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Speciation for Analysis of Organotin Compounds by GC AA and GC MS after Ethylation by Sodium Tetraethylborate

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A range of organotin compounds has been ethylated using the reagent sodium tetraethylborate in a simple one-step procedure. Analysis of the volatile, fully alkylated derivatives has been achieved by GC AA with confirmation of the identity of the resulting ethylated derivatives by GC MS. Conditions for the GC AA and GC MS analysis of the organometallic ethyl derivatives are given.

Keywords: Ethylation, analysis, organotins, sodium tetraethylborate, tributyltin, tricyclohexyltin, triphenyltin, gas chromatography, mass spectroscopy, atomic absorption

INTRODUCTION

The derivatization of low levels of organometallic or organometalloidal compounds in environmental samples has been achieved by gas chromatography (GC) with atomic absorption spectroscopy (AA) or mass spectroscopic (MS) detection and other techniques by several groups (for example Refs 1–4). These techniques rely on the derivatization of the relatively involatile environmental organometallic compounds bound to chlorides, oxides, hydroxides or to unknown counterions, etc., to their corresponding volatile hydrides, methyls, ethyls, pentyls, etc., with subsequent chromatographic separation. this is usually achieved by the use of sodium borohydride (for the hydride derivatives) or the appropriate Grignard agent for the methyls, ethyls, etc. Both of these methods have disadvantages when used for environmental samples. Derivatization using sodium borohydride ($NaBH_4$) has been found to be suppressed in the presence of diesel oil and sulphides, both of which may occur at high level in environmental samples under investigation, particularly in sediments.[5] Derivatization by Grignard reagents has not been found to be suppressed in the same way, but it is a complex procedure with likely sample loss with the usually small volumes to be manipulated in environmental analysis.

We have been interested in developing methods for derivatization which do not require multiple steps, and which, if possible, do not suffer from suppression by contaminants present in the samples. Sodium tetraethylborate ($NaBEt_4$) has previously been reported for the preparative or analytical ethylation of trimethyl-lead and dimethyl-lead compounds,[6–9] and we now report an extension of its use with organotin species. A wide range of organotin compounds has been derivatized, including methyltins, ethyltins, propyltins, butyltins, phenyltins and cyclohexyltins, and confirmation of the identity of the ethylated derivatives has been obtained by mass spectroscopy. Inorganic tin(IV) chloride has also been ethylated by us for analysis in this way. We have previously reported the use of on-column hydride derivatization for analysis.[10] In this method the sodium borohydride ($NaBH_4$) reagent is added directly to a GC column and the involatile organometallic or inorganic substrate is injected directly to the column, the volatile hydride analyte being generated by reaction with the $NaBH_4$ on the column. Similarly for ethylation we report here the technique adapted for on-column and also off-column use. Preliminary details have been reported in a communication.[11]

For a general survey of analytical methods in this area see for example Refs 12–14. Recently, details have been described for the ethyl generation method applied to mercury compounds.[15–18]

The use of $NaBEt_4$ for the detection of dimethyl- and trimethyl-lead ions was first reported by Rapsomanikis *et al.*[9] They were able to obtain better detection limits for lead owing to the use of higher volumes of analyte (50 cm^3) and by using a cryogenic trap to trap the whole of the

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evolved methylethyl-lead derivatives. This gave an absolute detection limit of around 10 pg from 50 cm^3 of standard solutions with a limit of quantification of around 30 pg. The technique described in the present paper is inherently direct, not involving a trapping phase, and the limit of detection at the detector is 1–2 ng for butyltin species without cryogenic tapping, but to date we have not explored the ultimate sensitivity of the on- or off-column methods for elements other than tin. Estimated detection limits for tin are given in the Experimental section. We have previously reported on the use of $NaBEt_4$ for environmental butyltin separation and analysis.[1] We have now adapted the method for phenyl- and cyclohexyltin compounds.

