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Journal of Chromatography A, 794 (1998) 211–218

JOURNAL OF CHROMATOGRAPHY A

Speciation of organo-tin compounds using liquid chromatography–atmospheric pressure ionisation mass spectrometry and liquid chromatography–inductively coupled plasma mass spectrometry as complementary techniques

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Abstract

A liquid chromatographic method for the determination of dibutyltin (DBT), tributyltin (TBT), diphenyltin (DPhT) and triphenyltin (TPhT) in sediments has been developed, which is compatible with both atmospheric pressure ionisation (API) mass spectrometry and inductively coupled plasma (ICP) mass spectrometry. As a result of this development both techniques may be used for the complementary speciation of organo-tin compounds. The chromatographic system comprises of a Kromasil-100 5 μm C_{18} (150×2.1 mm) column and a mobile phase of 0.05% triethylamine in acetonitrile–acetic acid–water (65:10:25), at a flow-rate of 0.2 ml min^{-1}. The optimisation of the LC–API-MS conditions is discussed, together with the analysis of a real sediment sample for DBT and TBT using selected ion monitoring (SIM).

Keywords: Organo-tin compounds; Dibutyltin; Tributyltin; Diphenyltin; Triphenyltin

1. Introduction

It is now accepted [1] that the toxicity and environmental impact of an element, such as tin, is dependent on its chemical form. Liquid chromatography–inductively coupled plasma mass spectrometry (LC–ICP-MS) has become a popular technique for organo-metallic speciation analysis due to its inherent selectivity and sensitivity [2,3]. As regulatory processes increase the pressure for the routine analysis for these compounds, method validation is becoming more important, especially for laboratory accreditation purposes. At the present time only the most elementary validation methods are commonly utilised for LC–ICP-MS methods, i.e., identification based on retention times of appropriate standard solutions. Unfortunately, this approach is highly dependent on the quality of the separation and the availability of standards of high purity [2]. In conjunction with this is the fact that although atomic detection devices such as ICP-MS are highly selective and sensitive and therefore able to analyse many environmental matrices at very low levels, their main drawback is that they are destructive in nature and much of the real information about organo-metallic compounds that the modern speciation analyst requires, i.e., molecular information, is lost.

One solution to both of these problems would be the development of chromatographic separation methodologies fully compatible with both ICP-MS and atmospheric pressure ionisation-mass spectrometry (API-MS) detection systems. While ICP-

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0021-9673/98/$19.00
PII S0021-9673(97)00805-4

MS has the advantage of superior sensitivity, API-MS has the capability to provide molecular ion confirmation of the organo-metallic species present. The use of LC–API-MS using ionspray/electrospray ionisation [4–7] and atmospheric pressure chemical ionisation (APCI) [4] sources, following direct loop injections, has been described for the characterisation of organo-tin species. Similarly ionspray/electrospray has been used for organo-arsenic [8] and organo-chromium [9] speciation. However, the use of direct loop injection of the organo-metallic species into the ionisation source would have serious limitations when used for the analysis of real sample extracts. In order to obtain useful information for organo-metallic speciation in real samples, using LC–API-MS, a chromatographic separation of the compounds of interest is required.

The use of a thermospray ionisation source for LC–MS speciation of organo-tin compounds has also been described [10].

The aim of this work was to develop an LC method capable of separating dibutyltin (DBT), tributyltin (TBT), diphenyltin (DPhT) and triphenyltin (TPhT), compatible with both API-MS and ICP-MS. The use of API-MS was investigated as a means to obtain intact molecular information of organo-tin compounds. A key aspect to the development required the discovery of an eluent system with low dissolved solids and high volatility, for compatibility with both mass spectrometer interfaces. The use of high-performance liquid chromatography (HPLC) for the separation of organo-tin compounds has recently been reviewed [11]. Of the systems incorporating LC–ICP-MS, a number of chromatographic mechanisms have been employed. The use of ion-exchange [12–16], ion pair [13,17–21] and micellar [22,23] LC systems tend to involve the use of non-volatile additives in the mobile phase, which is incompatible with API-MS instrumentation. The use of tropolone in the mobile phase [24,25] has been found problematic for use with LC–ICP-MS in this laboratory, as a highly pacified (i.e., tin free) LC system is essential.

