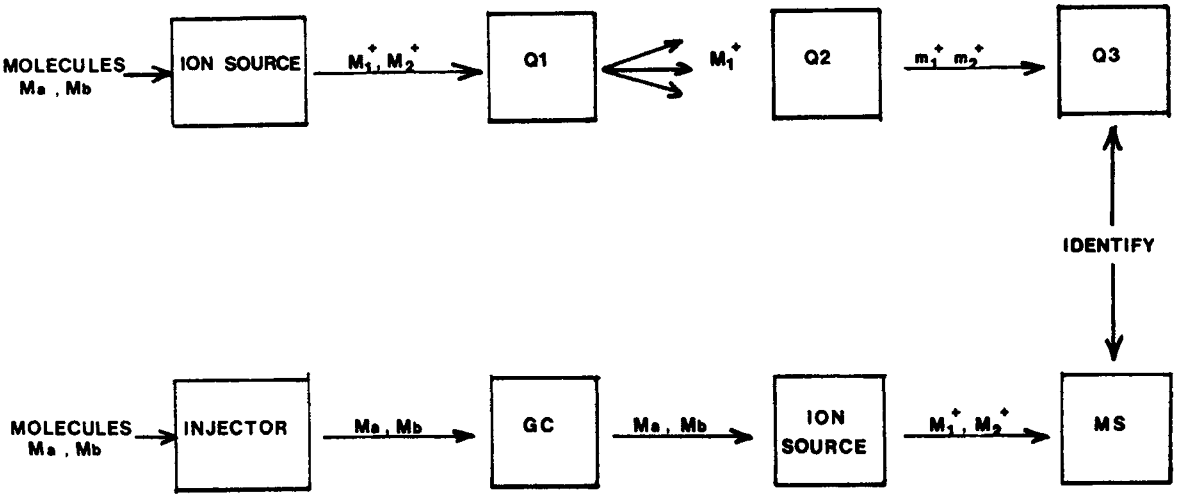


**Figure 4** Comparison of GC MS and MS–MS analytical approaches. (Adapted from Busch *et al.*, *MS/MS Techniques and Applications of Tandem Mass Spectrometry* with permission).

Table 1 Summary of organotin compounds

| Compound | Supplier | Purity (%) |
|---|---|---|
| Tetramethyltin | Aldrich | 99+ |
| Tetrabutyltin | Fluka | 98 |
| Tetra-n-butyltin | Aldrich | 93 |
| Butyltin trichloride | Aldrich | 95 |
| Phenyltin trichloride | Aldrich | 98 |
| Bis(tributyl tin) oxide | Aldrich | 96 |

*Note:* Purity and compound identification is as specified by the supplier.

occurs in time as each sequentially elutes from the column. This is contrasted with MS–MS, where ions are selected on the basis of mass-to-charge ($m/z$) ratios in the first mass spectrometer. In modern mass spectrometers separation according to $m/z$ can be achieved in milliseconds, whereas a chromatographic separation cannot usually be achieved in under one minute. Furthermore derivatization is not necessary since the sample can be introduced directly into the mass spectrometer via the direct insertion probe.

MS–MS experiments therefore have the potential to speciate the components of a mixture of organotin compounds without prior derivatization or the need for gas-chromatographic analysis.

## 3. EXPERIMENTAL

### 3.1 Determination of standard mass spectra and parent/daughter relationships

Authentic samples of a range of organotin compounds, as specified in Table 1, were obtained in order to calibrate the MS–MS instrument. The samples were loaded into the capillary probe tip, introduced into the mass spectrometer and then heated from ambient temperature to 400 °C at 230 °C min$^{-1}$. During this evolution of the sample, mass spectra were obtained under the operational parameters detailed below.

