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Speciation of phenyltin(IV) compounds using high-performance liquid chromatography. Part 2: The direct analysis of mixed standard solutions of triphenyltin halides/pseudohalide and of triphenyltin carboxylates containing functional group variations in the esteryl moiety

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Simultaneous speciation of mixed standard solutions of triphenyltin halides (triphenyltin chloride, bromide, iodide) and pseudohalide (triphenyltin isothiocyanate) has been achieved with reversed-phase high-performance liquid chromatography on a Waters Spherisorb S5W ODS-2 (octadecyl-silica) column. An isocratic mixture of 95:5 (v/v) acetonitrile:water was used as the mobile phase at a flow rate of 1 ml min^{-1}. A series of selected triphenyltin carboxylates, $Ph_3SnOCOZ$, where Z = Me, Ph, CH:CHPh, CH:NOMe, $CH_2SC_5H_4N$ and $CH_2SC(S)NMe_2$, was also similarly analysed using this system with two separate isocratic elutions using 100% acetonitrile and 96:4 (v/v) acetonitrile:water as the mobile phase. UV detection was done at 254 nm and the total run time for each analysis was less than 3 min. The detection limits for all the phenyltin(IV) compounds were in the range 0.01–0.03 ppm. Spiked water samples containing the triphenyltin carboxylates could also be simultaneously analysed by the above method without the need for any prior derivatization, following extraction with hexane. Pretreatment of the aqueous sample with NaCl/HCl and of the organic phase with hexamethylphosphoramide enabled recoveries of about 80% of the triphenyltins. Copyright © 2002 John Wiley & Sons, Ltd.

KEYWORDS: triphenyltin halides; triphenyltin isothiocyanate; triphenyltin carboxylates; organotin speciation; reversed-phase HPLC

INTRODUCTION

The high-performance liquid chromatography (HPLC) analysis of phenyltin compounds, often conjointly with other organotins, has been investigated by a number of workers[1–4] since the first report on the subject by Brinckman *et al.*[5] in 1977. The reversed-phase technique has featured dominantly in these studies. Two reviews by Harrington *et al.*[6] in 1996 and by Miller and Craig[7] in 1998 have summarized much of the recent efforts in the field. As pointed out by those authors, although the ease of detection by the standard UV detector (254 nm) is an inherent advantage with phenyltins, for environmental analysis the use of metal-specific detector systems that allow a better attainment of selectivity is generally preferred. Though speciation by means of HPLC of a mixture of mono-, di-, tri- and tetra-phenyltin compounds in laboratory or organic solvent-extracted environmental samples free of matrix

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interferences generally presents no problems, even with the use of a UV detector,[4] little or no work appears to have been carried out on speciation of phenyltins within a given structural class.

We have recently shown[8] that a mixture of tetraphenyltin with the three commercial triphenyltin biocides, Ph_3SnX (X = Cl, OH, OCOMe) could be well resolved by reversed-phase HPLC with UV detection on a Waters Spherisorb S5W ODS-2 (octadecylsilica) column using an isocratic mixture of 90:10 v/v acetonitrile:water as the mobile phase. The method proved not only sensitive (detection limits 0.01–0.02 ppm), but also free of any pre- or post-column derivatization requirements. This is of special relevance to the industry in facilitating quality control during manufacture of the triphenyltin products, often involving in the final stage of synthesis a hydrolysis, metathesis, condensation, esterification or transesterification step ($Ph_3SnX \rightarrow Ph_3SnY$). It was additionally shown that spiked water samples containing the three biocides could be directly analysed by the above method following extraction with toluene.