Phenyltin compounds have been analysed by a variety of methods. Woollins and Cullen used a combination of derivatization by $NaBH_4$ followed by capillary GC with flame ionization detection.[19] Soderquist and Crosby[20] converted the phenyltins to hydrides using $LiAlH_4$ and used packed-column gas chromatography with either flame ionization or electron capture detection. Derivatization to alkyl species by means of Grignard reagents has been used. Van den Broek *et al.*[21] converted triphenyltin to triphenylmethyltin and analysed the latter by packed-column GC with flame photometric detection. Wright *et al.*[22] have used a similar procedure but with capillary GC. Conversion of the triphenyltins with a Grignard reagent to give a higher alkyl derivative has also been undertaken. Ohhira and Matsui[23] used a phenyl Grignard to produce phenyltin pentyl derivatives which were analysed by capillary GC with a flame photometric detector.

Other methods have included complete disruption of the tin–carbon bonds using bromine followed by hydride generation and detection by quartz furnace AA.[24] This work was limited by its inability to separate a mixture of phenyltin species. An alternative method involves separation of the phenyltins using high-performance thin-layer chromatography, reaction with Morin and quantification using scanning densitometry.[25]

To date, the technique of derivitization with $NaBEt_4$ has not been reported for separation of phenyl- or cyclohexyl-tin species. We report here quartz furnace AA and/or MS for the detection of the phenyltin ethyls or cyclohexyltin ethyls produced after derivatization with $NaBEt_4$. We have used this derivatization method for environmental work with butyltin compounds.[1] The detection methods were as given here and followed an extraction of the butyltin from an environmental sediment using the method summarized in Scheme 1.

