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Enhanced detection levels in the GC MS analysis of organometallic compounds, based on pre- and post-acquisition data manipulation

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The different modes of data acquisition utilized in GC MS analyses of organometallic compounds are discussed. Comparisons of detection limits for each operating mode are reported and a lower detection limit of *ca* 5 pg organotin compound injected onto the column was determined. Mass spectral data for a range of organotin compounds are presented to facilitate the choice of species suitable for single (selected) ion monitoring (SIM)

Keywords: Organotin compounds, GC MS, selected ion monitoring (SIM), detection limits

1 INTRODUCTION

Gas chromatography–mass spectrometry (GC MS) has been applied to the investigation of analysis of environmental organotin compounds principally as a consequence of the ability of this technique to provide unique identification of derivatized compounds from the samples under investigation.[1-4] This ability has been allied with lower detection levels resulting from combination of more sophisticated computer techniques with developments in modern mass spectrometry. Some of these advances include changes in the manner in which the mass spectrometer (MS) acquires and processes raw data and also developments in equipment hardware, for example tandem MS instrumentation.[5] In this investigation the different approaches which can be adopted in data acquisition are discussed and examples are given highlighting advantageous techniques.

2 THEORY

2.1 Conventional scanning data collection

The general operating principles of the gas chromatograph are well understood. For the purposes of this work, a GC run consists of a sample injection, passage of components of the sample through the column, their detection and venting, and a final time period when the GC oven parameters return to the initial conditions. If a mass spectrometer is used as the GC detector, then as soon as the sample has been injected, the MS scan function is initiated. This means that the MS scans repetitively over a selected mass range, typically once every second, and continues to do so for the entire period of the GC analysis.[6] Such analysis may be of up to 120 min duration. The relationship between the GC run and the MS scans is shown in Fig. 1 as a function of time after injection (running left to right). The mass spectra shown indicate the data recorded as a result of each individual MS scan. The diagram clearly shows that during the elution of a peak from the GC the mass spectrometer records several (typically more than ten) full mass range scans and the data are stored in the computer. In order to recreate an equivalent GC trace using the mass spectral data, the total height (ion current) of all the peaks (m/z values) in the individual mass spectra are summed and plotted against time (Fig. 1c). This plot is composed of discrete segments corresponding to each MS scan. Where no compounds are leaving the GC column and entering the MS ion source, the only mass spectra observed correspond to residual air in the vacuum system and are consequently at the low level shown in the initial scans on the left-hand side of Fig. 1. When a compound elutes from the column into the MS, the resultant mass spectra change, with increases in both the range and height of the m/z values observed. The sum of these increases produces a much larger change in the recorded output (Fig. 1c). This computer-generated trace is known variously as the TIC (Total Ion Chromatograph) or RIC (Reconstructed Ion Chromatograph) trace, depending on the instrument manufacturer. As can be seen from Fig. 1(c), all peaks in the TIC trace are produced by

