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Speciation and GC retention indices of some organotin compounds in water

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Analytical methods have been developed for the quantitative determination of Bu_4Sn, Bu_3Sn^+, Bu_2Sn^{2+}, $BuSn^{3+}$, Me_3BuSn, Me_2Bu_2Sn, $MeBu_3Sn$, $MeBuSn^{2+}$, Me_2BuSn^+ and $MeBu_2Sn^+$ in water. Organotin compounds are extracted from water with tropolone at 0.1 % in n-pentane, derivatized with n-pentylmagnesium bromide and determined by gas chromatography with flame photometric detection or flame ionization detection. Absolute detection limits are 0.05–0.12 ng and 1.2–13 ng as tin, respectively. The method was applied to the analysis of spiked tap-water containing 0.3–1000 ng cm^{-3} of each of the organotin compounds.

Keywords: Organotin determination, gas chromatography, water samples, speciation, analysis

INTRODUCTION

Organotin compounds are used mainly as thermal and light stabilizers for plastics like poly(vinyl chloride) (PVC), as catalysts in the production of polyurethane foams, and also as biocidal agents (antifouling paints and for plant protection).[1]

The effective concentration of tin in the water by an antifouling paint surface approaches 1 μg cm^{-3}, sufficient to prevent fouling organisms such as algae and barnacles from attaching themselves. However, very much lower concentrations, about 1 ng cm^{-3} in seawater, are lethal to the larvae of many non-target invertebrates.[2] Even lower concentrations in water may affect growth rate and reproduction of commercial shellfish.[3] For this reason, the environmental water pollution caused by organotin compounds has led to studies for checking the levels of organotin compounds and their degradation products in the marine environment.[4–7]

Total tin has been determined by atomic absorption (AA) spectrometry with hydride generation in marine organisms[8] in the range 0.01–1.25 μg g^{-1} and in river water,[9] and with a graphite furnace in fresh water[10] and biological materials.[10,11] But in environmental studies there is a need for analytical techniques applicable to the quantitative determination of several organotin species simultaneously.

Hodge *et al.*[12] determined inorganic tin(IV), methyltin, dimethyltin, butyltin and dibutyltin in seawater and fresh water by generating the hydrides, which were collected in a trap cooled with liquid nitrogen. The hydrides were separated on the basis of their different boiling points and determined by atomic absorption spectrometry. A similar method has been used by Balls[13] for

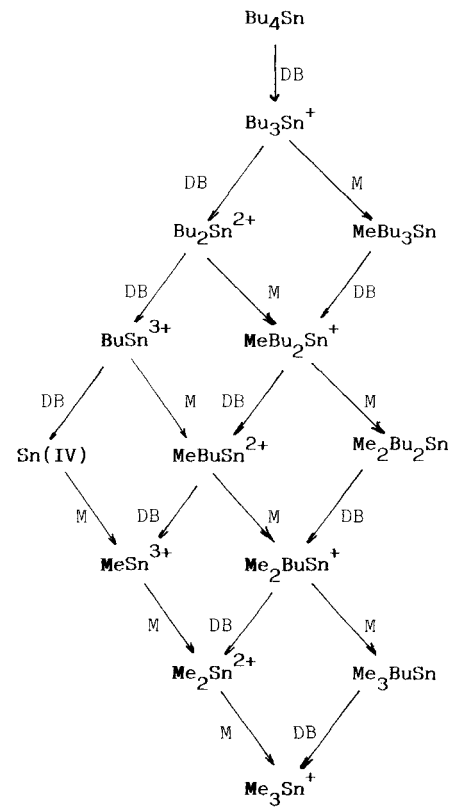

Figure 1 Degradation pathways for organotin compounds. DB, debutylation; M, methylation.

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determining tributyltin and dibutyltin in seawater, and by Chamsaz *et al.*[14] to analyse organotin compounds in seawater.

Gas liquid chromatography (GC) coupled to a variety of detectors has been demonstrated to be suitable for the quantitative speciation of tin, though for the analysis of some organotin compounds a prior derivatization is needed in order to produce volatile compounds. By using flame ionization detection (GC FID), Wollins and Cullen[15] proposed a method for the extraction from aqueous solution and subsequent determination of several organotin compounds of the type R_nSnX_{4-n} (R = Me, Et, Bu, Ph; $n = 2$, 3) by generating the corresponding hydrides, and Hansen *et al.*[16] determined tributyltin oxide in marine paints and triphenyltin hydroxide in apple-tree leaves. Gas chromatography–electron capture detection has also been applied to the determination of tributyltin in water,[17,18] seawater[19] and sediments.[18–21] Gas chromatography–mass spectrometry (GC MS) has been applied to the determination of butyltin compounds in water, after extraction with benzene in the presence of 0.05 % tropolone and methylation,[22] and of methyltin and butyltin species in natural waters.[23] Gas chromatography coupled to an atomic absorption spectrometer (GC AA) has been used by Chau *et al.*[24,25] for the determination of tin(IV) and methyltin compounds in several waters from harbours and heavily industrialized areas; by using 5–10 dm^3 of sample, Me_3Sn^+ was rarely found, but significant amounts of Me_2Sn^{2+} (0.02–0.40 $\mu g\ dm^{-3}$) and $MeSn^{3+}$ (0.06–1.22 $\mu g\ dm^{-3}$) were detected. Craig and co-workers[26] have achieved the determination of butyltin species based on a gas-chromatographic separation of the hydride or ethyl derivatives and detection by atomic absorption spectrometry.