EXPERIMENTAL

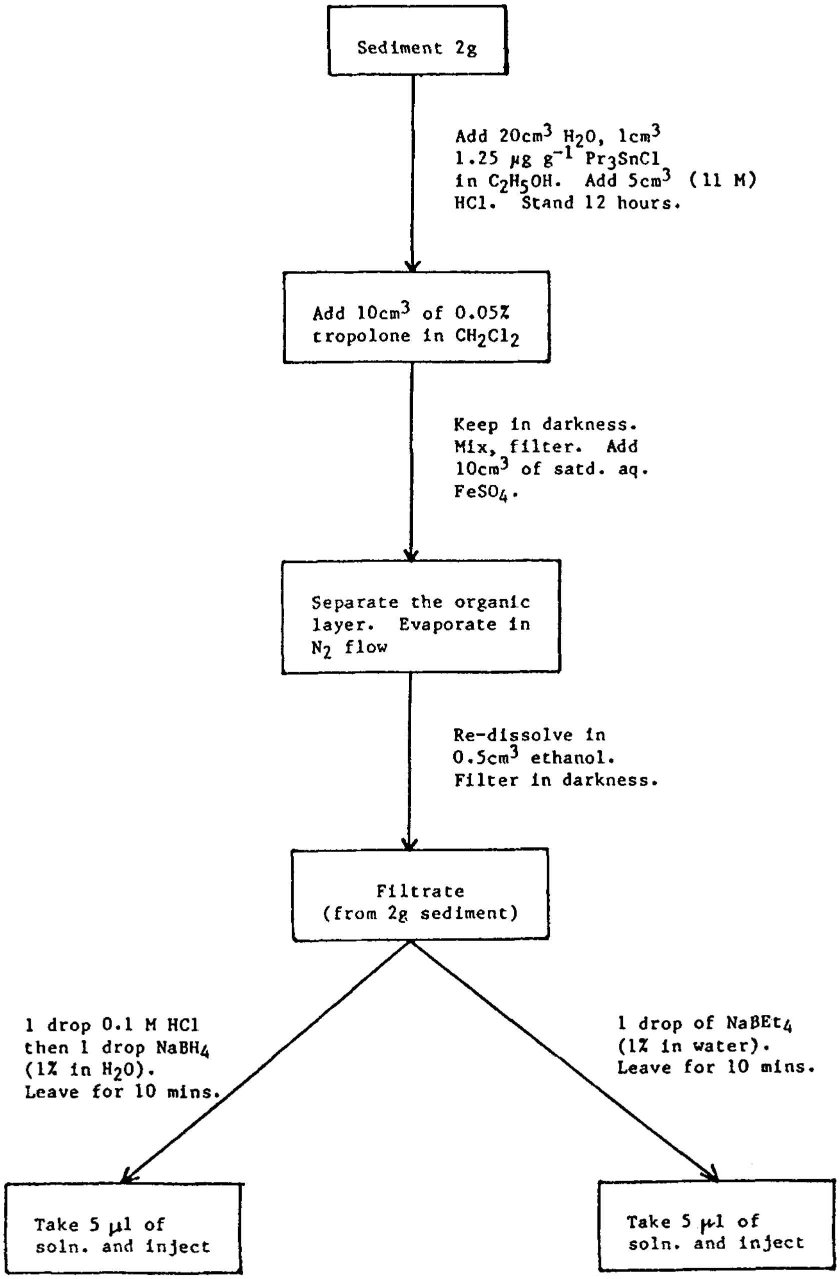
Reagents

Sodium tetraethylborate ($NaBEt_4$), diphenyltin dichloride (Ph_2SnCl_2), dimethyltin dichloride (Me_2SnCl_2), diethyltin dichloride (Et_2SnCl_2), triethyltin chloride (Et_3SnCl) and cyclohexyltin bromides ($(c\text{-}C_6H_{11})_{4-n}SnBr_n$) were obtained from Alfa Ventron, USA. Tributyltin chloride (Bu_3SnCl) and triphenyltin chloride (Ph_3SnCl) were obtained from Fluka, USA, and phenyltin trichloride ($PhSnCl_3$) was purchased from Strem Chemicals, Germany. They were used as purchased.

Stock solutions of the organotin compounds were made up in dichloromethane (approximately 2 mg g^{-1}) and diluted weekly to the appropriate concentration (approximately 2 $\mu g\ g^{-1}$) in ethanol. sodium tetraethylborate (2%), was made up daily in spectroscopic-grade ethanol or water as required.

Apparatus

Analysis was by gas chromatography–atomic absorption spectrometry (GC AA) or gas chromatography–mass spectroscopy (GC MS). For GC AA the gas chromatograph (Pye–Unicam 104) was fitted with a 1-metre column (4 mm i.d.) packed with 3% OV101 on Chromosorb W-HP, 80–100 mesh, for derivatives of methyltin, ethyltin, butyltin and tripropyltin. For the phenyltin and cyclohexyltin derivatives, 3% OV17 on W-HP, 80–100 mesh, was used. This was linked by a stainless-steel, unpacked, transfer line at 180°C to a quartz furnace (950°C) modified atomic absorption spectrometer (Varian Model 100 apparatus, as described in detail elsewhere[17]), using the tin hollow-cathode lamp at 286.6 nm. Mass spectra were obtained with a Hewlett–Packard 5890 gas chromatograph, fitted with a 12 m capillary column packed with SE54 and linked to a VG Mass Lab Trio-3 triple-quadrupole mass spectrometer. Helium gas pressure was 7 psi (5×10^4 N m^{-2}). GC AA conditions



Scheme 1 Method for the extraction of butyltin compounds from aquatic bottom sediments.

for tin compounds are described in Table 1. For GC AA work, nitrogen at a flow rate of 60 cm^3 min^{-1} was used as the carrier gas. Hydrogen (flow rate 300 cm^3 min^{-1}) and air (flow rate 13 cm^3 min^{-1}) were supplied to the quartz furnace by Teflon lines. For GC MS work with butyltin compounds the oven temperature was held at 100°C for 3 min, then raised by 32°C min^{-1} to 25°C, with the injector temperature held at 220°C throughout. With these conditions GC MS retention times for tributylethyltin and tripropylethyltin, for example, were 5.7 min and 4.0 min

Table 1 GC AA conditions and retention times for ethylated organotin compounds[a]