In a continuation of the above work, we sought to discover whether our HPLC method could, in principle, be applied to the identification and resolution of mixtures of more closely related triphenyltin systems, such as that of the halides and carboxylate esters. The halides chosen were the chloride, bromide and iodide; the pseudohalide, isothiocyanate (NCS), was also included for comparison purposes. In respect of the carboxylates, a random selection of these compounds, including those previously synthesized in our laboratories and shown to be biologically active,[9] was chosen, *viz*.: X = OCOZ, where Z = Me, Ph, CH:CHPh, CH:NOMe, $CH_2SC_5H_4N$ and $CH_2SC(S)NMe_2$. As with our previous work, analysis was performed on mixed standard solutions of the halides and carboxylates. For the carboxylates, their spiked water samples were also analysed following extraction with hexane to gauge the potential applicability of the method to real systems. It must, however, be emphasized here that in attempting the speciation of the randomly mixed halides or esters, the purpose was essentially to test the versatility of the method in probing small changes in the anionic X group of Ph_3SnX. Hence no major variations in the operating conditions were made, except for exploratory compositional variations in the acetonitrile:water mobile phase.

EXPERIMENTAL

Instrumentation

The HPLC equipment consisted of a Thermo Separation Products Model ConstaMetric 4100 Quaternary Solvent Delivery System, SHM 4 Solvent Degassing System, AS3000 Variable-loop Autosampler, UV3000 detector and a PC1000 Chromatography Workstation. The analytical column used was Waters Spherisorb S5W ODS-2 (5 μm particle size; 150 mm × 4.6 mm i.d.). Sample volumes injected were 10–20 μl for each chromatographic run, with the column at room temperature (27 ± 1 °C). UV detection was set at 254 nm.

Reagents and chemicals

Triphenyltin chloride (Ph_3SnCl, 99%) and triphenyltin acetate ($Ph_3SnOCOCH_3$, 97%) were obtained from Merck–Schuchardt (Hohenbrunn, Germany). Triphenyltin iodide (Ph_3SnI), m.p. 122–124 °C, triphenyltin bromide (Ph_3SnBr), m.p. 124–125 °C, and triphenyltin isothiocyanate (Ph_3SnNCS), m.p. 172–173 °C, were synthesized by standard methods.[10] The 1:1 complexes[11,12] of triphenyltin chloride with Ph_3PO (m.p. 163–164 °C) and Ph_3AsO (m.p. 212–214 °C), and the stannate salt,[13] $[Me_4N]^+[Ph_3SnCl_2]^-$ (m.p. 294–296 °C), were prepared according to published procedures. The triphenyltin carboxylates, $Ph_3SnOCOZ$, where Z = Ph[10] (m.p. 84–86 °C), CH:CHPh[14] (m.p. 138–139 °C), CH:NOMe[15] (m.p. 167–168 °C), $CH_2SC_5H_4N$[16] (m.p. 161–163 °C) and $CH_2SC(S)NMe_2$[17] (m.p. 160–161 °C) were prepared in our laboratories by duplicating methods previously reported.

HPLC-grade acetonitrile, hexane, toluene, chloroform, dichloromethane, diethyl ether, cyclohexane, and carbon tetrachloride were purchased form BDH, as also were the inorganic salts, NaCl and NH_4Cl, of analytical grade. The mineral acids, HCl (36% fuming) and HNO_3 (65%), and glacial CH_3COOH (99.5%) were purchased from R & M Chemicals. Tropolone (98%), 8-hydroxyquinoline (oxine) and hexamethylphosphoramide (HMPA, 99%) were purchased from Aldrich Chemicals. Deionized water with a resistivity of 18 MΩ cm was obtained using a Millipore MilliQ water purifier. The organic and aqueous HPLC solvents were filtered through Durapore 0.22 μm membrane filters prior to chromatographic use. Both the pure organic solvent and its binary mixture with water in varying proportions were employed in the studies at the fixed flow rate of 1 ml min^{-1}.

Standard stock solutions of each phenyltin compound (1000 ppm) were prepared in HPLC-grade acetonitrile. These solutions were stored at 4 °C in dark glass bottles, and appropriate working solutions were freshly prepared daily using HPLC-grade acetonitrile for dilution.

All glassware was rinsed in deionized water, soaked overnight in 10% HNO_3 solution, and then rinsed again.

Spiking procedure

1 mg of each of the five triphenyltin carboxylates, $Ph_3SnOCOZ$, where Z = Ph, CH:CHPh, CH:NOMe, $CH_2SC_5H_4N$ and $CH_2SC(S)NMe_2$, were separately dissolved in 1 ml each of acetonitrile and the solutions then spiked into 1 l of deionized water. The spiked solution was stirred overnight using a magnetic stirrer to obtain a homogeneous clear solution.

