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Speciation of phenyltin(IV) compounds using high-performance liquid chromatography: Part 1. The direct analysis of mixed standard solutions of tetraphenyltin, triphenyltin chloride, triphenyltin hydroxide and triphenyltin acetate

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A rapid speciation high-performance liquid chromatography (HPLC) method has been developed for the simultaneous determination of phenyltin compounds. The commercially important products of triphenyltin-chloride, -acetate, -hydroxide and tetraphenyltin were separated by reversed-phase HPLC on a Waters Spherisorb S5W ODS-2 (octadecylsilica) column using an isocratic mixture of 90:10 (v/v) acetonitrile:water as the mobile phase at a flow rate of 1 ml min^{-1}. The phenyltin compounds were detected by UV detection at 254 nm and the total elution time is 8 min. The elution order is triphenyltin-chloride, -acetate, -hydroxide and tetraphenyltin. Detection limits were 0.01 ppm for each of the triphenyltin compounds and 0.02 ppm for tetraphenyltin. Spiked water samples containing the three biocidal triphenyltin compounds could also be analysed simultaneously by the above method without the need for any prior derivatization, following extraction with toluene. The versatility of the method in sensing substituent group variations on the phenyl ring was also demonstrated by the successful resolution of the hydroxides, tris(*p*-chlorophenyl)tin hydroxide, diphenyl(*p*-chlorophenyl)tin hydroxide and triphenyltin hydroxide. Copyright © 2002 John Wiley & Sons, Ltd.

KEYWORDS: phenyltin; organotin speciation; reversed-phase HPLC

INTRODUCTION

Organotin compounds are industrially well-established chemicals that find application on a wide front, including as stabilizers for PVC, catalysts for RTV silicone and polyurethane production, antifouling agents for marine paints, and as timber and crop protectants for the control of a host of fungal and insect pathogens.[1–5] The biological effects are particularly manifested by the triorganotin structural class, of which the triphenyltins find selective use in agriculture on account of their relatively lower phytotoxicity compared with alkyl analogues such as tributyltins. Indeed, the use of the compounds triphenyltin acetate ($Ph_3SnOCOCH_3$; 'Brestan') and triphenyltin hydroxide (Ph_3SnOH; 'Du-ter') in agriculture date back[6] to the early 1960s. The industrial preparative route[7,8] of these compounds involves the conversion of tetraphenyltin (Ph_4Sn) to triphenyltin chloride (Ph_3SnCl) and subsequent hydrolysis of the latter to the hydroxide; the esterification of the hydroxide, in turn, affords the acetate. Quality control in the industrial preparation of these chemicals requires that the contaminant levels of the various intermediary products be kept minimal. During application, there is also the concomitant need to monitor the entry of these compounds, as well as their degradation products, into the aquatic ecosystem via leaching and run-off from agricultural fields.[9–11]

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A number of techniques, many of them hyphenated, have been introduced for the analysis of organotin compounds, and a recent review on the subject exists.[12] In respect of phenyltins, their relative ease of detection by a standard UV detector (254 nm) has resulted in the earliest reported use of the high-performance liquid chromatography (HPLC) technique being directed towards their analysis.[13] For other organotins, the use of HPLC has been somewhat restricted by the complex problem of detector interface, although the use of HPLC–Inductively Coupled Plasma Mass Spectrometry (ICP-MS) is a very sensitive technique for the absolute detection of organotins at sub-picogram levels.[14]

Reviews on the speciation of organotin compounds have also appeared in the recent literature,[15,16] and these include a discussion of the speciation of mono-, di- and tri-phenyltins derivatized to their chloride form. This derivatization step is not without its complications, as triphenyltin compounds are known to undergo some degree of disproportionation in the work-up of their solutions, including during recrystallization.[6]

It was the purpose of this study to develop a rapid and accurate method for the simultaneous determination of the industrially important triphenyltin biocides in their admixtures, without recourse to prior derivatization, in the hope that it would be of value to the manufacturing and environmental monitoring sectors of the industry. The study has included the analysis of these triphenyltin compounds in spiked water samples. An extended application of the method in distinguishing between ring-substituted phenyltin hydroxides has also been explored. Additional applications of the technique in the analysis of triphenyltin halides/pseudohalides and triphenyltin carboxylates containing functional group variations in the esteryl moiety are described in Part 2 of this work.[17]

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 four analytical columns used were Waters μBondapak C_{18}, Waters Nova-Pak C_{18}. Inertsil ODS-2 and Waters Spherisorb S5W ODS-2. Sample volumes injected were 10 μl for each chromatographic run, with the column at room temperature (27 ± 1 °C). UV detection was set at 254 nm.