Compound derivatized	Column packing	Column temp. (°C)	Ramp rate (°C min^{-1})	Retention time (min)
$SnCl_4$	OV101[b]	120	Isothermal	4.4
$MeSnCl_3$	OV101[b]	120	Isothermal	2.7
Me_2SnCl_2	OV101[b]	120	Isothermal	1.8
Me_3SnCl	OV101[b]	120	Isothermal	1.0
Et_2SnCl_2	OV101[b]	250	Isothermal	0.7
Pr_3SnCl	OV101[b]	120–210	32	4.6
$BuSnCl_3$	OV101[b]	120–210	32	4.0
Bu_2SnCl_2	OV101[b]	120–210	32	5.7
Bu_3SnCl	OV101[b]	120–210	32	6.8
$PhSnCl_3$	OV101[b]	270	48	1.0
Ph_2SnCl_2	OV17[c]	270	Isothermal	2.0
Ph_3SnCl	OV17[c]	270	Isothermal	5.1
$(cC_6H_{11})SnCl_3$	OV17[c]	300	Isothermal	0.6
$(cC_6H_{11})_2SnCl_2$	OV17[c]	300	Isothermal	3.2
$(cC_6H_{11})_3SnCl$	OV17[c]	300	Isothermal	5.4

[a] Ethyl generation *off* the column (see text). Other conditions: H_2 flow rate = 300 cm^3 min^{-1}; air flow rate = 13 cm^3 min^{-1}; injector temperature 140°C; transfer line, 180°C; 2 μl injected. [b] For OV101, N_2 flow rate 60 cm^3 min^{-1}. [c] For OV17, N_2 flow rate 100 cm^3 min^{-1}.

respectively (Table 3). GC AA calibration was achieved by ethylating solutions of various concentrations of (for example) mono-, di- and tributyltin chlorides containing a constant concentration of tripropyltin, and a calibration plot of the ratio of the peak heights of the butylethyltins to tripropylethyltin against the concentration of the butyltin chloride was constructed. Calibration was linear for the range 0–10 μg g^{-1}

Table 2 GC MS conditions and retention times for ethylated organotin compounds[a]

Compound derivatized	Column temp. (°C)	Ramp rate (°C min^{-1})	Retention time (min)
$SnCl_4$	60–100	24	5.5
$MeSnCl_3$	60–100	24	5.1
Me_2SnCl_2	60–100	24	4.5
Me_3SnCl	60–100	24	3.6
Et_2SnCl_2	60–100	24	5.5
Pr_3SnCl	50–250	20	4.0
$BuSnCl_3$	50–250	32	3.5
Bu_2SnCl_2	50–250	32	4.6
Bu_3SnCl	50–250	32	5.7
$PhSnCl_3$	150–240	20	2.6
Ph_2SnCl_2	150–240	20	5.4
Ph_3SnCl	150–240	20	8.6
$(cC_6H_{11})SnCl_3$	150–240	20	2.1
$(cC_6H_{11})_2SnCl_2$	150–240	20	4.8
$(cC_6H_{11})_3SnCl$	150–240	20	7.5

[a] Ethyl generation *off* the column (see text). All samples were analysed using an SE54 capillary column (see text for details). The temperature was maintained for 0.2 min prior to ramp for all analyses.

Sample preparation and derivatization

Standard solutions of alkyltin (except methyltin) compounds (both alone or in mixed solutions) were made up from the stock solutions to a final concentration of approximately 2 μg g^{-1} in ethanol. To 5 cm^3 of this solution was added approximately 0.2 cm^3 of the 2% sodium tetraethylborate solution. Approximately 2 μl of the resulting solution (i.e. 2 ng of analyte) was injected into the GC AA system, or 1 μl for the GC MS system. A blank solution containing ethanol and the appropriate amount of ethylating agent was injected into the GC column prior to the injection of the organotin compound to eliminate memory effects and also as a blank determination. A daily injection of 10% methyl iodide in ethanol was also found to eliminate any possible build-up of organotin compounds on the column. Solutions containing ethylated butylin compounds at the μg g^{-1} (ppm) level were found to be stable for at least a week when stored in the dark at 3°C. After this