Table 1. Retention times of triphenyltin halides and pseudohalide

Compound	100% acetonitrile (P' = 5.80)[a]	95:5 (v/v) acetonitrile:water (P' = 6.02)[a]	90:10 (v/v) acetonitrile:water (P' = 6.24)[a]
Ph_3SnI	1.24	1.08	1.02
Ph_3SnNCS	1.53	1.25	1.12
Ph_3SnBr	1.54	1.38	1.25
Ph_3SnCl	2.50[b]	1.55	1.43

[a] Solvent polarity parameter.[18]
[b] Pronounced tailing.

Extraction procedure

A 100 ml sample of the spiked solution was taken into a separating funnel and extracted with three successive 20 ml portions of the organic solvent, typically hexane. An orbital shaker was used to facilitate the extraction. The separated organic layers were combined, dried over anhydrous Na_2SO_4 and then filtered. The filtrate was concentrated to dryness on a water bath using a rotary evaporator, and the residue reconstituted with 1 ml acetonitrile before being injected into the HPLC system.

Pretreatment of aqueous/organic phases

The extraction procedure described above was repeated with the stock organotin-containing aqueous solution being pretreated with modifiers such as NaCl or NH_4Cl (25 g) in the co-presence or otherwise of mineral acids, HCl and HNO_3 (1 ml) or glacial CH_3COOH (5 ml). Pretreatment of the organic phase with complexing agents such as tropolone (0.05% w/v), oxine (0.05% w/v) and HMPA (0.05% v/v) was additionally performed with the aim of getting improved extractability of the organotins from the aqueous phase. For this purpose the aqueous phase used was that containing NaCl and HCl.

RESULTS AND DISCUSSION

Analysis of triphenyltin halides and pseudohalide mixtures

As with our earlier study[8] involving standard mixtures of Ph_3SnCl, $Ph_3SnOCOCH_3$, Ph_3SnOH and Ph_4Sn, the use of 100% acetonitrile as the mobile phase in the Waters Spherisorb S5W ODS-2 column resulted in co-elution of the halides and pseudohalide mixture, with pronounced tailing displayed by the chloride. Clear separation of the compounds was achieved when water was introduced into the mobile phase, with the retention times decreasing with increasing water content for all the compounds (Table 1).

Satisfactory resolution of the compounds with sharp peak characteristics was achieved with the binary mobile phase composition 95:5 (v/v) acetonitrile:water (Fig. 1).

The retention times followed the sequence Ph_3SnI $<Ph_3SnNCS$ $<Ph_3SnBr$ $<Ph_3SnCl$. This trend parallels the strength of the respective tin–halogen bonds,[19,20] which makes the iodide the most polar among the halides and, therefore, the most responsive to polarity change in the mobile phase. In as much as the order of elution remained unchanged with increasing polarity of the binary mobile phase achieved with increasing water addition, the HPLC result may be regarded as a direct measure of the relative polarities of the halide and pseudohalide compounds. Though water, with its known donor properties to tin, may