#### 3.1.1 Standard EI mass spectra

Instrument VG TRIO 3, Q1 only

| | | |
|---|---|---|
| Q1: | Scanning | $m/z$ 35–500 in 1 s |
| | Resolution | >1000 |

#### 3.1.2 Parent–daughter relationships

Instrument VG TRIO 3, Q1, Q2 and Q3

Q1: Set at $m/z$ values preselected from results of section 3.1.1

| | | |
|---|---|---|
| Q2: | Collision gas | Argon at 2–3 mT |
| | Ion collision energy | 6.0 eV |
| Q3: | Scanning | $m/z$ 35–500 in I S |
| | Resolution | >1000 |

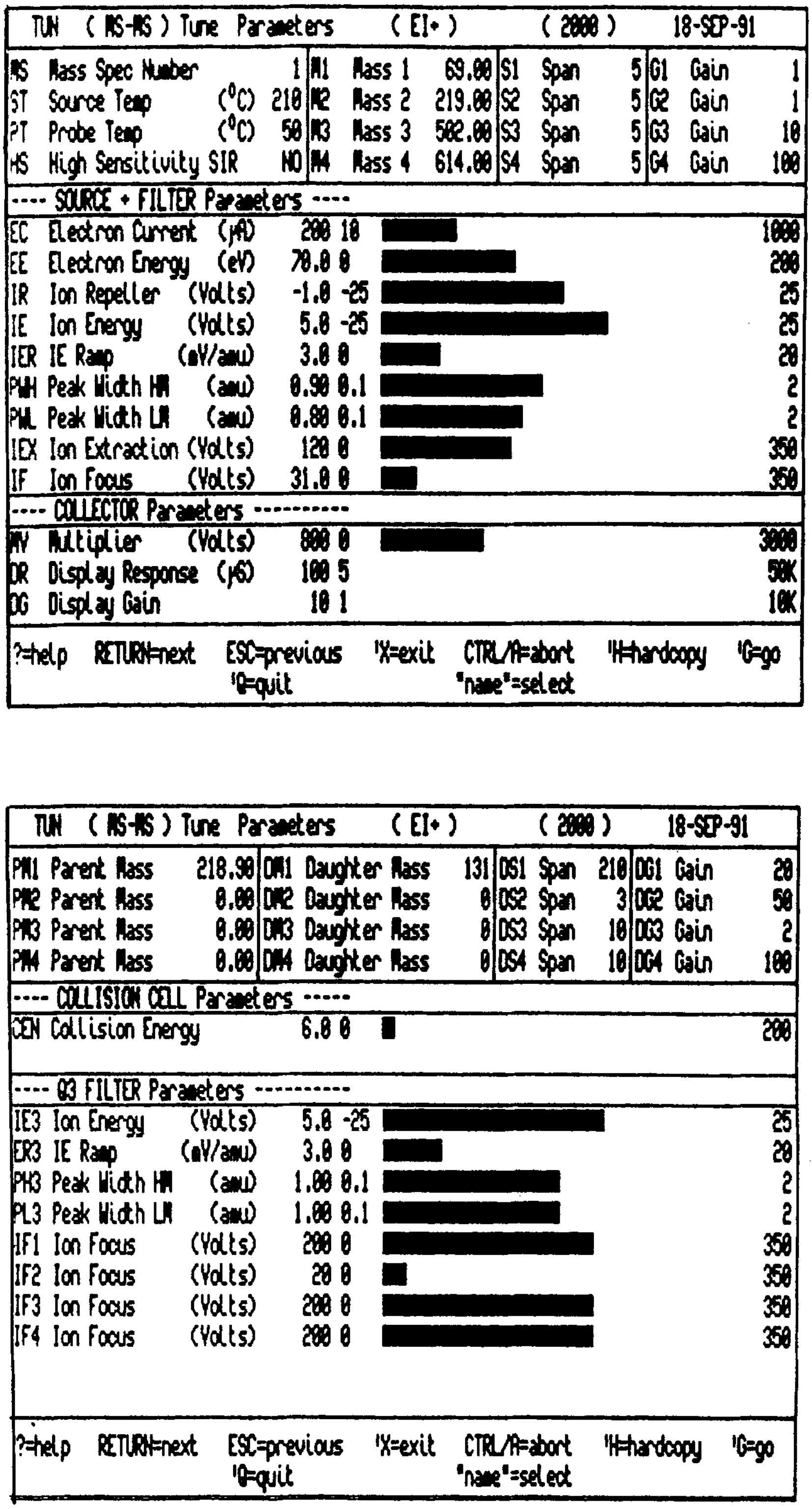
### 3.2 Analysis of a test mixture

The MS–MS approach to the separation and speciation of the complex components of a mixture of organotin compounds was tested by subjecting known examples to the procedure. Samples of the mixture were introduced into the mass spectrometer using the direct insertion probe. The operating parameters of Q1, the collision cell and the final mass spectrometer were controlled by the TRIO 3 software and are detailed in Fig. 5.