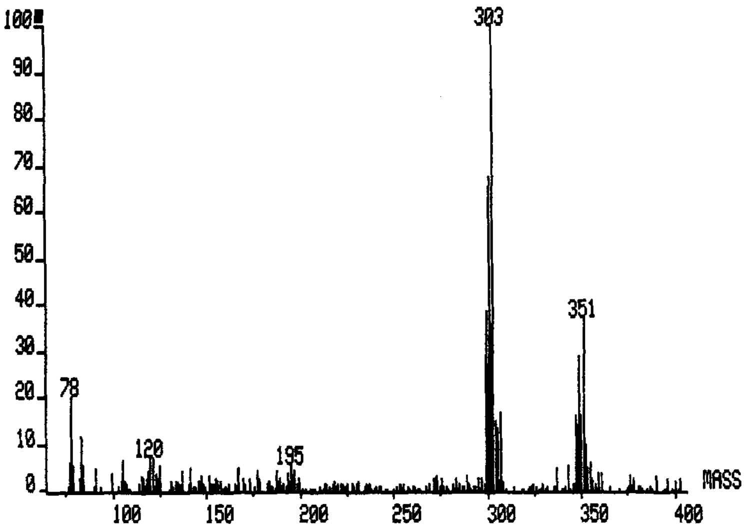


Figure 1 Mass spectrum of $(C_6H_5)_3SnC_2H_5$.

time dismutation of tributylethyltin to dibutylethyltin and monobutylethyltin occurred.

Headspace analysis following ethylation was carried out only for methyltin compounds in water. Thus, 1 cm^3 of a solution of approximately 3 $\mu g\,g^{-1}$ of methyltin compound in water was placed in a 50 cm^3 vial and sealed with a crimp-on cap. then 2 cm^3 of 2% $NaBEt_4$ in water was injected into the vial and 0.1 cm^3 (6 ng of tin) of the headspace was withdrawn using a gas-tight syringe for analysis, Up to 15 min after addition of $NaBEt_4$ was allowed for complete generation of ethyltin derivative before the sample was analysed.

For the phenyl- and cyclohexyl-tin derivatives a solution at approximately 6 $\mu g\,g^{-1}$ of each reagent was made up in ethanol and ethylated as described above for butyltin compounds and analysed using the 3% OV17 packed column of the same dimensions for GC AA. Conditions are given in Table 1. GC MS details are given in Table 2.

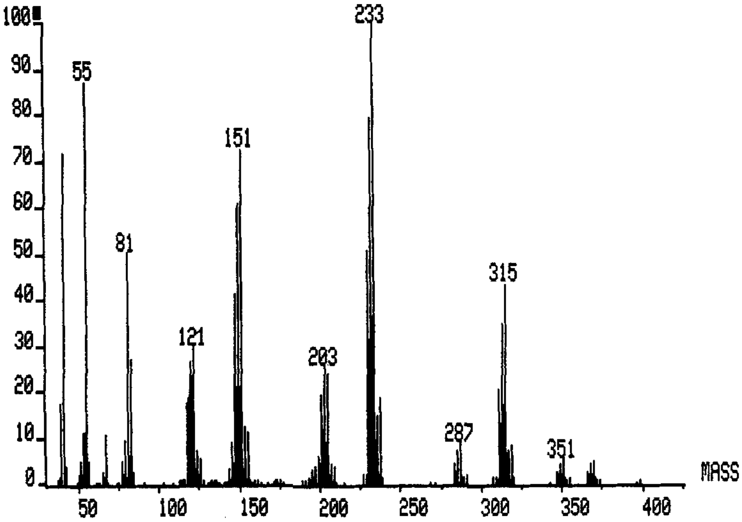


Figure 2 Mass spectrum of $(cC_6H_{11})_3SnC_2H_5$.