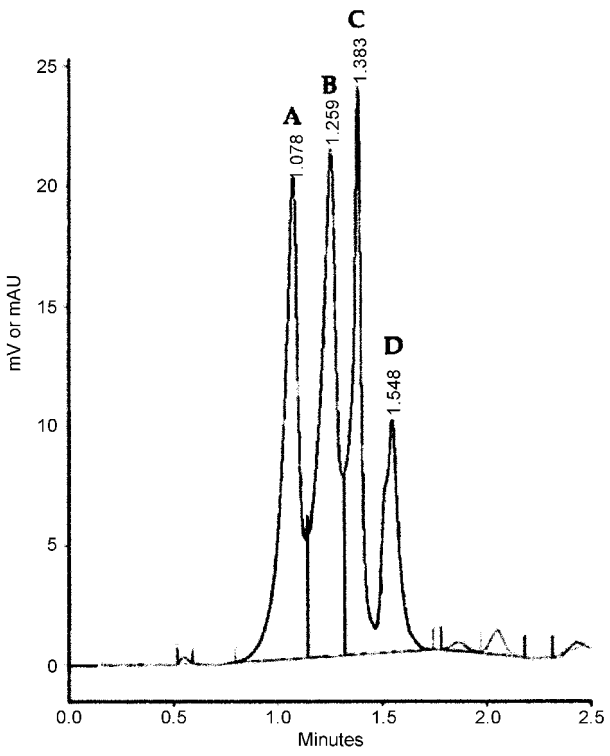

Figure 1. Chromatogram of a mixed standard solution of triphenyltin halides and pseudohalide. (A) Ph_3SnI (1.0 ppm), (B) Ph_3SnNCS (1.0 ppm), (C) Ph_3SnBr (1.0 ppm) and (D) Ph_3SnCl (0.5 ppm) obtained with injection of 20 µl of standard solution. Mobile phase, 95:5 (v/v) acetonitrile:water; flow rate 1 ml min^{-1}.

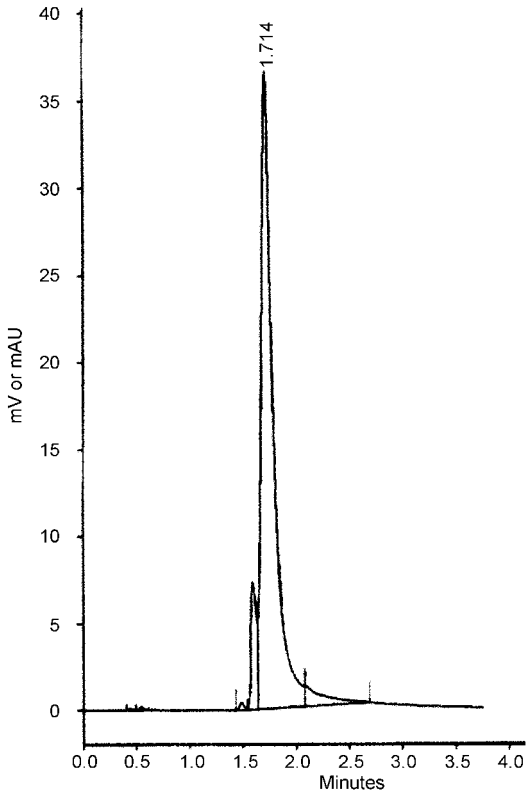

Figure 2. Chromatogram of $[Ph_3SnCl_2]^-[Me_4N]^+$ obtained with injection of 10 µl of its standard solution (3.0 ppm). Mobile phase, 100% acetonitrile; flow rate 1 ml min^{-1}.

be expected to exert some degree of coordinative interaction with the compounds in the relative order of their acceptor strengths[19] (I <Br <Cl), no unusual selectivity of one or more of these compounds towards water exists, as this would have otherwise elicited marked changes in the elution profiles with increasing water content of the mobile phase. The Lewis acidity of the compounds can also be a factor in their partitioning from the stationary phase on account of possible interactions with the residual silanol groups on the column, with the interaction being particularly strong with Ph_3SnCl, as evidenced by the pronounced tailing observed for this halide in the chromatogram. The tailing is diminished when the water content of the mobile phase, and hence its polarity, is progressively increased. This implies that the water molecules bring about a competitive disruption of the interactions of the silanol groups with the organotin.

In the context of the above findings, we were interested to know the behaviour of neutral and ionic complexes of Ph_3SnCl when subjected to HPLC analysis under the same conditions. It was noted that the 1:1 adducts of Ph_3SnCl with Ph_3PO and Ph_3AsO underwent complete dissociation in 100% acetonitrile and eluted as their separate components. However, this was not the case with tetramethylammonium dichlorotriphenylstannate $[Me_4N]^+[Ph_3SnCl_2]^-$ which retained its chemical integrity and eluted as a sharp peak with no tailing (Fig. 2). The retention time for the stannate (t_R = 1.71 min) is shorter than that of Ph_3SnCl (t_R = 2.50 min) in this medium.