## 4. RESULTS

The conventional electron impact (EI) mass spectra of the organotin compounds are shown in Fig. 6. The alkyl-substituted compounds clearly show the sequential loss of alkyl groups from both the methyl and butyl derivatives. The tetrabutyltin compound shows fragment peaks at $m/z$ 291, 235 and 179 corresponding to the loss of a butyl group followed by the loss of two $C_4H_8$ groups. Similar peaks, i.e. at $m/z$ 291, 235 and 179, are seen in the mass spectrum of bis(tributyl tin) oxide. There is little structural information available from the fragmentation patterns of butyltin trichloride and phenyltin trichloride. Indeed, in this latter compound the major peak in the mass spectrum, at $m/z$ 112, appears to result from a rearrangement reaction leading to the formation of $C_6H_5Cl^+$.

The fragmentation patterns are further complicated by the large number of isotopic variations potentially available from a species containing one tin atom and three halogens. This complexity of molecular ions reduces the relative intensity of the ions with $m/z$ values (i.e. little fragmentation)



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 TUN  ( MS-MS ) Tune  Parameters     ( EI+ )        ( 2000 )      18-SEP-91
MS  Mass Spec Number          1 M1  Mass 1   69.00 S1  Span    5 G1  Gain    1
ST  Source Temp       (°C)  210 M2  Mass 2  219.00 S2  Span    5 G2  Gain    1
PT  Probe Temp        (°C)   50 M3  Mass 3  502.00 S3  Span    5 G3  Gain   10
HS  High Sensitivity SIR     NO M4  Mass 4  614.00 S4  Span    5 G4  Gain  100
---- SOURCE + FILTER Parameters ----
EC  Electron Current  (µA)    200 10                               1000
EE  Electron Energy   (eV)   70.0 0                                 200
IR  Ion Repeller   (Volts)   -1.0 -25                                25
IE  Ion Energy     (Volts)    5.0 -25                                25
IER IE Ramp       (mV/amu)    3.0 0                                  20
PWH Peak Width HM    (amu)   0.90 0.1                                 2
PWL Peak Width LM    (amu)   0.80 0.1                                 2
IEX Ion Extraction (Volts)    120 0                                 350
IF  Ion Focus      (Volts)   31.0 0                                 350
---- COLLECTOR Parameters ----------
MV  Multiplier     (Volts)    800 0                                3000
DR  Display Response  (µS)    100 5                                 50K
DG  Display Gain               10 1                                 10K
?=help  RETURN=next  ESC=previous  'X=exit  CTRL/A=abort  'H=hardcopy  'G=go
                     'Q=quit                *name*=select
```

```
 TUN  ( MS-MS ) Tune  Parameters     ( EI+ )        ( 2000 )      18-SEP-91
PM1 Parent Mass   218.90 DM1 Daughter Mass  131 DS1 Span  210 DG1 Gain   20
PM2 Parent Mass     0.00 DM2 Daughter Mass    0 DS2 Span    3 DG2 Gain   50
PM3 Parent Mass     0.00 DM3 Daughter Mass    0 DS3 Span   10 DG3 Gain    2
PM4 Parent Mass     0.00 DM4 Daughter Mass    0 DS4 Span   10 DG4 Gain  100
---- COLLISION CELL Parameters -----
CEN Collision Energy          6.0 0                                 200

---- Q3 FILTER Parameters ----------
IE3 Ion Energy     (Volts)    5.0 -25                                25
ER3 IE Ramp       (mV/amu)    3.0 0                                  20
PH3 Peak Width HM    (amu)   1.00 0.1                                 2
PL3 Peak Width LM    (amu)   1.00 0.1                                 2
IF1 Ion Focus      (Volts)    200 0                                 350
IF2 Ion Focus      (Volts)     20 0                                 350
IF3 Ion Focus      (Volts)    200 0                                 350
IF4 Ion Focus      (Volts)    200 0                                 350

?=help  RETURN=next  ESC=previous  'X=exit  CTRL/A=abort  'H=hardcopy  'G=go
                     'Q=quit                *name*=select
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**Figure 5** Software control parameters for the tandem analyses.