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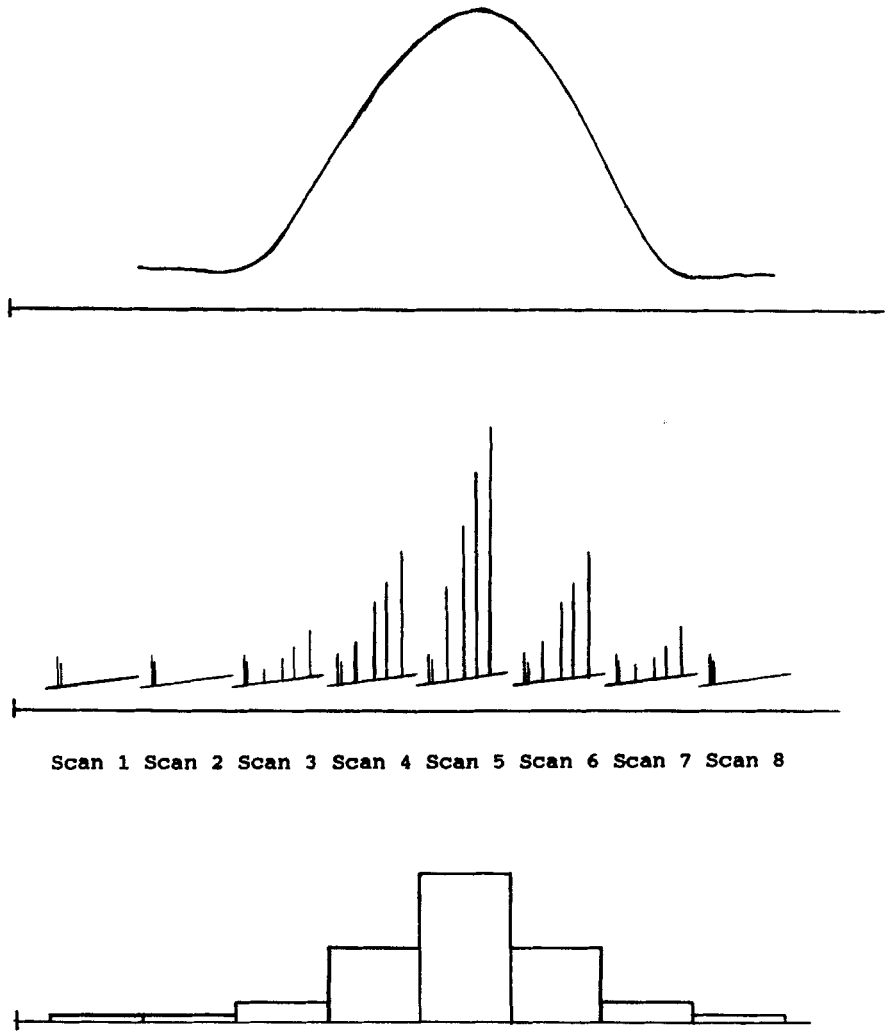

Figure 1 Generation of a reconstructed ion chromatogram from the mass spectral data generated by a GC MS instrument. (a) Trace indicating a compound eluting from the GC column and entering the ion source of the mass spectrometer. (b) Repetitive mass spectral scans showing the change in data as the compound enters the ion source. (c) Sum of all the ions per individual scan plotted in histogram form to re-create the original peak.

step functions, in most instruments however, the steps are much smaller than those shown here for illustrative purposes, and consequently they are usually non-discernible.

There are some advantages and several disadvantages associated with the respective scanning approaches for the collection of GC MS data. The single and most obvious advantage is the presentation of mass spectral data for each component eluting from the GC which allows independent compound identification/speciation and hence the determination of the appropriate retention parameters. The fact that many complete mass spectra are acquired and stored implies that much of the analyte that leaves the gas chromatograph is never actually 'seen' by the mass spectrometer and is essentially therefore wasted. This is a result of the mass spectrometer being required to detect for example, 200 masses (scanning over the range 40–240 amu) of which only five may be significant to the analysis of interest. On this basis, virtually all of the data recorded by the MS (97%) are redundant; as a consequence, the majority of the analyte ions are deliberately not detected, since the MS is tuned to other m/z values. This problem can be exacerbated if several contaminants