By ensuring that the LC conditions are compatible with both the API-MS and ICP-MS instruments, the two techniques could be used to give complementary information about the organo-tin species present in environmental samples. This is the basis for providing a robust method for organo-tin speciation analysis, which would underpin sound validation.

2. Experimental

2.1. Reagents

Methanol and acetonitrile (HPLC grade) were obtained from Fisher Scientific (Loughborough, UK). Triethylamine (HPLC grade) and glacial acetic acid (analytical-reagent grade) were obtained from Merck (Lutterworth, UK).

Dibutyltin dichloride, tributyltin chloride, diphenyltin dichloride and triphenyltin chloride, were obtained from Aldrich (Gillingham, UK). Stock solutions (1000 mg l^{-1}) were prepared by dissolving 0.1 g in 100 ml methanol. Working standards (both individual and composite) were prepared by dilution of the stock solutions using deionised water (>18 MΩ conductivity) as required. All standards were stored in the dark at 4°C when not in use.

2.2. LC–API-MS instrumentation

A Waters (Watford, UK) LC system comprising a 600S system controller, 616 gradient pump and 717plus autosampler was connected to an SSQ7000 mass spectrometer (Finnigan MAT, Hemel Hempstead, UK) using an API source, fitted with either of two probes; electrospray ionisation (ESI) or APCI.

The mode of ionisation (positive or negative), the fragmentation voltage (octapole offset), the capillary temperature and the vaporiser temperature (for APCI only) were optimised for the organo-tin compounds under investigation—see Section 3. A summary of the optimised conditions is given in Table 1.

When using ESI, the spray voltage was fixed at 4.5 kV, while for APCI the spray current was set at 5 μA. The multiplier voltage remained at 1300 V for both ESI and APCI.

In scanning mode, a typical mass range of 150 to 450 Daltons was used with a scan time of 0.5 s. In selected ion monitoring (SIM) mode, mass windows of 0.4 u and a cycle time of 0.5 s were used. A summary of the SIM masses used is given in Table 2 and the reasons for their selection is given in Section 3.4.

Table 1
Optimised LC–API-MS conditions

Column	Kromasil 100-5C18 (150×2.1 mm)
Mobile phase	MeCN–HOAc–water–TEA (65:10:25:0.05)
Flow-rate	0.2 ml min^{-1}
Injection volume	50 μl
Ionisation mode	APCI (+ve)
Vaporiser temperature	450°C
Capillary temperature	150°C
Corona current	5 μA
Octapole offset	5 V
Multiplier voltage	1300 V
SIM parameters	simwidth = 0.4 u, scan time = 0.5 s

2.3. LC–ICP-MS instrumentation

The LC–ICP-MS system consisted of a Perkin-Elmer (Beaconsfield, UK) series 410 gradient HPLC pump, Rheodyne injection valve, an Elan 5000A ICP-MS (Perkin-Elmer, Beaconsfield, UK). The LC column was connected directly to the nebulizer of the ICP-MS using a 5 cm length of 0.25 mm I.D. polyether ether ketone (PEEK) tubing.

The normal Ryton corrosion resistant spray chamber was replaced by a double skinned, silvered glass spray chamber cooled by a RTE-110 chiller unit (Neslab Instruments, Nottingham, UK) with a mixture of ethyleneglycol–water (50:50, v/v), in order to reduce organic solvent loading. Typical ICP-MS operating conditions are given in Table 3. Before coupling the ICP-MS to the HPLC system the ICP-MS was optimised for maximum signal for ^{120}Sn isotope by the aspiration of a 10 μg l^{-1} Sn solution in a methanol–water (80:20) mixture.

All chromatographic data were exported in computer format and data manipulation was performed off-line in Excel (Microsoft, UK).

Table 2
Ions monitored in SIM mode

Time window (min)	Analyte	Ions monitored (*m*/*z*)	Nature of ions
0 to 4	DPhT	329, 331, 333	$[M+OAc]^+$
4 to 8	DBT	289, 291, 293	$[M+OAc]^+$
	TPhT	347, 349, 351	$[M]^+$
8 to 15	TBT	287, 289, 291	$[M]^+$

Table 3
ICP-MS operating conditions

ICP	
Power	1125–1250 W
Plasma gas	15.0 l min^{-1}
Auxiliary gas	0.8 l min^{-1}
Nebuliser gas	0.90–0.95 l min^{-1}
Oxygen	20–25 ml min^{-1}
Cones	Pt
Lenses	
P	44 (switch settings)
B	48
S2	45
E1	25
Chiller Unit	−10°C to −15°C
Data acquisition	
Mass	120
Dwell time	1000 ms
Sweep/reading	1
Readings/replicates	1
Number of replicates	300
Points across peak	1
Resolution	Normal