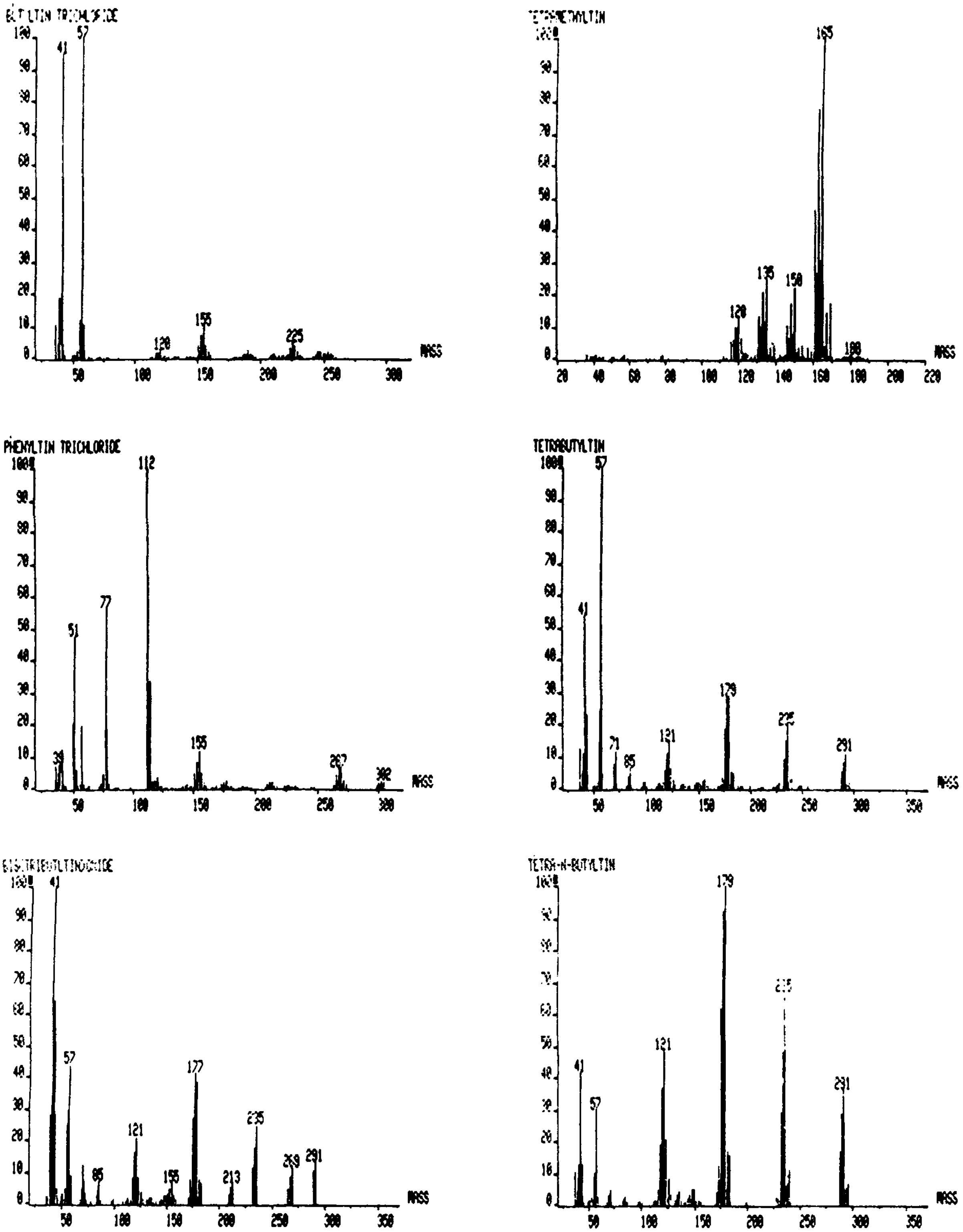

**Figure 6** Conventional electron impact (70 eV) mass spectra of the selected organotin compounds.

which exhibit the greatest potential to provide structural information when undergoing CID reactions.

Furthermore, it can be seen from these data that the conventional EI mass spectra would provide little help in identifying the individual components of a mixture of either other organotin compounds or other contaminants present in an environmental sample. There are however several significant features of the results which merit discussion elsewhere, particularly the reactions leading to the fragmentation pattern exhibited by phenyltin trichloride.