Table 3. Limits of detection of triphenyltin halides and pseudohalide

Compound	Limit of detection (ppm)
Ph_3SnI	0.02
Ph_3SnNCS	0.02
Ph_3SnBr	0.02
Ph_3SnCl	0.01

Calibration plots of mixed standard solutions of triphenyltin halides and pseudohalide and their reproducibility

Calibration graphs were established by plotting peak areas against concentration for standard solutions of the four compounds. Excellent linearity of the calibration curves was observed for product concentrations of up to 10 ppm tested in two stepwise interval ranges. Table 2

Table 2. Calibration curves ($y = A + Bx$)[a] and regression data for triphenyltin halides and pseudohalide. Number of data points is ten

Compound	Concentration range (ppm)	Intercept A	Slope B	Correlation coefficient R^2
Ph_3SnI	0.1–1.0	393	105 989	0.9997
	1.0–10.0	−611	103 858	0.9997
Ph_3SnNCS	0.1–1.0	735	126 647	0.9997
	1.0–10.0	12 521	108 376	0.9996
Ph_3SnBr	0.1–1.0	649	77 812	0.9996
	1.0–10.0	−4194	78 345	0.9996
Ph_3SnCl	0.1–1.0	−809	101 559	0.9997
	1.0–10.0	4215	96 280	0.9997

[a] Peak area (arbitrary counts) on *y*-axis; concentration (ppm) on *x*-axis.

Table 4. Retention times of triphenyltin carboxylates in acetonitrile–water media of varying compositions

Compound		Retention time (min)					
Name	Formula	100% CH_3CN	96:4 (v/v) $CH_3CN:H_2O$	90:10 (v/v) $CH_3CN:H_2O$	85:15 (v/v) $CH_3CN:H_2O$	80:20 (v/v) $CH_3CN:H_2O$	75:25 (v/v) $CH_3CN:H_2O$
Triphenyltin acetate	$Ph_3SnOCOCH_3$	1.72	1.96	2.32	2.50	2.71	3.10
Triphenyltin benzoate	$Ph_3SnOCOPh$	1.71	1.51	1.49	1.44	1.37	1.22
Triphenyltin *N,N'*-dimethyldithiocarbamylacetate	$Ph_3SnOCOCH_2SC(S)NMe_2$	1.71	0.95	0.93	0.92	0.90	0.87
Triphenyltin cinnamate	$Ph_3SnOCOCH{:}CHPh$	1.72	0.94	0.92	0.91	0.88	0.86
Triphenyltin 4-pyridylmercaptoacetate	$Ph_3SnOCOCH_2SC_5H_4N$	1.94	0.94	0.93	0.91	0.89	0.86
Triphenyltin glyoxalate *O*-methyloxime	$Ph_3SnOCOCH{:}NOMe$	2.47	0.94	0.93	0.92	0.89	0.87

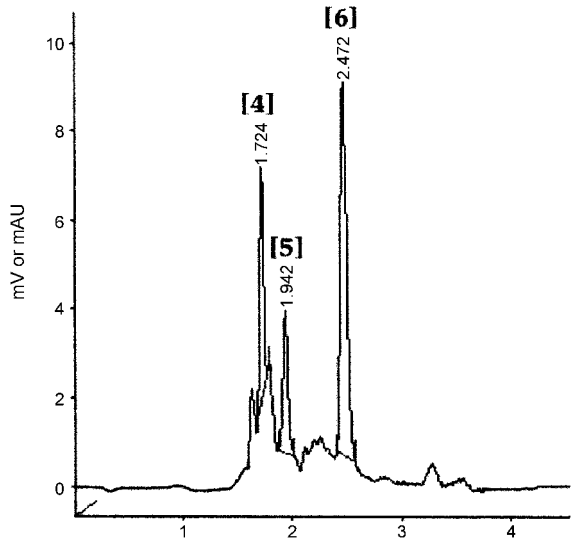

Figure 3. Chromatogram of a mixed standard solution of three triphenyltin carboxylates. [**4**]: $Ph_3SnOCOCH$:CHPh (0.1 ppm); [**5**]: $Ph_3SnOCOCH_2SC_5H_4N$ (0.1 ppm); [**6**]: $Ph_3SnOCOCH$:NOMe (0.2 ppm); obtained with injection of 10 μl of standard solution. Mobile phase, 100% acetonitrile; flow rate 1 ml min^{-1}.