REAGENTS AND CHEMICALS

Ph_3SnCl (99%) and $Ph_3SnOCOCH_3$ (97%) were obtained from Merck–Schuchardt (Hohenbrunn, Germany). Ph_3SnOH (98%) was obtained from Tokyo Kasei. Ph_4Sn, m.p. 227–229 °C, and tris(*p*-chlorophenyl)tin hydroxide, m.p. 114–118 °C, were prepared by literature methods.[18,19] Diphenyl (*p*-chlorophenyl)tin hydroxide, m.p. 109–110 °C, was synthesized as described elsewhere.[20]

HPLC-grade acetonitrile, methanol, *i*-propanol, tetrahydrofuran, hexane, chloroform and toulene were purchased from 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 a 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 Ph_3SnCl, Ph_3SnOH and $Ph_3SnOCOCH_3$ were separately dissolved in 1 ml each of acetonitrile and the solutions spiked into 1 l of deionized water. The spiked solution was stirred overnight using a magnetic stirrer to obtain a homogeneous clear solution.

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 toluene. 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 NH_4Cl and glacial CH_3COOH.

RESULTS AND DISCUSSION

Optimization of chromatographic conditions

Separation of the four phenyltin compounds was, in the first instance, investigated using different solvents (methanol, acetonitrile, *i*-propanol, tetrahydrofuran) admixed with varying amounts of water on the μBondapak C_{18} column. Of these, methanol, *i*-propanol and tetrahydrofuran were found to be unsuitable, as their use resulted in long retention times and poor peak shapes. Improved peak shapes at shorter retention times were obtained when acetonitrile was used as the organic solvent. The use of this solvent, admixed with varying amounts of water (0–40%), was used in the optimization study. Three other C_{18} columns with different packing characteristics (*see* Table 1) were also included in the optimization study. In all cases, the eluent flow rate was set at 1 ml min^{-1}; UV detection was at 254 nm.

In order to improve the resolution, the effect of mobile phase composition (acetonitrile–water ratio) on capacity factor k' was examined for all four of the C_{18} columns. This is illustrated in Fig. 1.

The capacity factors k' of all the compounds were found to decrease with increasing amounts of acetonitrile with all four of the columns, with the notable exception of Ph_3SnCl in the Waters Spherisorb S5W ODS-2 column. This compound exhibited considerable tailing when the mobile phase was 100% acetonitrile. This 'anomalous' behaviour of Ph_3SnCl could be occasioned by the presence on the column of a larger number of residual silanol groups, which can interact with the phenyltins, particularly so with Ph_3SnCl, which has the strongest Lewis acidity.[21,22] This interaction is countered by acetonitrile, with which the phenyltin halide can engage in dipole–dipole interaction. The observed tailing is probably reflective of this dual interaction. When water is introduced along with acetonitrile, the solvent polarity increases, and this favours the delivery of the more polar Ph_3SnCl into the mobile phase. Thus, while the other phenyltins respond to the reduction[23] in solvent strength by showing increased retention times, Ph_3SnCl registers a shorter retention time. Although phenyltins cannot be classified as being hydrophilic, the presence of water, with its known donor properties to tin, in the acetonitrile medium conceivably serves to engage the Lewis acidic Ph_3SnCl in coordinative interactions, thereby disrupting its interactions with the silanol groups. Reduced tailing is the consequence.

With the μBondapak C_{18} and Nova-Pak C_{18} columns, all the triphenyltins co-eluted as a single peak (Fig. 1A and B), irrespective of the composition of the binary mobile phase, although here again peak tailing was most pronounced when the mobile phase was exclusively acetonitrile. With the Inertsil ODS-2 column, it was possible to separate only Ph_3SnOH from the other triphenyltins (Fig. 1C). All three of the triphenyltin compounds were well separated when the Waters Spherisorb S5W ODS-2 column was employed. Ph_4Sn, however, was well resolved with all four of the columns.

Satisfactory resolution of mixed standard solutions of the four phenyltins was readily achieved only with the Waters Spherisorb S5W ODS-2 column using the binary 90:10 (v/v) acetonitrile–water mobile phase. A typical chromatogram is depicted in Fig. 2. The respective retention times under optimized conditions are shown in Table 2.