Gas chromatography with flame photometric detection (GC FPD) has been used by Braman and Tompkins[27] for the determination of tin(IV) and methyltin compounds in a variety of samples, such as saline, estuarine, fresh, tap- and rainwaters, in shells and in human urine. They found that up to 60 % of the total tin in water was present in the methylated form, whilst in human urine only 18 % of it corresponded to methyltin forms. In sea shells, they found concentrations of

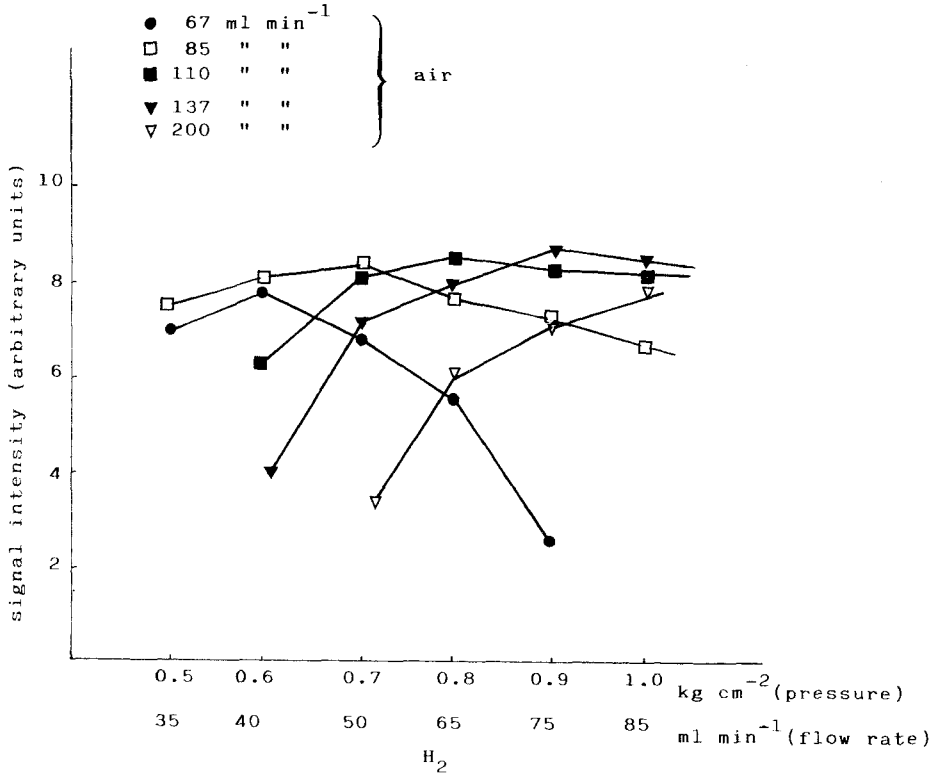

Figure 2 Effect of hydrogen and air flow rate on the FPD signal for Me_2Bu_2Sn. Air at: A, 67 $cm^3\ min^{-1}$; B, 85 $cm^3\ min^{-1}$; C, 110 $cm^3\ min^{-1}$; D, 137 $cm^3\ min^{-1}$; E, 200 $cm^3\ min^{-1}$.

Table 1 Retention times and Kovats retention indexes for organotin compounds

Compound	Retention time (min)[a]				Corrected Kovats retention index
	a	b	c	d	
Me_3BuSn	3.65	4.76	6.91	13.89	827.9
Me_2BuSn	6.30	8.90	12.22	33.19	1215.4
$Me_2BuPeSn$	7.11	10.20	13.86	39.41	1299.0
Me_2Pe_2Sn	7.90	11.43	15.40	45.29	1379.1
$MeBu_3Sn$	8.55	12.31	16.48	49.47	1443.1
$MeBu_2PeSn$	9.15	13.40	17.86	54.70	1531.8
$MeBuPe_2Sn$	9.80	14.45	19.15	59.66	1616.6
Bu_4Sn	10.22	15.01	19.84	62.78	1669.9
Bu_3PeSn	10.81	15.95	21.00	66.84	1758.8
Bu_2Pe_2Sn	11.29	16.85	22.11	71.02	1843.8
$BuPe_3Sn$	11.87	17.70	23.18	75.06	1925.7

[a]Conditions: a, initial temperature 50 °C, rate 16 °C min^{-1}; b, initial temperature 50 °C, rate 10 °C min^{-1}; c, initial temperature 35 °C, rate 8 °C min^{-1}; d, initial temperature 35 °C, rate 2 °C min^{-1}. A 12 m × 0.53 mm i.d. BP − 1 glass capillary column was used.

methyltin compounds higher than those detected in the water in which they were collected, indicating the existence of a bioaccumulation process. They also detected other organotin compounds, but identification was not achieved. Maguire and Huneault,[28] also using GC FPD, proposed a method for the determination of tin(IV) and butyltin compounds in water by making the n-pentyl derivatives. When they applied this method to the analysis of water from Ontario lakes and rivers, they found concentrations of butyltin compounds in surface water 10^4 times greater than in subsurface water. GC FPD has also been applied to the analysis of organotins in fish[29,30] and harbour water.[31]

Our approach was to develop a GC FPD method for the determination in water of Bu_4Sn, Bu_3Sn^+ and their degradation products, arising either from dealkylation or from methylation. Figure 1 shows the possible pathways in the degradation of either Bu_4Sn or Bu_3Sn^+. Debutylation of Bu_3Sn^+ is well known,[1] and several reports have been published on the biomethylation[1,32–34] and chemical methylation[35,36] of inorganic and organic tin compounds.

Tetra-alkyltin can be readily extracted and analysed by gas chromatography, but the determination of tri-, di- and mono-alkyltin species requires derivatization in order to obtain volatile compounds. We chose to make the n-pentyl derivatives, since some ethyl and propyl derivatives are volatile enough to be lost during routine concentration procedures.[28] In this way, and by using GC FPD or GC FID, the quantitative and simultaneous determination in water of ten organotin compounds of the type Bu_4Sn, Bu_3Sn^+, Bu_2Sn^{2+}, $BuSn^{3+}$, Bu_3MeSn, Bu_2Me_2Sn, $BuMe_3Sn$, Me_2BuSn^+, $MeBu_2Sn^+$ and $MeBuSn^{2+}$ is feasible. Inorganic tin(IV) was not included in the determination because of its low toxicity. Besides, the determination of tin(IV) requires the use of very pure reagents in order to avoid very high tin blanks.[24,27]