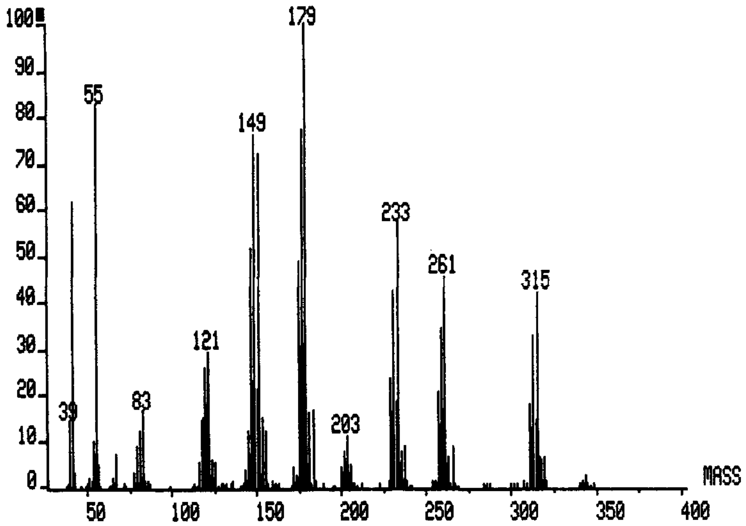


Figure 3 Mass spectrum of $(cC_6H_{11})_2Sn(C_2H_5)_2$.

RESULTS AND DISCUSSION

Using the GC AA or GC MS methodology, the simple alkyl derivatives of tin could be separated and detected without difficulty by this system. Environmental results for butyltin compounds have already been reported.[1] Phenyl- and cyclohexyl-tin solutions were also easily derivatized and detected by those methods.

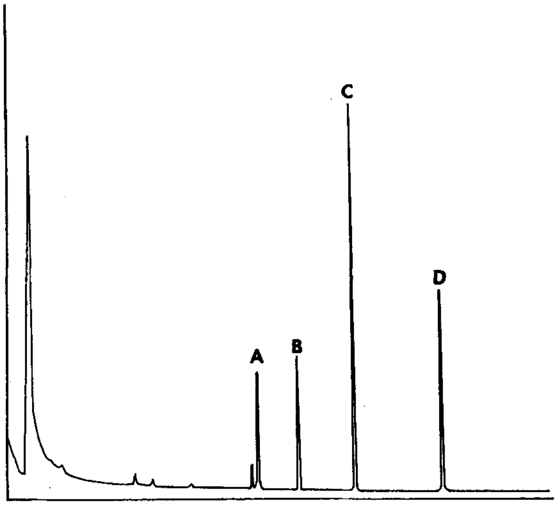


Figure 4 Total ion current trace of a derivatized mixed sample of butylethyltin compounds with $(C_3H_7)_3SnCl$ added as internal standard. A(=4.0), $C_4H_9Sn(C_2H_5)_3$; B(=4.6), $(C_3H_7)_3SnC_2H_5$; C(=5.7), $(C_4H_9)_2Sn(C_2H_5)_2$; D(=6.8), $(C_4H_9)_3SnC_2H_5$.

Using the 3% OV17 packed column, GC AA peaks for monocyclohexyltriethyltin, dicyclohexyldiethyltin, monophenyltriethyltin and diphenyldiethyltin were sharp and well resolved. Peaks for both tricyclohexylethyltin and triphenylethyltin were broader and the limit of detection (LOD) for derivatized tricyclohexyltin bromide was found to be 4 ng absolute compared with levels between 1 and 2 ng for the ethylated butyltin derivatives.