Calibration of mixed standard solutions and reproducibility

Calibration graphs were established by plotting peak areas against concentration for standard solutions of the four phenyltin compounds. Excellent linearity of the calibration curves was observed for both the low-level concentration range of 0.1 to 1.0 ppm and the high-level concentration range of 1.0 to 10 ppm. Higher concentration levels were not explored, as such levels of contamination are not expected in commercial samples of the individual phenyltin com-

Table 1. Packing characteristics of the C_{18} HPLC columns

Packing	Reversed-phase packings			
	μBondapak (C_{18})	Nova-Pak (C_{18})	Inertsil ODS-2 (C_{18})	Waters Spherisorb ODS-2 (C_{18})
Column length (mm)	150	150	150	150
Internal diameter (mm)	3.9	3.9	4.6	4.6
Particle size (μm)	10	4	5	5
Particle shape	irregular	spherical	spherical	spherical
Pore size (nm)	12.5	6.0	15.0	8.0
Carbon load (%)	10	7	18.5	11.5
Minimum plates per column	5000	8720	9750	11250
End-capped	yes	yes	yes	yes

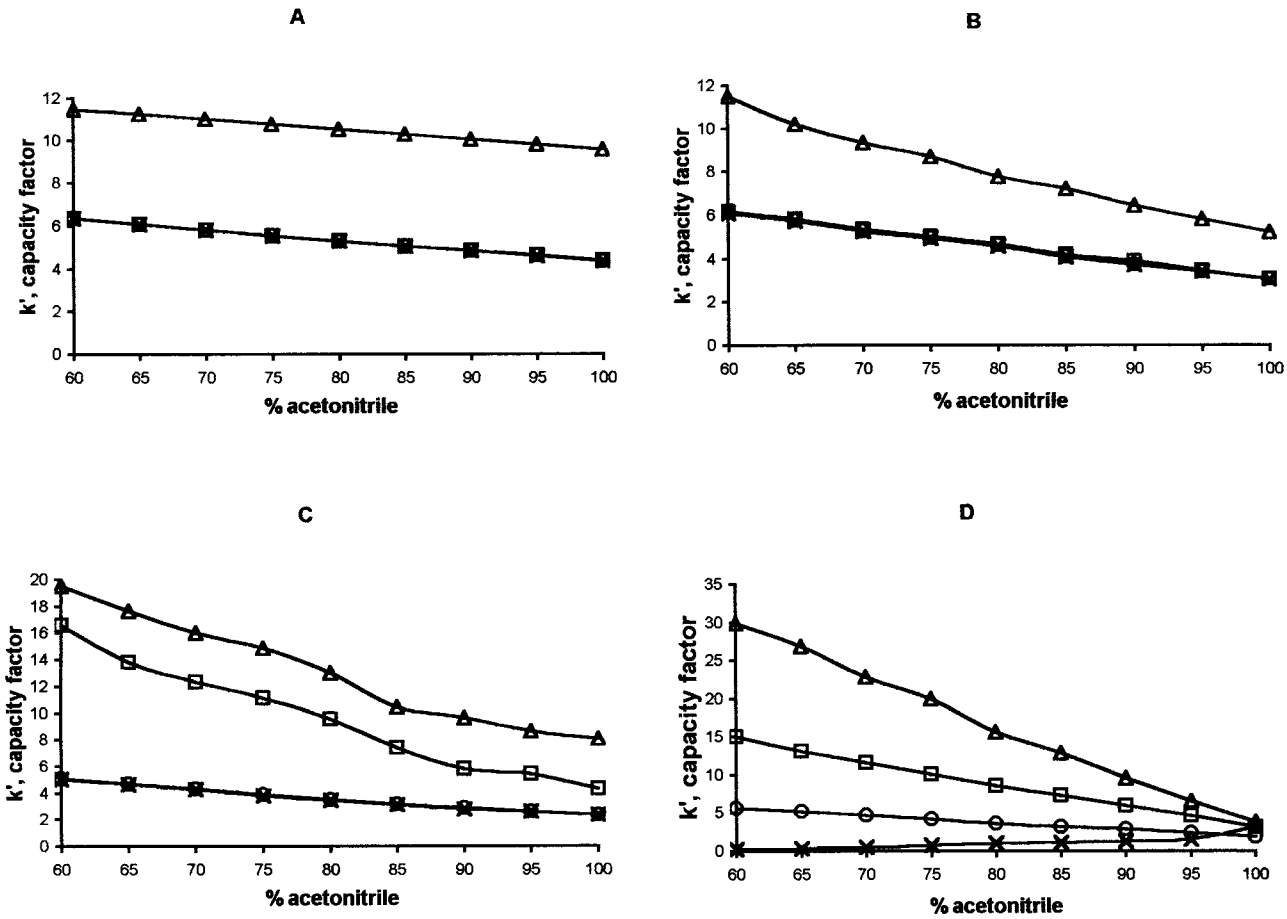

Figure 1. Effect of the acetonitrile–water composition on the separation of phenyltin compounds with various columns: (A) μBondapak (C_{18}); (B) Nova-Pak (C_{18}); (C) Inertsil ODS-2; (D) Waters Spherisorb S5W ODS-2; × Ph_3SnCl; ○ $Ph_3SnOCOCH_3$; □ Ph_3SnOH; △ Ph_4Sn.

pounds. Table 3 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 3. The relative standard deviations (RSD) were in the range 2–7% for all four phenyltin 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 4.

Analysis of mixtures of Ph_3SnOH with chloro-substituted phenyltin analogues