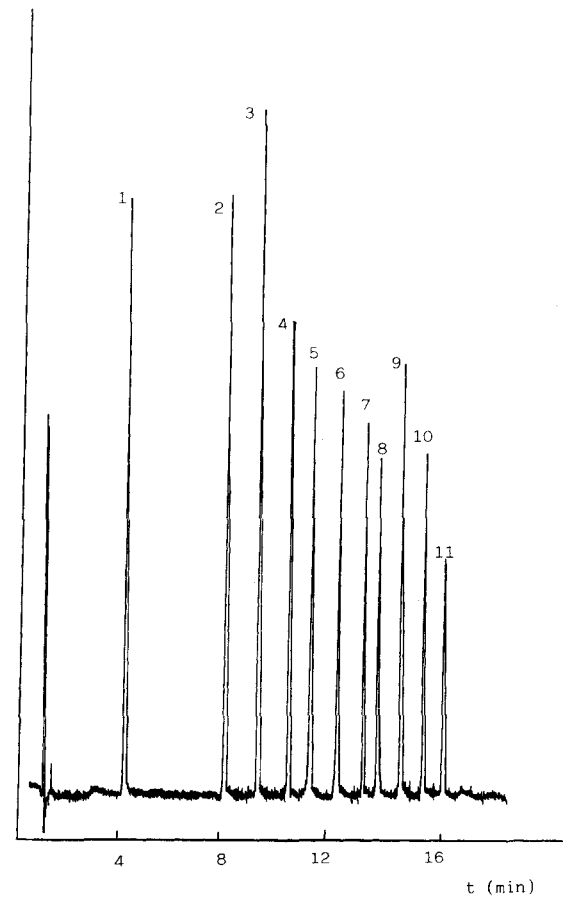

Figure 3 GC FPD programmed temperature chromatogram of organotin compounds using a 610 nm filter. 1, Me_3BuSn (20.6 ng); 2, Me_2Bu_2Sn (28.8 ng); 3, $Me_2BuPeSn$ (40.3 ng); 4, Me_2Pe_2Sn (28.0 ng); 5, $MeBu_3Sn$ (30.0 ng); 6, $MeBu_2PeSn$ (29.6 ng); 7, $MeBuPe_2Sn$ (31.2 ng); 8, Bu_4Sn (27.6 ng); 9, Bu_3PeSn (42.3 ng); 10, Bu_2Pe_2Sn (33.3 ng); 11, $BuPe_3Sn$ (32.3 ng).

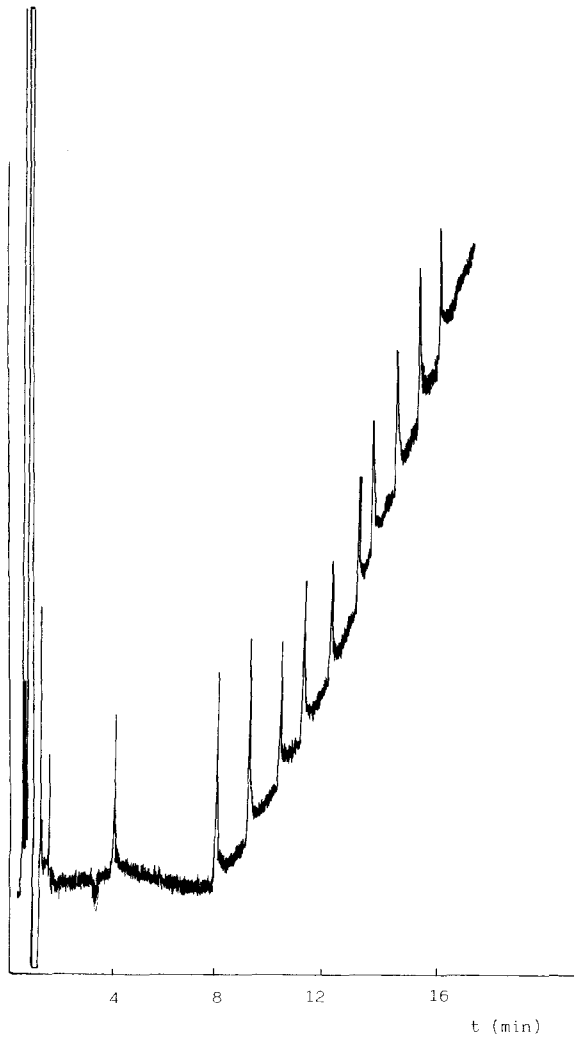

Figure 4 GC FPD programmed temperature chromatogram of about 5 ng of each of the organotin compounds using a $\frac{1}{8}$ in (0.32 cm) pin hole. Elution in the same order as in Fig. 3.

EXPERIMENTAL

Apparatus

A Shimadzu GC8A-FP gas chromatograph was equipped with a flame photometric detector with an EMI 9601B photomultiplier (range 300–800 nm, maximum at 380 nm) and 610 nm interference filter (Infrared Engineering), and a glass capillary column (12 m × 0.53 mm i.d. coated with a 3.0 μm film of BP-1). F33 Perkin Elmer gas chromatograph was equipped with a flame ionization detector and a glass capillary column (7 m × 0.23 mm i.d. coated with a 0.25 μm film of BP-1).

Reagents

Bu_4Sn, Bu_3SnCl, Bu_2SnCl_2, $BuSnCl_3$, Me_2SnCl_2, tropolone (2-hydroxy-2,4,6-cycloheptatrien-1-one) and n-pentyl bromide (PeBr) were obtained from Aldrich. Bu_4Sn, Bu_3SnCl and $BuSnCl_3$ were purified by distillation at reduced pressure. Bu_2SnCl_2 was recrystallized from hexane.

The standards $MeBu_3Sn$, Me_2Bu_2Sn and Me_3BuSn were prepared by Grignard methylation of Bu_3SnCl, Bu_2SnCl_2 and $BuSnCl_3$ respectively. Bu_3PeSn, Bu_2Pe_2Sn, $BuPe_3Sn$, $MeBuPe_2Sn$, $MeBu_2PeSn$, $Me_2BuPeSn$ and Me_2Pe_2Sn were obtained by Grignard n-pentylation of Bu_3SnCl, Bu_2SnCl_2, $BuSnCl_3$, $MeBuSnI_2$, $MeBu_2SnI$, Me_2BuSnI and Me_2SnCl_2 respectively. The detailed synthesis and purification of these standards have been described previously.[37] All standards were ⩾95% pure by GC FID and GC FPD. Solutions of these compounds containing 500–0.2 μg cm^{-3} were prepared in hexane.