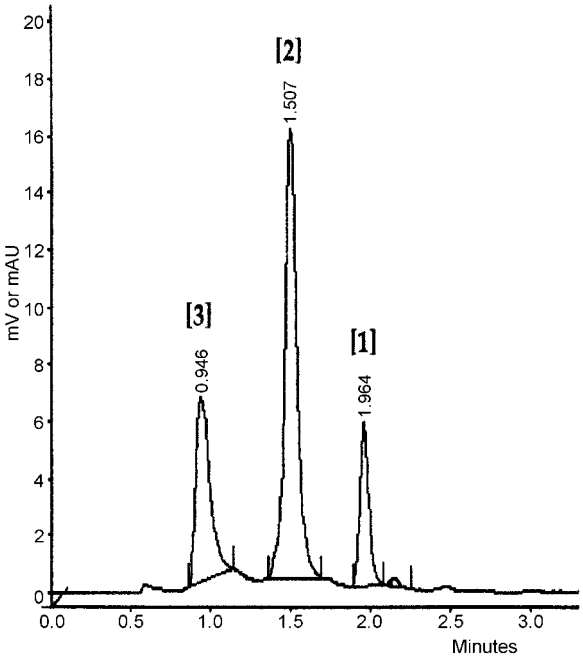

Figure 4. Chromatogram of a mixed standard solution of three triphenyltin carboxylates. [**3**]: $Ph_3SnOCOCH_2SC(S)NMe_2$ (0.2 ppm); [**2**]: $Ph_3SnOCOPh$ (0.4 ppm); [**1**]: $Ph_3SnOCOCH_3$ (0.1 ppm); obtained with injection of 10 μl of standard solution. Mobile phase, 96:4 (v/v) acetonitrile:water; flow rate 1 ml min^{-1}.

summarizes the calibration and regression data for the phenyltin compounds. Correlation coefficients R^2, obtained by using either peak areas or peak heights, were almost identical.

Reproducibility was studied by evaluating the relative standard deviations for six replicate injections for each chosen concentration within the standard concentration range shown in Table 2. The relative standard deviations (RSDs) were in the range 3–9% for all four of the compounds. Detection limits were calculated from a signal that was three times the noise. Detection limits obtained for the respective phenyltin compounds are tabulated in Table 3.

Analysis of triphenyltin carboxylate mixtures

Six randomly selected triphenyltin carboxylate esters were used for the HPLC analysis. Individual retention times of the triphenyltin esters with various acetonitrile:water mobile phase compositions are shown in Table 4. To the best of our knowledge, this represents the first reported study by HPLC on organotin carboxylates containing various functional residues on the esteryl moiety.

The data suggest that using 100% acetonitrile as the mobile phase can effect separations of mixtures of $Ph_3SnOCOCH$:CHPh (**4**) with $Ph_3SnOCOCH_2SC_5H_4N$ (**5**) and $Ph_3SnOCOCH$:NOMe (**6**), but not of mixtures of $Ph_3SnOCOCH_3$ (**1**), $Ph_3SnOCOPh$ (**2**), and $Ph_3SnOCOCH_2SC(S)NMe_2$ (**3**), and that resolutions of compounds **1**, **2** and **3** require the use of binary acetonitrile:water mobile phase. Indeed, a standard mixture of compounds **1**, **2**, **3** and **4** co-eluted as a single peak in 100% acetonitrile, but that of compounds **4**, **5** and **6** was satisfactorily resolved in this medium (Fig. 3). The elution order **4** < **5** < **6** suggests that triphenyltin gyloxalate *O*-methyloxime is the least polar among the ester compounds studied.