### 4.1 Parent-daughter ion investigations

Due to the complexity of the isotope patterns associated with these molecules, the most abundant ions with the least fragmentation from the parent molecule were selected for CID studies. The abundance of the daughter ions was expressed in a conventional relative measure based on the most abundant ion monitored by Q3. In all other respects a daughter ion spectrum (Fig. 7) looks like an exceptionally clean mass spectrum.

The results obtained from the authentic com-

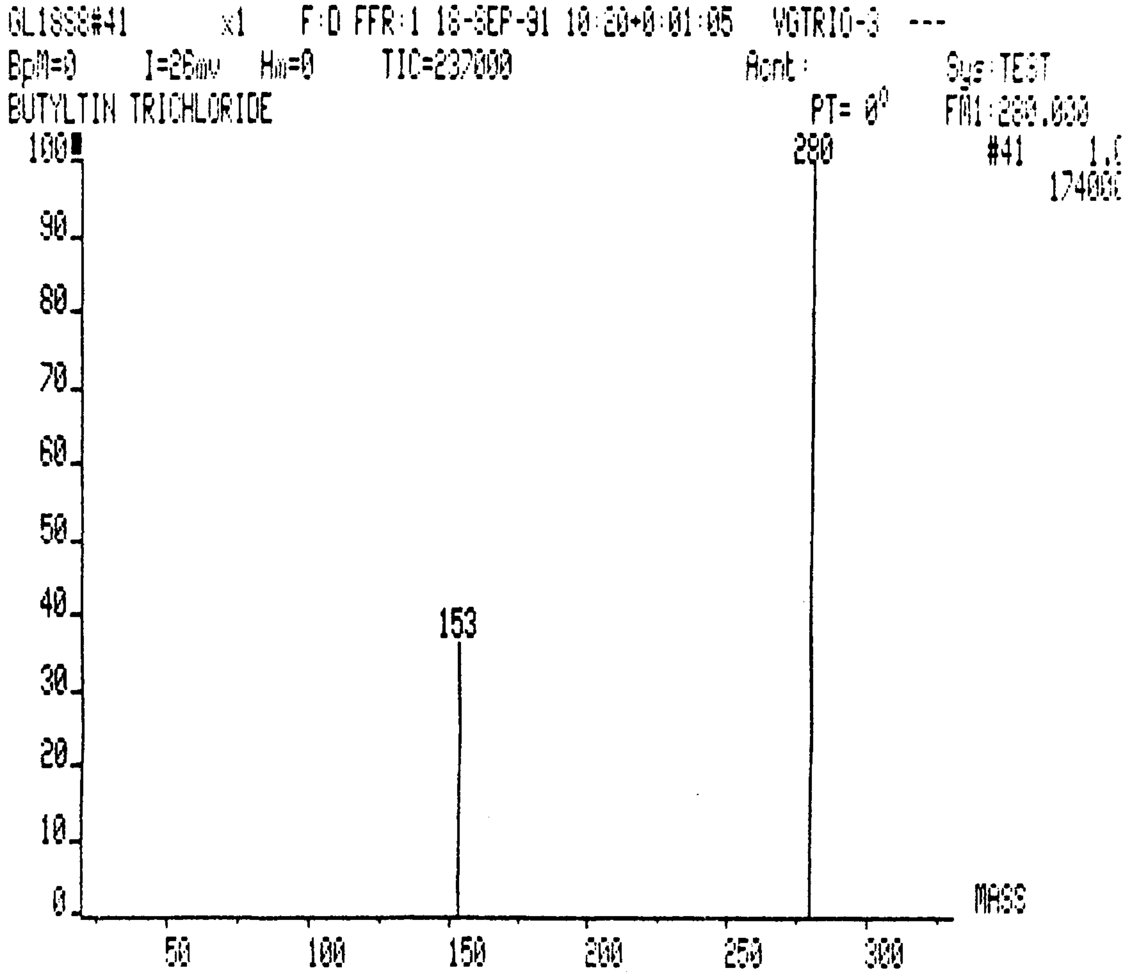

**Figure 7** Typical daughter ion mass spectrum. The chosen example shows the daughter ions from *m/z* 280 from butyltin trichloride, after collision with argon gas.