Me_2SnCl_2 was used as an internal standard. This compound was recrystallized from hexane and kept under a nitrogen atmosphere over silica gel. Standard stock solutions of this compound (*ca* 50 μg cm^{-3}) in absolute ethanol were prepared weekly.

Solutions of 0.1 % tropolone in n-pentane or toluene were prepared immediately before use, since these solutions have been reported to be fairly unstable.[28]

Solutions of 1 M n-pentylmagnesium bromide in diethyl ether were prepared in the normal manner by reaction of n-pentyl bromide with magnesium metal. This solution was prepared weekly and

Table 2 Response factors by GC FPD for organotin compounds

	Response factor relative to Bu_4Sn		Response for 10 ng of tin	
Compound	Area	Height	Area	Height
Me_3BuSn	2.57	2.34	10 105	1753
Me_2Bu_2Sn	2.00	1.72	9350	1533
$Me_2BuPeSn$	2.01	1.35	9894	1269
Me_2Pe_2Sn	1.35	1.26	7378	1262
$MeBu_3Sn$	1.34	1.16	7248	1202
$MeBu_2PeSn$	1.00	1.12	5645	1212
$MeBuPe_2Sn$	1.02	0.93	6061	1049
Bu_4Sn	1.00	1.00	6184	1181
Bu_3PeSn	1.78	0.83	11 472	1013
Bu_2Pe_2Sn	1.65	0.86	11 000	1093
$BuPe_3Sn$	1.43	0.61	9902	813

Table 3 GC FPD response curve data for organotin compounds by using peak areas

Compound	Linear range (ng)	Correlation coefficient	MDQ[a] (ng)		RSD[b] (%)
			As compound	As tin	
Me_3BuSn	0.4–85	1.0000	0.1	0.05	4.8
Me_2Bu_2Sn	0.6–120	1.0000	0.2	0.09	4.2
$Me_2BuPeSn$	0.6–125	0.9999	0.2	0.08	8.0
$MeBu_3Sn$	0.7–140	1.0000	0.3	0.12	5.8
$MeBu_2PeSn$	0.7–140	0.9999	0.3	0.11	3.1
$MeBuPe_2Sn$	0.7–75	0.9998	0.3	0.11	5.8
Bu_4Sn	0.7–70	0.9998	0.3	0.10	7.8
Bu_3PeSn	0.9–90	0.9998	0.2	0.06	6.5
Bu_2Pe_2Sn	1.3–75	1.0000	0.2	0.06	4.1
$BuPe_3Sn$	0.9–90	1.0000	0.3	0.09	8.5

[a]Minimum detectable quantity, evaluated as the amount of organotin that gives a signal three times higher than the noise level. [b]Evaluated by five injections of 6 ng of each of the organotin compounds.

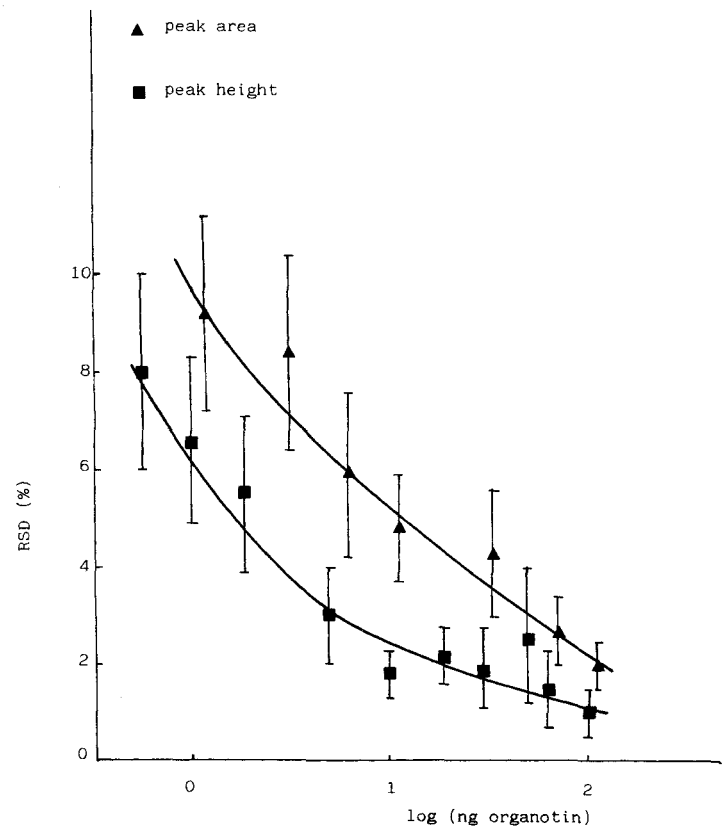

Figure 5 *Relative standard deviation as a function of the amount of organotin injected* by GC FPD and using Me_2Pe_2Sn as internal standard. A, using peak height; B, using peak area. Every point shows the mean and the standard deviation of the relative standard deviations obtained by five injections of each of the ten organotin compounds studied.

Table 4 Retention times and response factors by GC FID for organotin compounds

Compound	Retention time (min)[a]	Response factor relative to Bu_4Sn	Response for 100 ng of tin
Me_3BuSn	2.45	1.01	9468
Me_2Bu_2Sn	8.15	1.17	12 970
$Me_2BuPeSn$	10.20	1.04	12 186
Me_2Pe_2Sn	12.15	1.01	12 980
$MeBu_3Sn$	13.54	1.01	13 111
$MeBu_2PeSn$	15.31	1.01	13 576
$MeBuPe_2Sn$	16.90	0.89	12 476
Bu_4Sn	17.90	1.00	14 649
Bu_3PeSn	19.26	0.96	14 542
Bu_2Pe_2Sn	20.50	0.99	15 624
$BuPe_3Sn$	21.62	0.86	14 148

[a]Initial temperature 50 °C, rate 10 °C min^{-1}. A 7 m × 0.23 mm i.d. BP-1 glass capillary column was used.

shown to contain small amounts of Pe_4Sn, probably from tin contamination in the magnesium metal employed.