Detection of single or mixed phenyl- or cyclohexyl-tin solutions by GC MS using the SE54 capillary column gave sharp peaks for both tricycloethyltin and triphenylethyltin. The identity of the products from the ethylation of all other organotin compounds was also confirmed by GC MS. Mass spectra of the derivatives obtained from solutions of standard samples of tricyclohexyltin bromide and triphenyldiethyltin chloride are given in Figs 1 and 2. The mass spectra of monocyclohexyltriethyltin, dicyclohexyldiethyltin (Fig. 3) and tricyclohexylethyltin are in good agreement with those found by Muller and Bosshardt[26] after ethylation of standard samples of cyclohexyltin bromides with the Grignard reagent ethylmagnesium bromide. For tricyclohexylethyltin a weak molecular ion (clustered around *m/z* 398) is present (Fig. 2). Molecular ions were also obtained for dicyclohexyldiethyltin and tripropylethyltin only. Figure 4 shows the total ion current trace obtained during a GC MS analysis of a

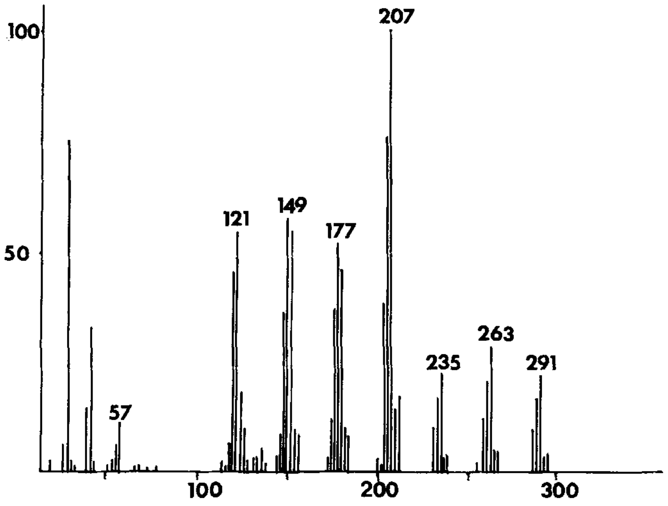


Figure 5 Mass spectrum of $(C_4H_9)_3SnC_2H_5$.

Table 3 MS peaks based on ^{120}Sn

Butyltriethyltin		Phenyltinethyls		Cyclohexyltinethyls	
m/z	origin	*m/z*	origin	*m/z*	origin
120	Sn^+	120	Sn^+	120	Sn^+
149	$SnC_2H_5^+$	149	$SnC_2H_5^+$	149	$SnC_2H_5^+$
177	$SnC_4H_9^+$	197	$SnC_6H_5^+$	178	$Sn(C_2H_5)_2^+$
206	$SnC_4H_9(C_2H_5)^+$	226	$SnC_6H_5(C_2H_5)^+$	203	$SncC_6H_{11}^+$
234	$Sn(C_4H_9)_2^+$	255	$SnC_6H_5(C_2H_5)_2^+$	232	$SncC_6H_{11}(C_2H_5)^+$
263	$Sn(C_4H_9)_2(C_2H_5)^+$	275	$Sn(C_6H_5)_2^+$	261	$SncC_6H_{11}(C_2H_5)_2^+$
291	$Sn(C_4H_9)_3^+$	284	$SnC_6H_5(C_2H_5)_3$	315	$Sn(cC_6H_{11})_2(C_2H_5)^+$
320	$Sn(C_4H_9)_3C_2H_5$	351	$Sn(C_6H_5)_3^+$	344	$Sn(cC_6H_{11})_2(C_2H_5)_2^+$
				369	$Sn(cC_6H_{11})_3^+$

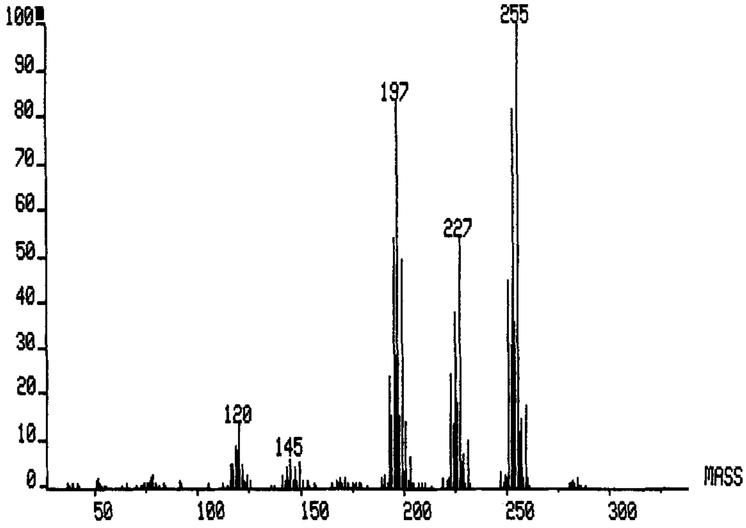


Figure 6 Mass spectrum of $C_6H_5Sn(C_2H_5)_3$.