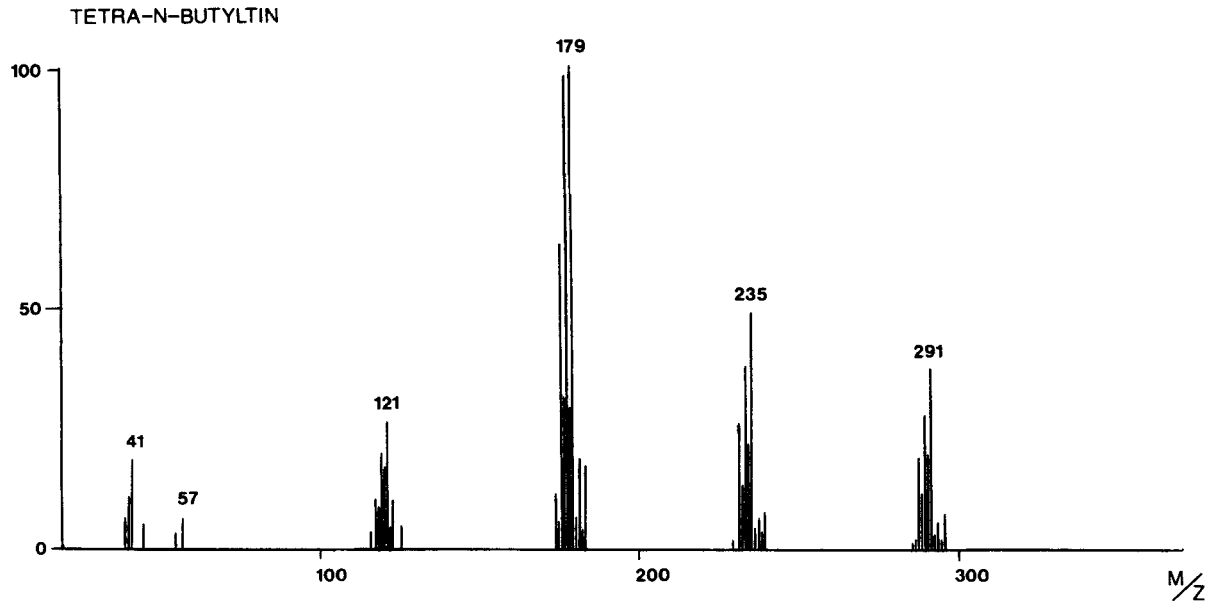

Figure 2 Mass spectrum of tetra-n-butyltin (TBT).

from an environmental sample co-elute with the organotin compound, causing the signal for the analyte to become lost in the noise produced by the other eluents.

Under these circumstances, both the production of mass spectral data and the identification of the analyte apparently lost in the noise are dealt with by post-acquisition data processing.

2.2 Post-acquisition data processing

The mass spectrum for an individual compound from a GC MS analysis is produced by retrieving the data acquired during the scan corresponding to the top of the individual GC (or RIC) peak (see Fig. 1), by specifiying the appropriate MS scan number. Any background *m/z* peaks can be removed by computer subtraction of the mass spectra recorded in scans on either side of the GC (or RIC) peak. Background subtraction is not always necessary, particularly for pure samples or where there is good chromatographic separation. This routine produces data similar to those shown for tetrabutyltin (Fig. 2) which can then be compared with mass spectral databases[7,8] and literature information.[9]

Post-acquisition data processing can be used to search all the accumulated data from a particular GC run for the occurrence of ions characteristic of the anticipated analyte. In this instance a pseudo chromatographic trace is produced which indicates the presence of these ions as a function of MS scan number. This plot is called a selected ion chromatograph and can be used to highlight species which may not have produced an identifiable GC peak on the TIC, or which may be hidden in a large group of co-eluting compounds, all of which contribute to the total ion chromatogram. This approach can only be adopted when standard mass spectral data for the compounds of interest are available, and providing also that the data to be searched are characteristic and unique to the analytes. On this basis, therefore, results derived from contaminated samples or poor chromatography can be retrospectively searched for the anticipated analytes.

2.3 Pre-acquisition data processing

The loss of signal resulting from the MS scanning and therefore not 'seeing' most of the analyte can be reduced or eliminated by reducing the number of *m/z* values observed. This approach is shown in Fig. 3, where the changes in instrumental scan mode are from all masses to just four selected masses;[10] perhaps finally just a single mass would be scanned. In this latter case the mass spectrometer becomes a single continuous detector monitoring a single *m/z* value, e.g. 165 or 120. In this format any compound eluting into the MS which produces ions of the selected mass will be detected with the maximum possible sensitivity,