All glassware was washed with distilled water, ethanol and diethyl ether in this order, to avoid possible cross-contamination between samples.

Extraction and pentylation procedures

Between 100 and 1000 cm^3 of distilled or tap-water spiked with organotin compounds was placed in a suitable separating funnel. The walls of the sample vessel were rinsed with 5–20 cm^3 of 48 % hydrobromic acid, which was added to the sample and the mixture allowed to stand for

Table 5 GC FID response curve data for organotin compounds by using peak areas

Compound	Linear range (ng)	Correlation coefficient	MDQ[a] (ng)	
			As compound	As tin
Me_3BuSn	30–1900	0.9999	25	13.4
Me_2Bu_2Sn	30–1600	0.9996	20	9.0
$Me_2BuPeSn$	30–1600	0.9999	24	10.3
$MeBu_3Sn$	20–1700	0.9999	13	5.1
$MeBu_2PeSn$	20–1700	0.9999	13	4.8
$MeBuPe_2Sn$	20–1800	0.9998	14	5.0
Bu_4Sn	15–1700	0.9996	6	2.0
Bu_3PeSn	10–1700	0.9994	7	2.3
Bu_2Pe_2Sn	10–1700	0.9996	4	1.3
$BuPe_3Sn$	10–1700	0.9999	4	1.2

[a]Minimum detectable quantity, evaluated as the amount that gives a signal three times higher than the noise level in the region in which the peak appears.

Table 6 Recovery of organotin compounds by using toluene and n-pentane as extractants and concentrating[a] to 1 cm^3

Compound	Recovery[b] (%)	
	Toluene	n-Pentane
Me_3BuSn	3	94
Me_2Bu_2Sn	11	95
Me_2BuSn^+	81	100
$MeBu_3Sn$	99	102
$MeBu_2Sn^+$	94	102
$MeBuSn^{2+}$	97	96
Bu_4Sn	107	100
Bu_3Sn^+	107	102
Bu_2Sn^{2+}	103	103
$BuSn^{3+}$	102	102

[a]Samples of 100 cm^3 of distilled water containing about 50 ng cm^{-3} of each of the organotin compounds. [b]Single determination by using 4.8 μg of Me_2SnCl_2 as internal standard.

15 min. It was then extracted twice with 15–20 cm^3 portions of a 0.1 % solution of tropolone in n-pentane, shaking vigorously for 1–2 min. The combined pentane phases were placed in a 250 cm^3 round-bottom flask, together with a suitable amount (~5 μg) of Me_2SnCl_2 dissolved in absolute ethanol, and were treated with 20 cm^3 of 1M-pentylmagnesium bromide solution in diethyl ether. The mixture was refluxed, under constant stirring for 1 h. Afterwards, the excess of Grignard reagent was destroyed by slowly adding 25 cm^3 of 0.5M sulphuric acid, the organic phase separated and the aqueous phase extracted twice with 10 cm^3 of diethyl ether. The combined organic phase was dried over anhydrous $MgSO_4$, placed in a Wheaton flask, and the $MgSO_4$ rinsed with 3 cm^3 of diethyl ether, which was also added to the organic phase. Then it was concentrated at reduced pressure and room temperature to about 1 cm^3, the glass walls of the flask rinsed with about 3 cm^3 of diethyl ether, the organic solution concentrated again to about 1 cm^3, the lower glass walls rinsed again with about 0.5 cm^3 of diethyl ether and the extract concentrated to exactly 1.0 cm^3, adding some diethyl ether to dilute to the mark if necessary. The extract was then ready for gas chromatographic analysis as described below.

GC FID and GC FPD conditions

For GC FID, the following conditions were used: injector and detector temperature 200 °C; initial column temperature 50 °C; heating rate 10 °C min^{-1} up to 250 °C; helium flow rate

through the column 3.8 $cm^3 min^{-1}$ and 110 $cm^3 min^{-1}$ through the splitter.

For GC FPD, the injector, detector, column temperatures and heating rate were held as for GC FID. Helium was also used as carrier gas, at a flow rate through the column of 8.5 $cm^3 min^{-1}$, and 37 $cm^3 min^{-1}$ through the splitter. Hydrogen and air flow rates for the flame photometric detector were 50 and 85 $cm^3 min^{-1}$, respectively.

Aliquots of 5–10 µl were injected, and peak areas when using GC FID or peak heights when using GC FPD were recorded. The amounts of organotins were determined from suitable calibration graphs using Me_2Pe_2Sn as internal standard.

RESULTS AND DISCUSSION

Gas chromatography with flame photometric detection

Optimization of tin response

Me_2Bu_2Sn was used to optimize hydrogen and air flow rates to the FPD. Maximum signal was obtained by using 85–110 $cm^3 min^{-1}$ of air and 40–85 $cm^3 min^{-1}$ of hydrogen (Fig. 2). Since noise increased when hydrogen flow rate increased, 50 $cm^3 min^{-1}$ of hydrogen and 85 $cm^3 min^{-1}$ of air were chosen. Under these conditions 5 µl of hexane or pentane can be injected without solvent flameout. Tests were also made by reversing the

Table 7 GC FPD recovery or organotin compounds from tap-water[a]