Using the binary acetonitrile:water mobile phase of composition 96:4 (v/v), it was also shown that a mixture of compounds **1**, **2** and **3** was well resolved (Fig. 4). The elution order **3** < **2** < **1** further attests to the influence of esteryl substituents on the overall polarity of the compounds, with the more polar molecules requiring more polar mobile phases for their partitioning from the stationary phase. No significant changes in the elution profiles were encountered upon increasing the water content in the mobile phase to 10, 15, 20 or 25% (v/v) levels. Thus, the complete speciation by HPLC of a standard mixture of all the six esters would necessitate two separate isocratic elutions, one using 100% acetonitrile and the other using a binary acetonitrile:water as the mobile phase.

Calibration plots of mixed standard solutions of triphenyltin carboxylate esters and their reproducibility

Calibration graphs were established by plotting peak areas

Table 5. Calibration curves ($y = A + Bx$)[a] and regression data for triphenyltin carboxylate esters using 100% acetonitrile mobile phase. Number of data points is ten

Compound	Concentration range (ppm)	Intercept A	Slope B	Correlation coefficient R^2
$Ph_3SnOCOCH{:}CHPh$	0.1–1.0	−570	192 393	0.9993
	1.0–10.0	−16 378	208 243	0.9993
$Ph_3SnOCOCH_2SC_5H_4N$	0.1–1.0	313	174 076	0.9994
	1.0–10.0	−4260	180 506	0.9993
$Ph_3SnOCOCH{:}NOMe$	0.1–1.0	−1086	213 096	0.9994
	1.0–10.0	−3913	212 457	0.9996

[a] Peak area (arbitrary counts) on y-axis; concentration (ppm) on x-axis.

Table 6. Calibration curves ($y = A + Bx$)[a] and regression data for triphenyltin carboxylate esters using 96:4 (v/v) acetonitrile:water mobile phase. Number of data points is ten

Compound	Concentration range (ppm)	Intercept A	Slope B	Correlation coefficient R^2
$Ph_3SnOCOCH_2SC(S)NMe_2$	0.1–1.0	−2001	225 597	0.9996
	1.0–10.0	−18 402	223 608	0.9994
$Ph_3SnOCOPh$	0.1–1.0	347	213 557	0.9996
	1.0–10.0	12 087	213 347	0.9996
$Ph_3SnOCOCH_3$	0.1–1.0	−555	230 469	0.9996
	1.0–10.0	22 635	208 523	0.9996

[a] Peak area (arbitrary counts) on y-axis; concentration (ppm) on x-axis.

against concentration for standard solutions of the six compounds. Excellent linearity was achieved for the concentration range of 0.1 to 10.0 ppm chosen for the investigation.

Tables 5 and 6 summarize the calibration and regression data for the compounds. The correlation coefficients R^2, obtained by using either peak areas or peak heights, were almost identical.

Reproducibility was studied by evaluating the relative standard deviations for six replicate injections for each chosen concentration within the standard concentration range shown in Tables 5 and 6. The RSDs were in the range 4–9% for all six of the compounds. Detection limits were calculated from three times the signal/noise ratio. Detection limits obtained for the respective triphenyltin esters are tabulated in Tables 7 and 8.

Analysis of spiked aqueous samples containing triphenyltin carboxylates

The experiments here were patterned on the work of Abalos *et al.*,[21] who studied the effects of several extraction variables, such as acid concentration and strength, the presence of complexing agents in the extracting mixture, and the solvent polarity, for native butyl- and phenyl-tin compounds in marine sediments.

For the present study, hexane proved to be more efficient than the other solvents as the extractant (Table 9). The percentage recovery data were based on HPLC analysis using the mobile phase compositions of 100% acetonitrile and 96:4 (v/v) acetonitrile:water mobile phase and performed under identical operating conditions as described in the foregoing sections.