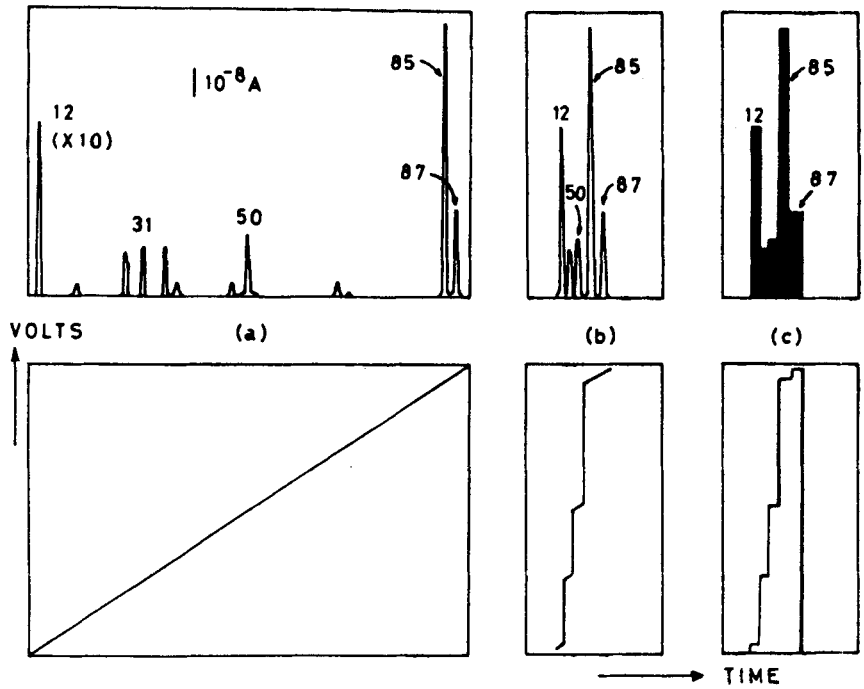

Figure 3 Mode of action of the programmable peak selector for a quadrupole mass filter. The upper traces show the possible types of ion current output and the lower traces depict the control voltage waveforms needed to generate the outputs. (a) Normal spectrum generated by a simple voltage ramp. (b) A series of short sections of the ramp have been compressed to produce a condensed mass spectrum containing selected peaks. (c) The short ramps have been replaced by horizontal steps to give the ion current output in histogram form.

since all the ions are intrinsically stable in the MS, i.e. none is rejected since there is no scanning to other m/z values. Operating in this mode the mass spectrometer can provide no speciation data unless it is an ultrahigh-resolution instrument where a precise mass measurement (correct to five decimal places) is sufficient to identify uniquely the species of concern. It can be readily appreciated, therefore, that single ion or selected ion monitoring (SIM) can produce a significant increase in sensitivity but that this is usually at the expense of specificity. This approach is directly analogous to the use of GC AA techniques, where the nature of the compound is inferred by the specificity of the detection in conjunction with the retention time under the given chromatographic conditions.

3 EXPERIMENTAL

In order to investigate the concepts discussed in Section 2, synthetic samples of organotin compounds in pure solvent were prepared over a known concentration range. Aliphatic hydrocarbons (gas oil and diesel) were introduced as the sample contaminants to mimic oil spillage in a marine environment. The purity of the organotin compounds investigated was better than 98% and these compounds were used as supplied by the manufacturers.

Table 1 Analytical conditions and instrumental parameters

Gas chromatograph	HP5890
Column	25 m silicone SE 54 equivalent capillary column
Oven programme	70–270 °C at 20 °C min^{-1}, then hold for 10 min
Carrier flow	Helium at 1 cm^3 min^{-1}
Split ratio	30:1
Mass spectrometer	VG TRIO 3
Full scan mode	
Scan range	35–500 amn
Scan time	0.002 s per mass
Selected ion monitoring	
Calibration sample	Heptacosaperfluorotributylamine
Selected ions (m/z)	179, 235, 291
Scan time	0.1 s per mass

Since the main purpose of this work was to confirm the effects of different data processing methods, the analytical conditions and instrumental parameters, once chosen, were maintained constant. These parameters were as shown in Table 1.