	Sample 1		Sample 2		Sample 3		Sample 4		Sample 5	
Compound	Added	Found	Added	Found	Added	Found	Added	Found	Added	Found
Me_3BuSn	850	865 ± 18	250	243 ± 9	125	120 ± 1	75.0	70.5 ± 2.9	—	0.4
Me_2Bu_2Sn	600	605 ± 11	218	218 ± 9	109	103 ± 2	65.4	63.1 ± 2.1	21.8	20.9 ± 1.8
Me_2BuSn^+	840	852 ± 19	168	158 ± 4	84	84 ± 2	50.4	50.2 ± 1.1	16.8	16.3 ± 1.4
$MeBu_3Sn$	630	627 ± 8	226	217 ± 7	113	112 ± 2	67.8	69.1 ± 1.6	22.6	21.7 ± 1.0
$MeBu_2Sn^{2+}$	948	941 ± 24	190	179 ± 6	95	89 ± 1	66.9	68.3 ± 2.3	19.0	18.3 ± 0.9
$MeBuSn^+$	582	590 ± 20	116	112 ± 4	58	56 ± 2	46.6	48.3 ± 1.0	11.6	12.1 ± 0.9
Bu_4Sn	1070	1086 ± 41	214	216 ± 7	107	114 ± 2	64.2	64.4 ± 0.9	21.4	21.7 ± 1.8
Bu_3Sn^+	953	951 ± 32	190	188 ± 6	95	91 ± 3	57.2	58.5 ± 1.3	19.1	20.4 ± 1.9
Bu_2Sn^{2+}	1019	1046 ± 34	204	215 ± 6	102	105 ± 3	61.2	62.8 ± 2.5	20.4	18.7 ± 1.8
$BuSn^{3+}$	685	685 ± 22	137	141 ± 3	68	58 ± 2	54.8	56.0 ± 3.0	13.7	14.0 ± 1.5
	Sample 6		Sample 7		Sample 8		Sample 9		Sample 10	
Compound	Added	Found	Added	Found	Added	Found	Added	Found	Added	Found
Me_3BuSn	7.5	8.2 ± 1.1	5.1	4.3 ± 1.0	6.8	7.1 ± 0.5	1.70	1.16 ± 0.29	0.51	0.80 ± 0.06
Me_2Bu_2Sn	6.5	6.9 ± 0.8	7.2	6.4 ± 1.1	3.0	3.2 ± 0.6	1.20	1.03 ± 0.30	0.36	0.31 ± 0.12
Me_2BuSn^+	5.0	5.0 ± 1.3	6.7	6.2 ± 0.4	4.2	4.5 ± 0.5	1.68	1.44 ± 0.34	0.54	0.77 ± 0.17
$MeBu_3Sn$	6.8	6.1 ± 0.4	10.1	11.1 ± 0.4	3.1	2.7 ± 0.3	1.26	1.05 ± 0.21	0.38	0.26 ± 0.09
$MeBu_2Sn^+$	5.7	5.5 ± 1.0	5.7	5.0 ± 0.8	4.7	4.4 ± 0.4	1.90	1.60 ± 0.20	0.57	0.55 ± 0.11
$MeBuSn^{2+}$	3.5	3.7 ± 0.5	3.5	3.4 ± 0.8	4.7	4.8 ± 0.5	1.16	0.98 ± 0.09	0.36	0.34 ± 0.06
Bu_4Sn	6.4	7.6 ± 0.6	17.1	17.8 ± 1.7	5.3	5.7 ± 0.3	2.14	2.10 ± 0.15	0.64	0.35 ± 0.10
Bu_3Sn^+	5.7	6.0 ± 0.9	38.1	41.1 ± 0.6	190.7	188.8 ± 6.3	1.91	1.78 ± 0.05	0.57	0.53 ± 0.08
Bu_2Sn^{2+}	6.1	6.2 ± 0.4	30.6	30.3 ± 0.5	20.4	19.9 ± 1.1	2.04	2.10 ± 0.10	0.61	0.48 ± 0.02
$BuSn^{3+}$	4.1	3.6 ± 0.6	5.5	5.1 ± 0.7	3.4	3.7 ± 0.3	1.37	1.26 ± 0.04	0.41	0.57 ± 0.06

[a]All concentrations in ng cm^{-3}. Sample volumes: 20 cm^3 for sample 1, 100 cm^3 for samples 2–8 and 1000 cm^3 for samples 9, 10. Results are given as $\bar{x} \pm s$ of three determinations.

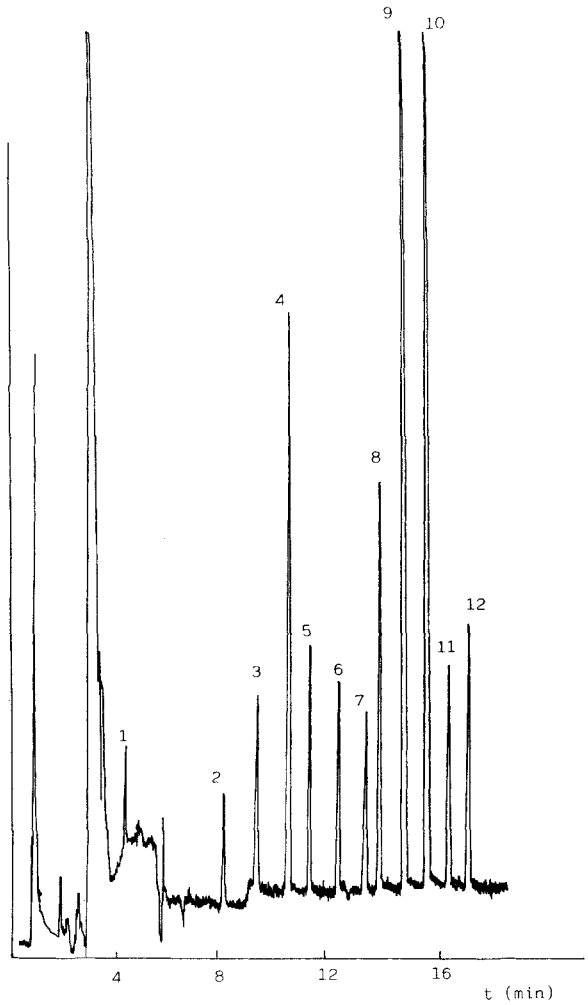

Figure 6 GC FPD chromatogram of water sample 7. 1, Me_3BuSn; 2, Me_2Bu_2Sn; 3, $Me_2BuPeSn$; 4, Me_2Pe_2Sn (internal standard); 5, $MeBu_3Sn$; 6, $MeBu_2PeSn$; 7, $MeBuPe_2Sn$; 8, Bu_4Sn; 9, Bu_3PeSn; 10, Bu_2Pe_2Sn; 11, $BuPe_3Sn$; 12, impurities of Pe_4Sn.

hydrogen and air inlets, which has been reported to increase signal-to-noise ratios and eliminate solvent flameout problems.[25,28,38] The results were unsatisfactory because flameout was produced even with 1 μl injections. This was probably due to the design of the Shimadzu burner used; this is very different from those employed in those earlier studies.