2.4. Chromatographic parameters

As discussed previously [21] a stationary phase of Kromasil 100 C_{18} has been found suitable for the separation of TBT and TPhT followed by ICP-MS detection. For this study a 150×2.1 mm column packed with Kromasil 100-5C18 was used (Hichrom, Reading, UK). Choice of mobile phase is discussed in Section 3.2. A flow-rate of 0.2 ml min^{-1} was used with an injection volume of 50 μl. The optimised conditions are summarised in Table 1.

2.5. Sample preparation and pre-concentration

For the sediment sample analysed in this study, 0.5–1.0 g of sample was extracted by adding 10 ml of a glacial acetic acid–methanol (2:8) solution and mechanically shaking for 12 h. The resultant supernatant was filtered and injected onto the LC–ICP-MS. For LC–API-MS analysis the extract was preconcentrated by reducing 4 ml to dryness at 40°C under a stream of nitrogen, then dissolving the residue in 200 μl of deionised water. This extraction procedure has not been optimised or validated to date—it was simply used as a means to qualitatively extract organo-tins from the sediment for LC–API-

MS and LC–ICP-MS analysis, in order to demonstrate the use of these techniques for organo-tin speciation.

3. Results and discussion

The optimisation of the LC–API-MS conditions was a complex process, with many of the factors studied being inter-dependent. Rather than discussing at length each experiment and its outcome, a summary of the findings is presented here. Note that for molecular, fragment and adduct ions, [M] refers to the organo-tin species without the associated chlorine atom(s).

3.1. Choice of ionisation mode

Loop injections (i.e., no LC column) of individual standard solutions of DBT, TBT, DPhT and TPhT were introduced onto the mass spectrometer, using both ESI and APCI probes in both positive and negative ionisation modes. From the spectra obtained for each compound under each ionisation mode, it was decided to proceed with positive ion APCI as the spectra observed in this mode were the most satisfactory, exhibiting intense $[M]^+$ and/or $[M+OAc]^+$ ions, with the characteristic tin isotope pattern clearly visible. It was noted that for TBT, the presence of an $[M-C_4H_9+OAc]^+$ ion cluster ($m/z=293$) overlapping with the $[M]^+$ ion cluster ($m/z=291$), observed using ESI [6], was minimal using positive-ion APCI.

3.2. Optimisation of chromatographic conditions

Previous work with LC–ICP-MS, using Kromasil 100-5C18 packing material [21], employed a mobile phase of 10 mg l^{-1} oxalic acid and 0.3% (v/v) triethylamine in methanol–acetic acid–water (82:2.5:15.5), for the separation of TBT and TPhT chlorides. However, the inclusion of oxalic acid in the mobile phase is unsuitable for use with the LC–API-MS interface, as it is non-volatile under the source conditions employed. Attempts to use this mobile phase without oxalic acid for the baseline separation of DBT, TBT, DPhT and TPhT using both 250×4.6 mm and 150×2.1 mm columns proved unsuccessful. Using the triethylamine–methanol–acetic acid–water mobile phase as a starting point, optimisation of the mobile phase composition was made with attention to the concentrations of triethylamine, acid and organic modifier (methanol or acetonitrile). The following observations were made:

The use of acetonitrile as the organic modifier rather than methanol gave significantly sharper peaks of greater intensity. An acetonitrile concentration of 65% was found to be suitable.

The presence of triethylamine (TEA) in the mobile phase increases the retention time of TBT and reduces peak tailing. Increasing the TEA concentration above 0.2% gave no further improvement. A TEA concentration of 0.05% was found to give optimum retention and peak shape for TBT. The presence of TEA in the mobile phase was not found to have significant effect on the retention or peak shape of the other organo-tin species under investigation.

An increase in the acetic acid concentration reduces retention times and significantly reduces peak tailing for DBT and DPhT. An acetic acid concentration of 10% was found to be optimal.

The use of a 2.1 mm I.D. column rather than the more traditional 4.6 mm I.D. column used previously [21], improves sensitivity and reduces the required flow-rate from 1 ml min^{-1} to 0.2 ml min^{-1}, thus reducing solvent usage which is advantageous for LC–ICP-MS as it reduces solvent loading.