It was also of interest to enquire whether the favourable differentiation of the anionic residues attached to the triphenyltin moiety achieved by the direct HPLC method could also be obtained for substituent group variations on the phenyl ring. For this purpose, Ph_3SnOH was admixed with tris(*p*-chlorophenyl)tin hydroxide and diphenyl(*p*-chlorophenyl)tin hydroxide and the mixture analysed. The chloro-substituted phenyltin compounds were chosen on account of their reported lower phytotoxicity,[24] superior antifungal activity[25] and reduced genotoxic potential[26] compared with Ph_3SnOH. The binary 90:10 (v/v) acetonitrile–water mobile phase enabled excellent resolution of the compounds (Table 5). Reducing the water content to 2% permitted faster retention times inside 4 min; good resolution was also obtained, as exemplified by the chromatogram depicted in Fig. 3. Calibration and regression data of these compounds are shown in Table 6. The limits of detection, as tabulated in Table 7, compared favourably with those obtained for the title compounds (Table 4).

Analysis of spiked aqueous samples containing Ph_3SnCl, Ph_3SnOH and $Ph_3SnOCOCH_3$

The experiments here were guided by the work of Abolas *et al.*[27] who studied the effects of several extraction variables, such as acid concentration and strength, the presence of

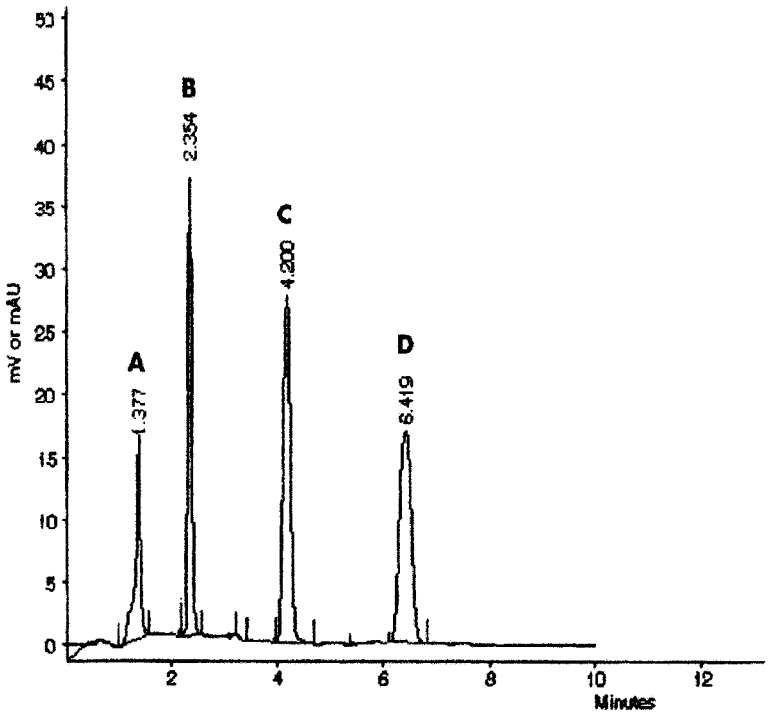

Figure 2. Chromatogram of a mixed standard solution of phenyltin compounds. (A) Ph_3SnCl (1.0 ppm); (B) $Ph_3SnOCOCH_3$ (1.0 ppm); (C) Ph_3SnOH (1.0 ppm); (D) Ph_4Sn (2.0 ppm) obtained with injection of 10 μl of standard solution. Column: Waters Spherisorb S5W ODS-2; mobile phase: 90:10 (v/v) acetonitrile–water; flow rate 1 ml min^{-1}; UV detection at 254 nm.