The recoveries with hexane were enhanced somewhat

Table 7. Limits of detection of triphenyltin carboxylate esters using 100% acetonitrile mobile phase

Compound	Limit of detection (ppm)
$Ph_3SnOCOCH{:}CHPh$	0.03
$Ph_3SnOCOCH_2SC_5H_4N$	0.03
$Ph_3SnOCOCH{:}NOMe$	0.03

Table 8. Limits of detection of triphenyltin carboxylate esters using 96:4 (v/v) acetonitrile:water mobile phase

Compound	Limit of detection (ppm)
$Ph_3SnOCOCH_2SC(S)NMe_2$	0.03
$Ph_3SnOCOPh$	0.02
$Ph_3SnOCOCH_3$	0.01

Table 9. Recoveries of triphenyltin carboxylates with various extracting solvents[a]

Compound	Recovery (%)						
	Hexane	Toluene	Chloroform	Dichloromethane	Diethylether	Cyclohexane	Carbontetrachloride
$Ph_3SnOCOCH:CHPh$	60	58	41	40	40	54	48
$Ph_3SnOCOCH_2SC_5H_4N$	61	56	42	41	42	52	46
$Ph_3SnOCOCH:NOMe$	62	57	41	41	41	50	45
$Ph_3SnOCOCH_2SC(S)NMe_2$	60	56	40	42	42	52	44
$Ph_3SnOCOPh$	61	57	42	40	40	50	45

[a] No pretreatment was applied either to the aqueous or organic phase.

Table 10. Effect of modifiers and acids in aqueous pretreatment[a]

Compound	Recovery with hexane (%)				
	NaCl	NH_4Cl	NaCl + HCl	NaCl + HNO_3	NaCl + CH_3COOH
$Ph_3SnOCOCH:CHPh$	68	66	71	68	68
$Ph_3SnOCOCH_2SC_5H_4N$	68	66	70	69	68
$Ph_3SnOCOCH:NOMe$	68	65	71	68	70
$Ph_3SnOCOCH_2SC(S)NMe_2$	70	68	72	71	70
$Ph_3SnOCOPh$	67	65	70	68	67

[a] Amount of modifiers, NaCl or NH_4Cl, used was 25 g; acids used were HCl (1 ml), HNO_3 (1 ml) and CH_3COOH (5 ml).

Table 11. Effect of complexing agents[a] on hexane extraction of pretreated[b] aqueous sample

Compound	Recovery with hexane (%)		
	Tropolone	Oxine	HMPA
$Ph_3SnOCOCH:CHPh$	78	76	82
$Ph_3SnOCOCH_2SC_5H_4N$	76	75	80
$Ph_3SnOCOCH:NOMe$	77	75	81
$Ph_3SnOCOCH_2SC(S)NMe_2$	76	75	80
$Ph_3SnOCOPh$	77	76	81

[a] 0.05% v/v or w/v in hexane.
[b] NaCl/HCl (see footnote of Table 10).

when the aqueous phase was pretreated with NaCl and HCl (Table 10). A significant improvement in recovery occurred when the organic phase was also pretreated with a complexing agent. HMPA proved to be most effective in this regard, yielding recoveries of 80% for the title compounds (Table 11).

CONCLUSION

An HPLC–UV method for the simultaneous determination of triphenyltin halides/pseudohalide, namely Ph_3SnCl, Ph_3SnBr Ph_3SnI and Ph_3SnNCS, has been developed. The method employs isocratic elution on a Waters Spherisorb S5W ODS-2 column with 95:5(v/v) acetonitrile:water mobile phase. The method has also been extended to probing functional group variations in the esteryl moiety, as exemplified by the resolution of a random mixture of triphenyltin carboxylates, $Ph_3SnOCOZ$, where Z = Me, Ph, CH:CHPh, CH:NOMe, $CH_2SC_5H_4N$ and $CH_2SC(S)NMe_2$, achieved with two separate isocratic elutions using 100% acetonitrile and 96:4 (v/v) acetonitrile:water as the mobile phase. Spiked water samples containing the triphenyltin carboxylates have been similarly analysed following extraction with hexane. Pretreatment of the aqueous sample with NaCl/HCl and of the organic phase with HMPA enabled recoveries of about 80% of the triphenyltins. The advantages of the method are its simplicity, non-requirement of any pre- or post-column derivatization and the ready availability of the necessary instrumentation.

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