A mobile phase of 0.05% TEA in acetonitrile–acetic acid–water (65:10:25) was found to give baseline separation of DBT, TBT, DPhT and TPhT within 15 min. The pH of this mobile phase was found to be approximately 3.5, which is within the column manufacturer's recommended range.

Typical chromatograms obtained for LC–API-MS and LC–ICP-MS are depicted in Fig. 1a and 1b, respectively, which illustrate the compatibility of the chromatographic conditions with both API-MS and ICP-MS. The peaks obtained using LC–ICP-MS (Fig. 1b) are slightly broader than those obtained using LC–API-MS (Fig. 1a). This could be attributed to the larger dead volume associated with the ICP-MS spray chamber.

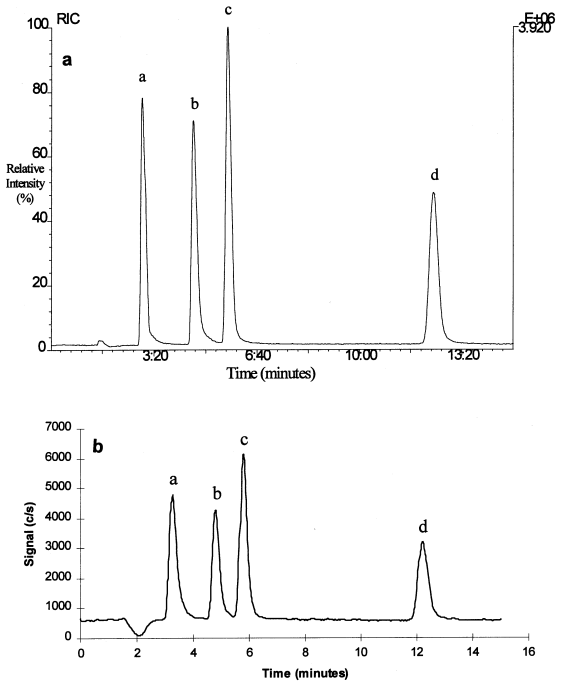

Fig. 1. (a) LC–API-MS chromatogram for organo-tin standards using positive ion APCI. (a) DPhT, (b) DBT, (c) TPhT, (d) TBT. 50 μg ml^{-1} as chlorides. (b) LC–ICP-MS chromatogram for organo-tin standards. (a) DPhT, (b) DBT, (c) TPhT, (d) TBT. 10 ng ml^{-1} as chlorides.

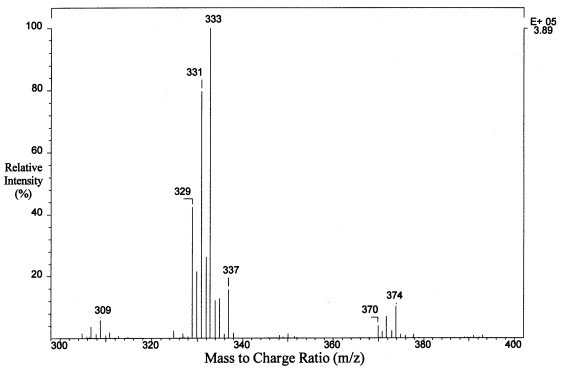

Fig. 2. Positive-ion APCI mass spectrum for diphenyltin.

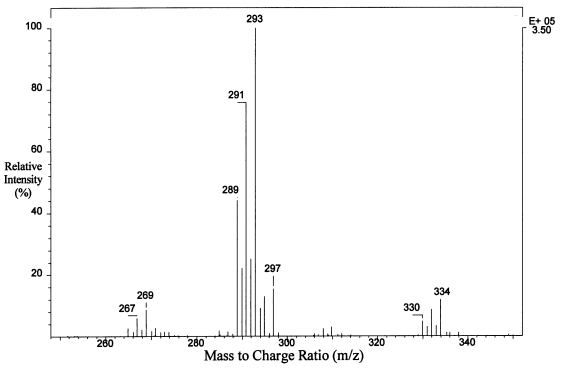

Fig. 3. Positive-ion APCI mass spectrum for dibutyltin.