Table 2. Retention times of phenyltin compounds using the Waters Spherisorb S5W ODS-2 column. Conditions: 90:10 (v/v) acetonitrile–water, flow rate 1 ml min^{-1}, UV detection at 254 nm

Compound	Retention time (min)
Ph_3SnCl	1.38
$Ph_3SnOCOCH_3$	2.35
Ph_3SnOH	4.20
Ph_4Sn	6.42

Table 4. Limits of detection of phenyltin compounds

Compound	Limit of detection (ppm)
Ph_3SnCl	0.01
$Ph_3SnOCOCH_3$	0.01
Ph_3SnOH	0.01
Ph_4Sn	0.02

Table 3. Calibration curves ($y = A + Bx$)[a] and regression data for phenyltin compounds. Number of data points is ten

Compound	Concentration range (ppm)	Intercept A	Slope B	Correlation coefficient R^2
Ph_3SnCl	0.1–1.0	−181	101791	0.9999
	1.0–10.0	−1789	101742	0.9999
$Ph_3SnOCOCH_3$	0.1–1.0	822	181159	0.9998
	1.0–10.0	7678	180494	0.9998
Ph_3SnOH	0.1–1.0	−1507	273897	0.9997
	1.0–10.0	−14757	272371	0.9997
Ph_4Sn	0.1–1.0	731	120292	0.9998
	1.0–10.0	4348	120731	0.9998

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

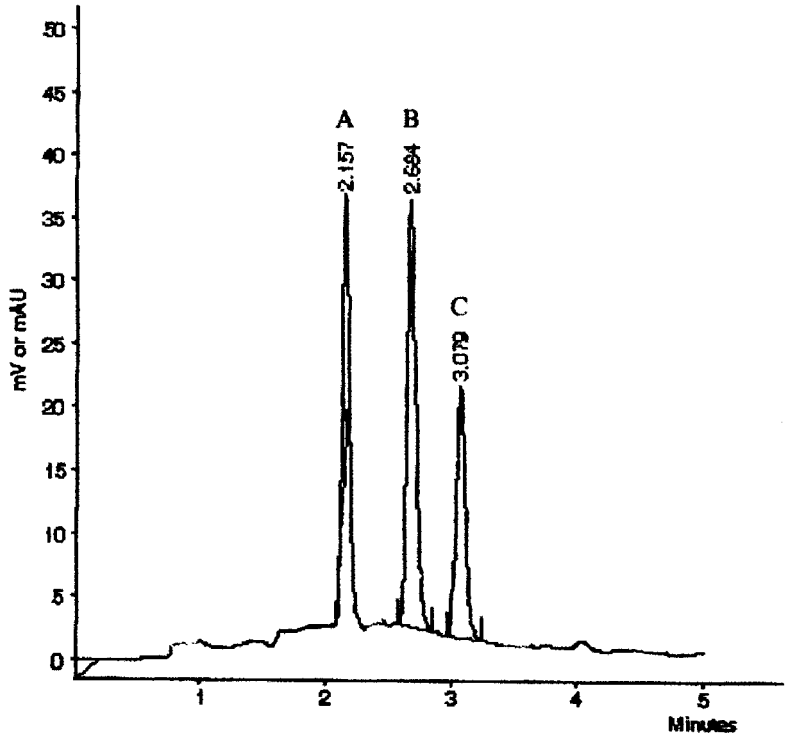

Figure 3. Chromatogram of a mixed standard solution of Ph_3SnOH with chloro-substituted phenyltin analogues. (A) (p-$ClC_6H_4)_3SnOH$ (0.3 ppm), (B) Ph_3SnOH (0.6 ppm) and (C) (p-$ClC_6H_4)Ph_2SnOH$ (0.4 ppm) obtained with injection of 20 μl of standard solution. Column: Waters Spherisorb S5W ODS-2; mobile phase: 98:2 (v/v) acetonitrile –water; flow rate 1 ml min^{-1}; UV detection at 254 nm.