4 EXAMPLES OF DATA MANIPULATION

4.1 Post-acquisition

Examples of post-acquisition data manipulation are shown in Fig. 4, where the two left-hand TIC traces were obtained from dilute solutions of tetra-n-butyltin (TBT) in methylene chloride (CH_2Cl_2). As can be seen, only a small peak is visible on the upper trace (retention approx. 600 scans) and no signal can be detected from the more dilute solution in the lower trace. The corresponding reprocessed traces (*m/z* 179) on the right-hand side of Fig. 4 both clearly show a peak present at approx. 600 scans indicating the probable presence of TBT. Furthermore, from the size of the peak in the lower trace, it is quite evident that the concentration of TBT in the solution can be further reduced, provided that this form of data manipulation is used. Similar information showing exactly the same increase in sensitivity has been obtained for TBT and tetraethyltin (TET).

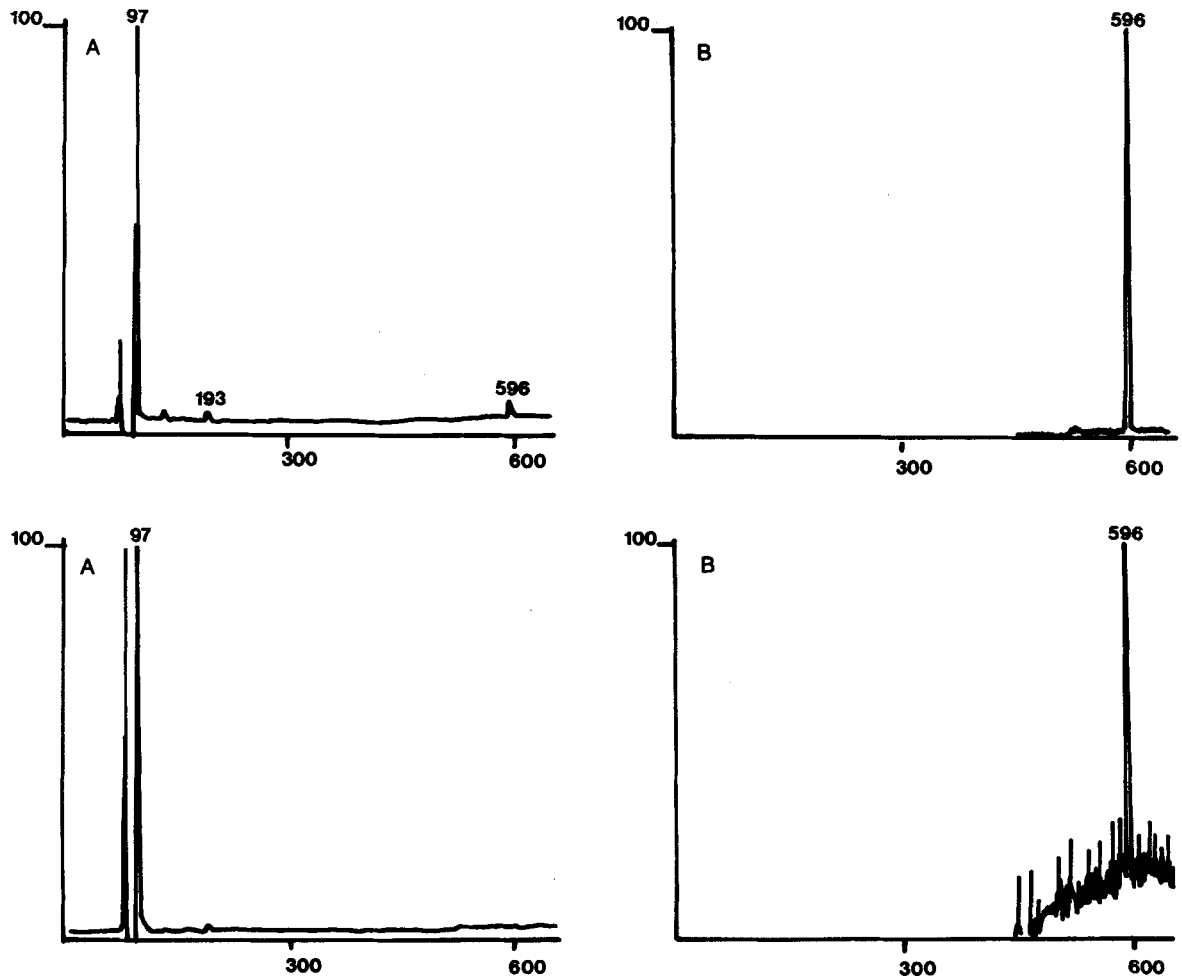

Figure 4 Detection level determination for TBT in solution in CH_2Cl_2: comparison of the results obtained from the full scan mode (left-hand side) and the post-acquisition mode (right-hand side). This latter technique clearly shows a better detection capability.