3.3. Optimisation of APCI parameters and fragmentation voltage

In positive-ion APCI mode the mass spectra obtained for DPhT and DBT exhibit intense $[M+OAc]^+$ adducts rather than molecular ions [6]. Attempts to prevent this adduct formation by varying the vaporiser and capillary temperatures proved unsuccessful, as did attempts to fragment the adduct be means of a fragmentation voltage applied to the octapole rods situated between the ionisation source and the quadrupole analyser. The spectra of both DPhT (Fig. 2) and DBT (Fig. 3) also show the formation of $[M+OAc+MeCN]^+$ and what is suspected to be $[M+H_2O+OH]^+$ adduct ion groups, all of which exhibit the tin isotopic pattern. The formation of doubly charged ions for DPhT and DBT was not observed (using a scan range of 50 to 500 Daltons).

The mass spectra obtained for TBT and TPhT exhibit intense $[M]^+$ ion clusters consistent with the expected tin isotopic ratios. In addition, the spectrum of TPhT (Fig. 4) shows the formation of $[M+MeCN]^+$ and $[M-Ph+OAc]^+$ adduct ions. The spectrum for TBT (Fig. 5) is more complicated, as

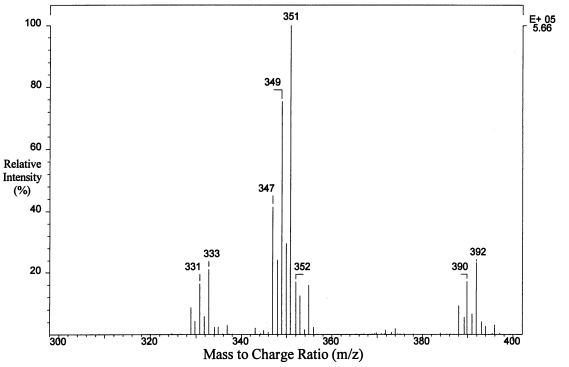

Fig. 4. Positive-ion APCI mass spectrum for triphenyltin.

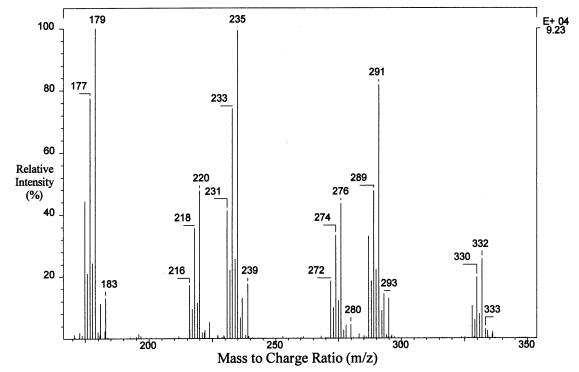

Fig. 5. Positive-ion APCI mass spectrum for tributyltin.

TBT fragments to give $[M-Bu+H]^+$ and $[M-2Bu+2H]^+$ ion clusters in addition to the $[M]^+$ molecular ions. In addition acetonitrile adducts are observed for each group of ions.

The assignments for each ion cluster from the mass spectra (Figs. 2–5) are listed in Table 4.

The APCI source temperatures (vaporiser and capillary) and the octapole offset voltage were optimised to give maximum intensities of the $[M+OAc]^+$ ions for DPhT and DBT, and of the $[M]^+$ ions for TPhT and TBT.

The optimum vaporiser and capillary temperatures were found to be 450°C and 150°C, respectively, with an octapole offset voltage of 5 V. Figs. 2–5 show the mass spectra of each analyte under these conditions.

Table 4
Assignment of ion groups observed in APCI mass spectra

Analyte	Ion cluster (m/z)	Ion assignment
DPhT (Fig. 2)	309	$[M+H_2O+OH]^+$
	333	$[M+OAc]^+$
	374	$[M+OAc+MeCN]^+$
DBT (Fig. 3)	269	$[M+H_2O+OH]^+$
	293	$[M+OAc]^+$
	334	$[M+OAc+MeCN]^+$
TPhT (Fig. 4)	333	$[M-Ph+OAc]^+$
	351	$[M]^+$
	392	$[M+MeCN]^+$
TBT (Fig. 5)	179	$[M-2Bu+2H]^+$
	220	$[M-2Bu+2H+MeCN]^+$
	235	$[M-Bu+H]^+$
	276	$[M-Bu+H+MeCN]^+$
	291	$[M]^+$
	332	$[M+MeCN]^+$

Note: the m/z ratio of each ion cluster refers to the most intense ion corresponding to the ^{120}Sn isotope.