In order to achieve good resolution of the peaks, different conditions were tested. An injector and detector temperature of 200 °C was found to be the lowest for not getting broad peaks. Four different temperature programs were tested. The retention times for the organotin compounds, as well as the Kovats retention indices, are shown in Table 1. A good separation was achieved by using an initial column temperature of 50 °C and a heating rate of 10 °C min^{-1} (Fig. 3). By stopping the program at 250 °C every chromatogram took 20 min and only 10 min was needed to cool the oven back to 50 °C. Further cooling of the oven to 35 °C required another 10 min. Under these conditions reproducibility of retention times was very good, all peaks appearing in ranges of ±0.03 min.

After flow rates and temperature conditions were optimized, the detector performance was tested by using a 610 nm interference filter [maximum transmission (82%) at 610 nm] or a round sheet of metal foil which had a $\frac{1}{8}$ in (0.32 cm) or $\frac{1}{16}$ in (0.16 cm) diameter hole in the centre. A good response was obtained with the $\frac{1}{8}$ in pin hole: but the detector became 100 times more sensitive to hydrocarbons than by using the interference filter, and the signal-to-noise ratio was 3 times lower. By using the 610 nm filter the peaks were close to symetrical (fig. 3), whereas with the $\frac{1}{8}$ in pin hole they tailed badly and the baseline drifted strongly (Fig. 4). These results disagree with those obtained by other other authors, who found that the *open mode* technique (no filter) provided the best overall performance,[39,40] probably because of the different configuraiton of the Shimadzu burner. Besides, the photomultipliers used in that work showed a very low response at 610 nm.

The response of this detector, using either peak areas or peak heights, is quite variable depending on the organotin injected (Table 2) and, though it is more homogeneous when referred to a fixed amount of tin in the compound, the response is still not strictly proportional to the tin content.

Calibration, precision and detection limits

GC FPD calibration curves for the organotin compounds studied, when using peak areas, were linear within the concentration range given in Table 3. The minimum detectable quantities estimated are based upon the amounts which give signals three times higher than the noise level.

In order to improve the accuracy of the determination, Me_2Pe_2Sn was used as internal standard. The calibration curve for this compound, using either areas or peak heights, was linear within the range 0.7–130 ng of Me_2Pe_2Sn, with a correlation coefficient of 0.9997. The minimum detectable quantity was 0.2 ng (0.08 ng of tin), and in the determination of 6.0 and 18.0 ng of Me_2Pe_2Sn, the relative standard deviations

were 6.6 and 3.8 % respectively when using areas, and 3.0 and 2.1 % respectively when using peak heights (ten injections). When using Me_2Pe_2Sn as internal standard, calibration curves were linear within the range 0.6–100 ng of each of the organotin compounds, either using areas or peak heights, with correlation coefficients of 0.9997–1.0000. Minimum detectable quantities are depicted in Table 3.

Relative standard deviations were lower by using peak heights than by using areas (Fig. 5), and they were about half those when the internal standard was not used. For this reason, in all further work Me_2Pe_2Sn (or Me_2SnCl_2 if a pentylation step was involved) was used as internal standard and peak heights were recorded.

Gas chromatography with flame ionization detection

For the GC FID determination of organotins, conditions were chosen similar to those described for the GC FPD. The only differences were the flow rates, specially in the splitter flow rate, which was increased up to 110 $cm^3 min^{-1}$ of helium in order to achieve a good separation between the solvent peak and the Me_3BuSn peak. The response of this detector when using peak areas is quite similar for all the organotin compounds (Table 4), but different when it is referred to a fixed amount of tin, obviously because this is a carbon-sensitive and not a tin-sensitive detector. The retention times, under the GC FID conditions used, are shown also in Table 4. By GC FID, Me_2Pe_2Sn was also used as internal standard. Similar results were obtained by recording either peak heights or peak areas but, because by using areas slightly lower relative standard deviations were obtained, these were recorded in all further work. The results obtained from the calibration graphs are shown in Table 5.

Extraction from water and pentylation procedures

Solutions of tropolone in benzene have been used to extract methyltin[24] and butyltin[22] species from water acidified with hydrobromic acid (HBr). Other solvents such as hexane,[24] pentane,[41] toluene, chloroform and methylene chloride,[22] in combination with tropolone, have been reported to extract the organotin compounds with good recoveries. Our work was centered on the use of 0.1 % tropolone solutions in toluene or pentane, discarding benzene *a priori* because of its toxicity, and chloroform and methylene chloride because they react with the Grignard reagent. Hexane was not tested because its properties are similar to those of pentane. Toluene has been reported to interfere with the detection of Me_3BuSn, since both compounds have similar retention times in gas chromatography,[22] but with the capillary column used in this work a satisfactory separation was achieved.

Because some organotin compounds are fairly volatile, especially the methyltin compounds, they can be lost during solvent stripping. Experiments were carried out with 10 cm^3 of toluene or pentane spiked with 10 μg of each of the organotin compounds and concentrating the solution to small volumes. The results showed that a significant amount of Me_3BuSn was lost when the toluene extract was reduced to 3 cm^3, but no losses were observed by using pentane, even concentrating to 1 cm^3. Furthermore, when 100 cm^3 of spiked distilled water containing about 50 ng cm^{-3} of each of the organotins was treated according to the recommended procedure but using toluene as extracting solvent, and the organic phase reduced to 1 cm^3, low recoveries weere detected for Me_3BuSn, Me_2Bu_2Sn and Me_2BuSn^+ (Table 6). On the other hand, no significant losses were observed when pentane was used, and the concentration step took only a quarter of the time required for toluene. Therefore pentane was selected as extractant solvent.

The internal standard Me_2Pe_2Sn was added to the extracts just before the pentylation step. It must not be added to the water sample because HBr suppresses the extraction of this species,[24] whilst for the recovery of $BuSn^+$ and Bu_2Sn^{2+} the presence of HBr[22] is necessary.