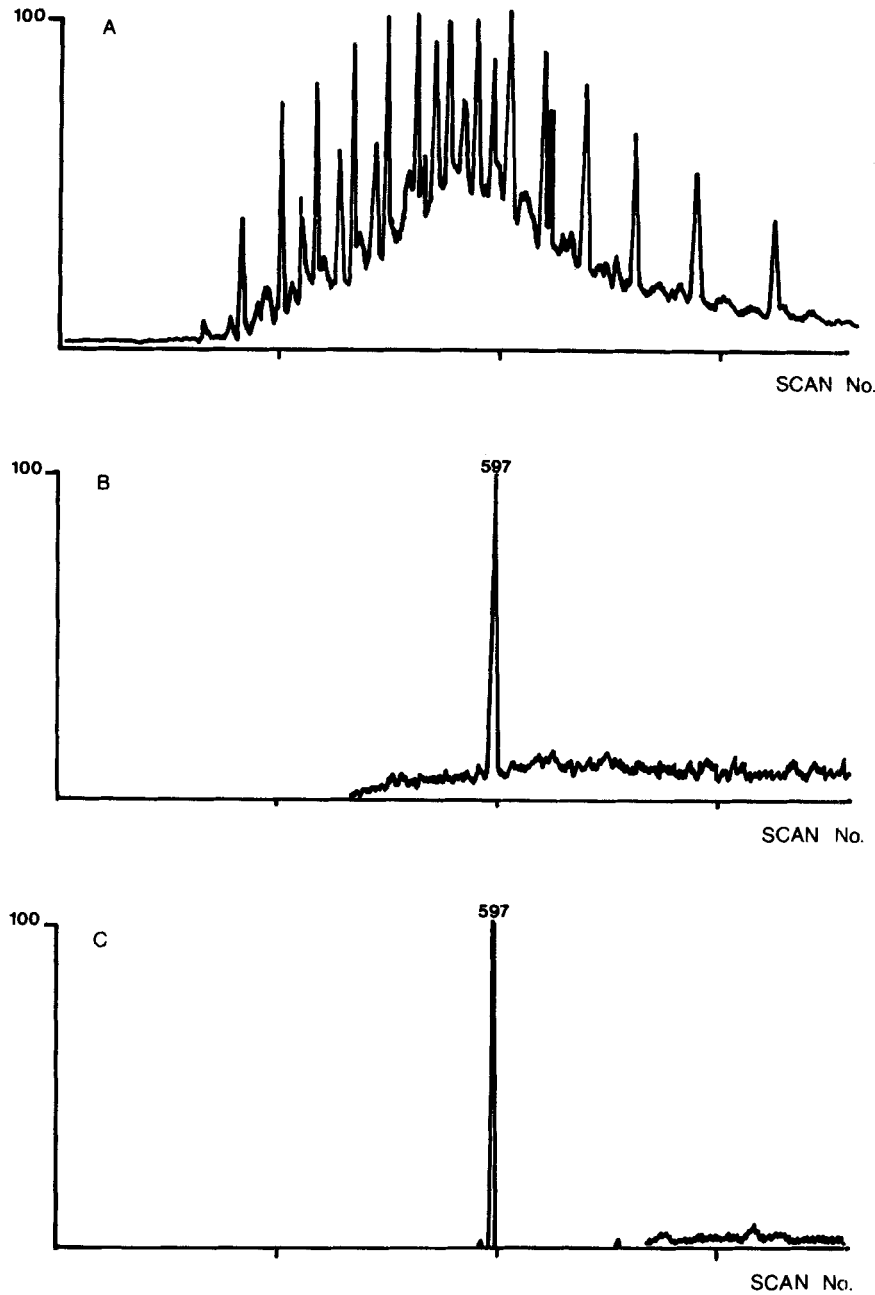

Figure 5 Post-acquisition data reprocessing to show the presence of TBT in a sample contaminated with gas oil. (a) Raw data. (b) Selected ion chromatography for *m/z* 235. (c) Similar, to (b) but with *m/z* 291.

The instrumental clean-up of a heavily contaminated sample, in this case TBT in gas oil, can be appreciated from the data in Fig. 5. The conventional total ion chromatograph (Fig. 5a) shows so many peaks that the presence of TBT cannot be confirmed. Reprocessing the data to produce the *m/z* 179 chromatograph (Fig. 5b) reduces the number of possible peaks; several remain in the trace, however, and these data can be further refined by the additional use of *m/z* 291 (Fig. 5c). The selected ions at *m/z* 179, 235 and 291 are characteristic of TBT which, from calibration determinations, has a retention time of approximately 600 scans. The results from the test

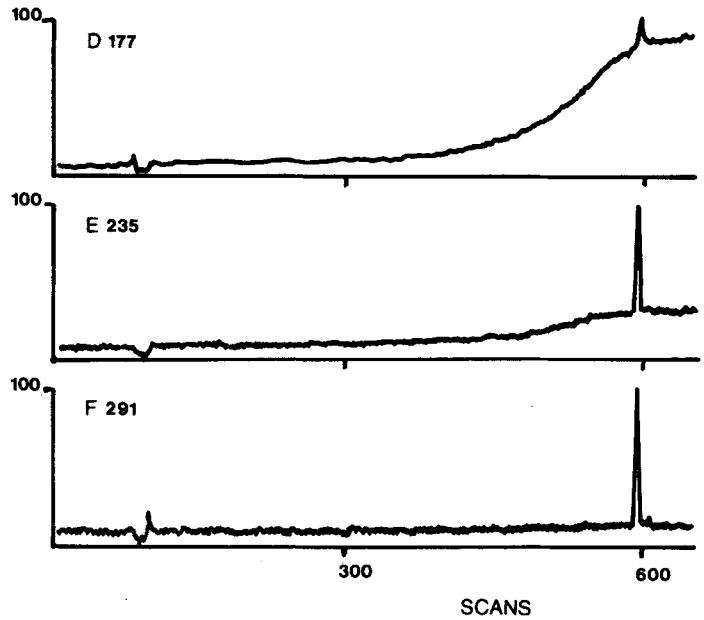

Figure 6 Results obtained from specific ion monitoring experiments for TBT at 0.1 mg kg^{-1} in CH_2Cl_2 solution. Increased selectivity is demonstrated when moving from *m/z* 177→235→291.

sample (Fig. 5b) shows the occurrence of a selected ion chromatography peak for each characteristic ion. These peaks all occurred around 597 scans, the expected retention time, and therefore this combination of data is indicative of the presence of TBT in the contaminated sample.

4.2 Pre-acquisition

This technique is the inverse of the production of a selected ion chromatograph. In this instance only ions of a limited number of masses are transmitted and recorded by the mass spectrometer. These *m/z* values should be characteristic of the analyte and can be of any magnitude within the capabilities of the instrument and the limitations of any background problems (i.e. the chosen peaks must be analyte-selective). In practical applications, the choice of at least three ions for selected monitoring is optimal but more can be chosen if necessary. The analysis of dilute solutions of TBT could therefore be carried out using any of the major ions from Fig. 2, for example *m/z* 291, 235, etc. The SIR data (Fig. 6) obtained from a TBT solution two orders of magnitude more dilute than previously studied clearly show that the characteristic ions (of TBT) can be readily detected. This demonstrates an increase in instrumental sensitivity with no other change in operational conditions. Similar experiments were carried out using TET and tetrapropyltin (TPT) as the test materials and monitoring in the SIR mode using the ions specified in Table 2. These ions were chosen to provide a reasonable sensitivity towards the compounds, coupled with a high degree of selectivity. The ions and the appropriate relative abundances (%) as cited in Table 2 were obtained from conventional electron impact mass spectra of the test materials.