**Table 2** Parent–daughter ion relationships for selected organo tin compounds

| Compound | Parent ion | Daughter ions (relative abundance) |
|---|---|---|
| Tetramethyltin | 180 | 180 (12%), 165 (100%) |
| | 178 | 178 (35%), 163 (100%), 148 (17%) |
| | 165 | 165 (100%), 150 (50%), 135 (30%) |
| Tetra(n-butyl)tin | 291 | 291 (50%), 235 (100%), 179 (75%) |
| Tetrabutyltin | 291 | 291 (60%), 235 (100%), 179 (85%) |
| Butyltin trichloride | 284 | 284 (100%), 57 (50%) |
| | 282 | 282 (100%), 155 (55%) |
| | 280 | 280 (100%), 153 (40%) |
| | 225 | 225 (100%), 190 (5%), 155 (5%) |
| Phenyltin trichloride | 304 | 304 (65%), 114 (52%), 112 (100%) |
| | 302 | 302 (70%), 114 (22%), 112 (100%) |
| | 300 | 300 (70%), 114 (18%), 112 (100%) |
| | 269 | 209 (100%), 215 (5%), 157 (10%), 77 (10%) |
| Bis(tributyl tin) oxide | 291 | 291 (100%), 235 (85%) |

pounds are recorded in Table 2 and show that in all cases the CID process was incomplete with significant levels of the parent ion being detected by Q3. Some apparently anomalous CID reactions were observed, for example in butyltin trichloride *m/z* 284→57 reprsents

$$C_4H_9Sn^+Cl_3 \rightarrow C_4H_9^+ \qquad [2]$$

whereas *m/z* 282→155 is presumably attibutable to

$$C_4H_9Sn^+Cl_3 \rightarrow Sn^+Cl \qquad [3]$$

The possible isotopic variations for the parent ion in [2] are $C_4H_9{}^{120}Sn^{35}Cl_2{}^{37}Cl$ and $C_4H_9{}^{118}Sn^{37}Cl_2{}^{35}Cl$; and for [3] similar considerations produce the possibilities of $C_4H_9{}^{120}Sn^{35}Cl_3$ or $C_4H_9{}^{118}Sn^{35}Cl_2{}^{37}Cl$. Within the limits of the experimental system it is not possible to differentiate readily between these alternatives but the lack of a peak at *m/z* 153 would mitigate against the second alternative suggested for Eqn [3]. Further study of this reaction type shows that a parent ion of mass 280 dissociates to 153 in accordance with Eqn [3]. Other exchange reactions involving polychlorinated species have been observed in this laboratory and have also been reported by Safe *et al.*[13]

Despite these anomalies there are sufficient characteristic data in Table 1 to facilitate the identification of the compounds of a mixture of any of these species.

In order to investigate a mixture of organotin compounds for the presence of species cited in Table 2, the presence of the specified parent ions must first be determined. The absence of (for example) *m/z* 180 indicates that tetramethyltin is not present in the sample at a detectable level. The parent ion 291 may indicate an organotin compound to be present, but only if the daughter ions 235 and 179 are observed at the appropriate abundances.

Table 3 details the results obtained from a CID investigation of a mixture of phenyltin trichloride and butyltin trichloride. Initially Q1 only was scanned to determine the *m/z* values of potential parent ions and these were then individually selected for the subsequent CID experiments. In this instance there was no significant signal for *m/z* 180 and 291, thus eliminating several of the possible components of the mixture. The results clearly show the presence of the characteristic daughter ions resulting from *m/z* 204, 302 and 300 from phenyltin trichloride, and more significantly the anomalous data from the butyltin trichloride are reproduced in this analysis. Not only are the correct daughter ions observed but the relative abundances are reproducible within the anticipated experimental error.

**Table 3** Parent–daughter ion analyses for a mixture

| | | |
|---|---|---|
| Mixture | 304 | 304 (55%), 114 (55%), 112 (100%) |
| | 302 | 302 (60%), 114 (25%), 112 (100%) |
| | 300 | 300 (50%), 114 (17%), 112 (100%) |
| | 284 | 284 (100%), 57 (60%) |
| | 282 | 282 (100%), 155 (55%) |
| | 280 | 280 (100%), 153 (28%) |

## 5 CONCLUSIONS

The results obtained demonstrate the potential of the approach for the speciation of organotin compounds in complex mixtures without prior derivatization and chromatographic separation. Work is already in hand to study more complex mixtures and also to determine the potential of the technique in quantitative experiments.

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