Table 5. Retention times of Ph_3SnOH and chloro-substituted phenyltin analogues

Compound	Retention time (min)				
	100% CH_3CN (P' = 5.80)[a]	98:2 (v/v) CH_3CN:H_2O (P' = 5.89)[a]	95:5 (v/v) CH_3CN:H_2O (P' = 6.02)[a]	90:10 (v/v) CH_3CN:H_2O (P' = 6.24)[a]	88:12 (v/v) CH_3CN:H_2O (P' = 6.33)[a]
(p-$ClC_6H_4)_3SnOH$	2.11	2.16	2.25	2.45	2.53
Ph_3SnOH	2.52	2.68	3.42	4.22	4.60
(p-$ClC_6H_4)Ph_2SnOH$	2.90	3.08	4.38	5.88	6.57

[a] Solvent polarity parameter.[23]

Table 6. Calibration curves ($y = A + Bx$)[a] and regression data for Ph_3SnOH and chloro-substituted phenyltin analogues. Number of data points is ten

Compound	Concentration range (ppm)	Intercept A	Slope B	Correlation coefficient R^2
(p-$ClC_6H_4)_3SnOH$	0.1–1.0	146	172329	0.9999
	1.0–10.0	2593	172776	0.9998
Ph_3SnOH	0.1–1.0	−1785	273455	0.9998
	1.0–10.0	−20149	291566	0.9998
(p-$ClC_6H_4)Ph_2SnOH$	0.1–1.0	−577	253808	0.9998
	1.0–10.0	−7700	276669	0.9998

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

Table 7. Limits of detection of Ph_3SnOH and chloro-substituted phenyltin analogues

Compound	Limit of detection (ppm)
$(p\text{-}ClC_6H_4)_3SnOH$	0.02
Ph_3SnOH	0.01
$(p\text{-}ClC_6H_4)Ph_2SnOH$	0.02

Table 8. Recoveries of triphenyltin compounds with various extracting solvents[a]

Compound	Recovery (%)		
	Hexane	Toluene	Chloroform
Ph_3SnCl	66	72	50
$Ph_3SnOCOCH_3$	65	70	47
Ph_3SnOH	68	73	50

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

complexing agents in the extracting mixture and solvent polarity, for native butyl- and phenyl-tin compounds in marine sediments. According to these authors, the toluene–CH_3COOH mixture yielded the highest extraction efficiency for the analytes.

For the study at hand, toluene proved to be more efficient than either hexane or chloroform as the extractant (Table 8). The percentage recovery data were based on HPLC analysis using the 90:10 (v/v) acetonitrile–water mobile phase and performed under identical operating conditions as described in the above sections.

The recoveries with toluene were enhanced somewhat when the aqueous phase was pretreated with NH_4Cl and glacial CH_3COOH (Table 9). 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 88% for the title compounds (Table 10).

A fuller discussion on this aspect of the work, also embracing a wider range of triphenyltin compounds, will be reported in Part 3 of this work.[28] For the present, the data presented here serve to validate the application of this HPLC method to the analysis of the triphenyltin compounds in an aqueous environment without the need for any prior derivatization step.

Table 10. Effect of complexing agents[a] on toluene extraction of pretreated[b] aqueous sample

Compound	Recovery with toluene (%)		
	Tropolone	Oxine	HMPA
Ph_3SnCl	86	83	88
$Ph_3SnOCOCH_3$	85	82	87
Ph_3SnOH	86	84	89

[a] 0.05% v/v or w/v in toluene.
[b] NH_4Cl/CH_3COOH (see footnote of Table 9).

CONCLUSION

An HPLC–UV method for the simultaneous determination of phenyltin compounds has been developed. The method employs isocratic elution on a Waters Spherisorb S5W ODS-2 column and has enabled the successful resolution of standard mixtures of the industrially important chemicals Ph_4Sn, Ph_3SnCl, Ph_3SnOH and $Ph_3SnOCOCH_3$. The applicability of the technique for analysing spiked water samples containing the above-mentioned triphenyltin biocides, as well as for sensing substituent group variations on the phenyl ring, as exemplified by the resolution of a mixture of Ph_3SnOH with tris(*p*-chlorophenyl)tin hydroxide and diphenyl (*p*-chlorophenyl)tin hydroxide, has been demonstrated. The advantages of the method developed are its simplicity, non-requirement of any pre- or post-column derivatization and the ready availability of the necessary instrumentation.

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Table 9. Effect of modifiers and acids in aqueous pretreatment[a]

Compound	Recovery with toluene (%)				
	NaCl	NH_4Cl	$NH_4Cl + HCl$	$NH_4Cl + HNO_3$	$NH_4Cl + CH_3COOH$
Ph_3SnCl	74	75	75	76	78
$Ph_3SnOCOCH_3$	72	73	74	73	76
Ph_3SnOH	73	75	75	76	78

[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).

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