Derivatization was carried out under refluxing conditions to ensure the quantitative reaction of the di- and mono-alkyltin species.[28] The yield of derivatization for Me_2SnCl_2 to give Me_2Pe_2Sn, tested through all this work, was 99 ± 3 %. To destroy the excess of Grignard reagent 25 cm^3 of 0.5 M-sulphuric acid (H_2SO_4) was employed. After separation of the organic layer, the remaining organotin compounds in the aqueous phase were extracted with diethyl ether, because in a preliminary study it was found that this solvent can recover high amounts of tetra-alkyltin compounds with a single extraction.

Recovery of organotin compounds from glass vessels

Recovery of organotin compounds has been reported to decrease slowly with time due to adsorption onto the glass wall of the vessel.[22] In order to find a safe time of storage, samples were prepared in distilled water and analysed three hours one day and four days after they were spiked with about 20 μg of each of the organotin compounds. They were analysed according to the recommended procedure and the results obtained showed that no significant losses of organotins were produced over a period of four days. This could be due to the HBr added to rinse the glass walls. Storing of samples acidified with HBr has also been reported.[22] Other authors[25,27] stored samples at low temperatures until analysis was performed.

Determination of organotin species in tap-water

To test the practical utility of the method, a series of experiments was carried out by analysing Aberdeen tap-water spiked with organotin compounds. Table 7 shows the results obtained by GC FPD. Satisfactory results were obtained by analysing 100 cm^3 samples containing 3.0–1000 ng cm^{-3} of each of the organotin compounds, but for the determination of lower concentrations, 0.3–2 ng cm^{-3}, 1 dm^3 of water was employed. The sensitivity of the method, by using one litre of sample, is about 0.05 ng cm^{-3}. This sensitivity can be improved by using larger water samples, although the use of larger volumes becomes cumbersome and a decrease in accuracy has to be expected. Actually, in the analysis of Sample 10 (about 0.5 ng cm^{-3}), recoveries were within the range 55–157 %, with relative standard deviations of 4–33 %. Samples 7 and 8 were prepared simulating the composition of waters contaminated with butyltin compounds, in which biochemical degradation has produced small amounts of other organotin species. As was expected because of the good separation between peaks, no overlapping problems were detected (Fig. 6), and good results were obtained in the determination of all the organotins.

The extracts obtained from Samples 1–4 were also analysed by GC FID. The results obtained are shown in Table 8. The determinations with this detector are rather difficult because a large number of other peaks appears in the chromatogram, and it is impossible for Me_3BuSn because this compound shows up together with the by-products of the Grignard pentylation. For the other organotin compounds, and by using 100 cm^3 samples, the sensitivity of the method is about 30 ng cm^{-3}. The use of greater volumes of sample is not recommended because the noise level would increase proportionally.

CONCLUSIONS

With the analytical methods described in this report, trace amounts of ten organotin species of the type Bu_4Sn, Bu_3Sn^+, Bu_2Sn^{2+}, $BuSn^{3+}$, Me_3BuSn, Me_2Bu_2Sn, $MeBu_3Sn$, Me_2BuSn^+, $MeBu_2Sn^+$ and $MeBuSn^{2+}$, either individually or simultaneously present in aqueous solutions, can

Table 8 GC FID recovery of organotin compounds from tap-water[a]

	Sample 1		Sample 2		Sample 3		Sample 4	
Compound	Added	Found	Added	Found	Added	Found	Added	Found
Me_3BuSn	850	—	250	—	125	—	75.0	—
Me_2Bu_2Sn	600	604 ± 15	218	216 ± 8	109	110 ± 7	65.4	78.2 ± 1
Me_2BuSn^+	840	857 ± 15	168	167 ± 7	84	88 ± 7	50.4	60.7 ± 0
$MeBu_3Sn$	630	628 ± 14	226	225 ± 9	113	116 ± 8	67.8	72.2 ± 2
$MeBu_2Sn^+$	948	938 ± 20	190	189 ± 3	95	94 ± 4	66.9	67.2 ± 1
$MeBuSn^{2+}$	582	590 ± 15	116	120 ± 6	58	53 ± 2	46.6	48.8 ± 2
Bu_4Sn	1070	1074 ± 19	214	208 ± 4	107	109 ± 3	64.2	55.8 ± 5
Bu_3Sn^+	953	943 ± 24	190	185 ± 5	95	94 ± 4	57.2	54.7 ± 4
Bu_2Sn^{2+}	1019	1027 ± 14	204	230 ± 9	102	105 ± 4	61.2	62.1 ± 1
$BuSn^{3+}$	685	686 ± 20	137	141 ± 6	68	67 ± 3	54.8	51.7 ± 3

[a]All concentrations in ng cm^{-3}. Sample volumes: 200 cm^3 for sample 1 and 100 cm^3 for samples 2–4. Results are given as $\bar{x} \pm s$ of three determinations.

be accurately determined. The methods can be extended without any modification to the determination of inorganic tin(IV) and other organotin species, such as mono-, di- and tri-phenyltin compounds, though for the determination of tin(IV), magnesium free of tin has to be used for the preparation of the Grignard reagent, and every chromatogram would take about 30 min for the determination of phenyltin compounds.

The method has proved to be applicable to samples much more highly contaminated than tap-water. Salmon tissue has been analysed to reveal the degradation of tributyltin to the di- and mono-butyltins, whilst an estuarine sediment was shown to contain Me_2BuSn and $MeBu_2Sn$ as major components following degradation of some tributyltins.[42]

The use of Me_2SnCl_2 as internal standard improves the precision of the determinations. There are no problems of high values for this internal standard from contamination from the water samples since the highest content of Me_2SnCl_2 found in heavily contaminated surface water[12,25,27] was *ca* 0.4 ng cm^{-3}, and by using HBr only 6–9 % of the total amount in water is extracted.[24]

Obviously, the GC FPD method is much better than the GC FID method, since it is selective and more sensitive. Actually, during the course of this work the FPD detctor proved to be 10^5–10^6 times more sensitive to tin compounds than to carbon compounds. This value is similar to those obtained by other authors.[27] The GC FPD method is suitable either for environmental analysis or for laboratory studies on biochemical degradation and the effects of small amounts of organotin compounds on invertebrates. The GC FID method is not sensitive enough for this kind of study but it can be applied for monitoring effluents highly contaminated with organotin compounds.

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