3.4. Selected ion monitoring (SIM) and limits of detection

In order to achieve detection of organo-tin compounds at environmental levels it is necessary to operate the mass spectrometer in SIM mode to improve sensitivity. To this end three isotopic ions are monitored for each analyte, corresponding to the ^{116}Sn, ^{118}Sn and ^{120}Sn isotopes. These ions were selected from the full scan spectra (Figs. 2–5) and are listed in Table 2 with the molecular nature of each group of ions.

In order to achieve optimum sensitivity in SIM mode it is desirable to monitor as few ions as possible. To this end the mass spectrometer was programmed to switch between three sets of SIM masses during the course of each run (15 min). The mass windows and cycle time were kept constant at 0.4 u and 0.5 s, respectively. The details of the time programme are listed in Table 2. Note that while a further improvement in sensitivity could be achieved by monitoring only one ion for each organo-tin compound (say the ion corresponding to the ^{120}Sn isotope), this would provide no tin isotopic confirmation and hence reduce the specificity of the technique.

A tentative study of the limits of detection for the four compounds of interest has been made. Using the SIM conditions described above, the limits of detection in the injected extract (based on a 50 μl injection volume) are approximately 50 ng ml^{-1} for DPhT and TPhT and 100 ng ml^{-1} for DBT and TBT. While these limits are not as low as those achievable by LC–ICP-MS (approx. 200 pg ml^{-1}), improvements in extraction efficiency and a more effective pre-concentration step should enable the use of LC–API-MS for the confirmation of organotins in a range of matrices at environmental levels.

3.5. Analysis of real sediment sample

Using the extraction procedure outlined in Section 2.5, a real sediment sample from Portsmouth Harbour (UK) was found to contain DBT and TBT at 6 and 15 μg g^{-1}, respectively, following LC–ICP-MS

Table 5
Isotopic ratios obtained in SIM mode for the analysis of a real sediment sample

Ion ratio	Dibutyltin $[M+OAc]^+$ ions			Tributyltin $[M]^+$ ions		
	289/293	291/293	293/293	287/291	289/291	291/291
Theoretical	0.43	0.75	1.00	0.43	0.75	1.00
Standard	0.39	0.73	1.00	0.39	0.74	1.00
Sample	0.41	0.74	1.00	0.38	0.74	1.00

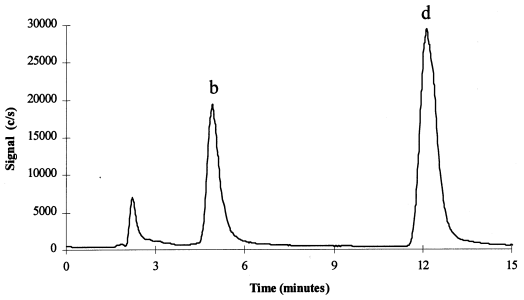

Fig. 6. LC–ICP-MS chromatogram for sediment sample extract (b) DBT, (d) TBT.

analysis. An LC–ICP-MS chromatogram for this sample is shown in Fig. 6. The sample extract was subjected to a twenty-fold concentration and injected onto the LC–API-MS system, operating in SIM mode, for qualitative analysis. Both DBT and TBT were detected in the extract and the ion ratios for each, together with those for a composite standard, are presented in Table 5. There is a good correlation between the standard and sample ion ratios for both DBT and TBT, which in turn are comparable with the theoretical values.

4. Conclusions

A method has been developed for the HPLC separation of DBT, TBT, DPhT and TPhT followed by mass spectrometric detection using APCI (Table 1). This chromatographic system is also compatible with ICP-MS allowing both techniques to be used to provide complementary information. While the use of ICP-MS has the advantage of superior sensitivity coupled with selectivity, LC–API-MS provides molecular information of the intact organo-tin species. Thus each technique can be used as a means of validation for the other, giving the analyst greater confidence in the speciation of organo-tin compounds.

Following appropriate modifications to the extraction and pre-concentration steps and validation by analysis of reference materials, the LC–API-MS procedure presented here could be used for routine confirmation of organo-tin compounds.

Acknowledgements

The work described in this paper was supported under contract with the Department of Trade and Industry as part of the National Measurement System Valid Analytical Measurement Programme.

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