The detection limits are assessed on the basis of the quantity of analyte injection onto the column. This quantity was determined from the concentration of the calibration solutions initially prepared. Calibration solutions were prepared over the concentration range 0.01–10 mg kg^{-1}; within this range the mass spectrometer output was linear over approximately three orders of magnitude,

Table 2 *m/z* values suitable for SIR determinations of TBT, TET and TPT

Sample	*m/z*[a]				
$(C_4H_9)_4Sn$ (TBT)	291 (40)	235 (52)	234 (38)	179 (100)	178 (98)
$(C_3H_7)_4Sn$ (TPT)	249 (78)	248 (60)	207 (100)	206 (72)	165 (90)
$(C_2H_5)_4Sn$ (TET)	178 (64)	179 (84)	206 (68)	207 (88)	149 (100)

[a] Values in parentheses are relative abundances (%).

Table 3 Detection levels for different operating conditions determined using TBT, TET and TPT

Tin compound injected (ng)	Signal detection mode		
	Full scan	Reprocessed	SIR
100	√[a]	√	√
10	×[a]	√	√
1.0	×	×	√
0.1	×	×	√
0.01	×	×	×
LOD (ng)	8–12	1.0–3.0	0.03–0.04

[a] Symbols: √, detected. ×, not detected.

depending on the chosen operating parameters (multiplier gain, etc.). The absolute detection values cited here will change with different conditions of GC split, etc., but it is the *relative differences* in detection limits, for the given instrumental parameters, which are important.

For the materials studied in this work (TBT, TET and TPT) the changes in detection limits are detailed in Table 3, which also includes an estimate of the absolute limit of detection (LOD) based on a signal 2× the noise level. This Table shows that there is no detectable variation in the response to these different compounds within the limits of experimental error. Thus uniformity of response is as predicted. Cullen *et al.*[1] have carried out determinations of a range of organotin compounds using SIR techniques for the quantification stage, and they specify a detection limit of less than 10 pg for splitless injection. This compares with an equivalent level of *ca* 1 pg for this work if similar splitless conditions were used.

In order to use this technique more widely, suitable mass spectral data, giving examples of characteristic *m/z* values, must be available. A range of suitable data for organotin compounds, collected from our own work and other literature sources, has been compiled in Table 4. Whilst this compilation is not meant to be proscriptive, nevertheless the data may be used as a guide to suitable values for use in selected ion recording.

Table 4 Ions suitable for SIR (SIM) investigations of selected organotin compounds

Organotin compound	*m/z*
$c(C_6H_{11})_3SnC_2H_5$	233, 232, 151, 315
$C(C_6H_{11})_2Sn(C_2H_5)_2$	179, 233, 261, 263
$(C_4H_9)_3SnC_2H_5$	207, 206, 177, 277
$C_6H_5Sn(C_2H_5)_3$	255, 197, 254, 302
$(C_6H_5)_2Sn(C_2H_5)_2$	303, 275, 197
$(C_6H_5)_3SnC_2H_5$	302, 303, 351
$(C_4H_9)_3SnCl$	349, 327, 291, 269
$(C_4H_9)_2SnCl_2$	351, 327, 293, 268
$C_4H_9SnCl_3$	363, 327, 305, 309
$(C_6H_5)_2SnCl_2$	391, 367, 333
$C_4H_9Sn(CH_3)_3$	165, 163, 161
$(C_4H_9)_2Sn(CH_3)_2$	207, 205, 203
$(C_3H_7)_4Sn$	249, 247, 245
$(C_4H_9)_3SnCH_3$	193, 191, 189
$c(C_6H_{11})_2Sn(CH_3)_2$	233, 231, 229
$c(C_6H_{11})_3SnCH_3$	219, 217, 215

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