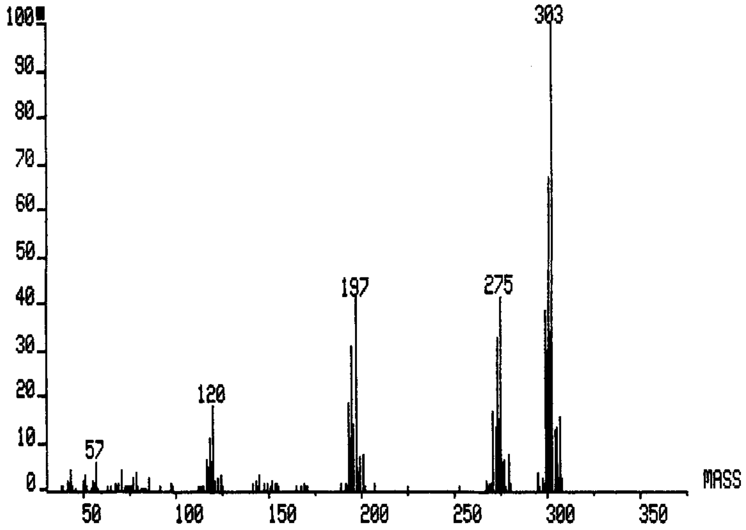


Figure 7 Mass spectrum of $(C_6H_5)_2Sn(C_2H_5)_2$.

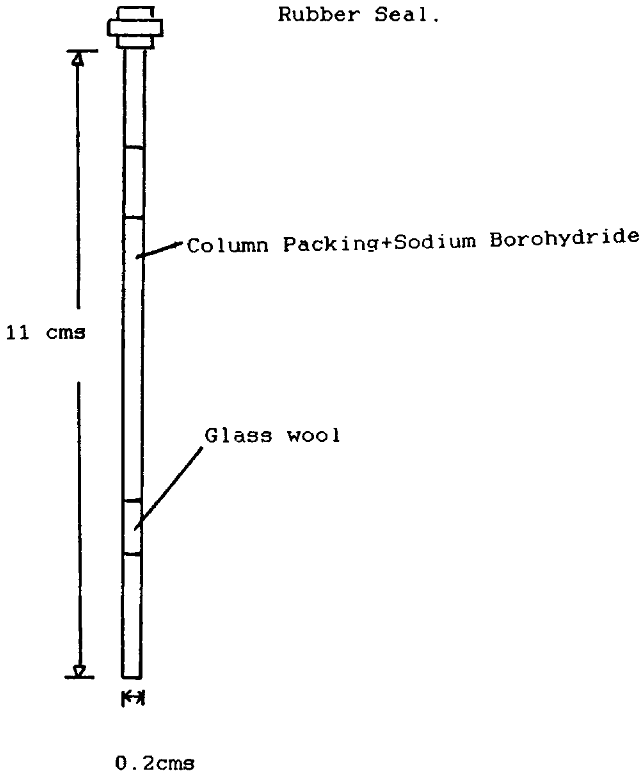


Figure 8 Insert for on-column generation of hydride or ethyl derivatives.

solution containing a mixture of mono-, di-, and tri-butyltin chlorides and tripropyltin chloride, derivatized as described above. The mass spectrum of the tributylethyltin derivative thus obtained is shown in Fig. 5. Identities of *m/z* ions for spectra shown in the Figures are given in Table 3.

For the GC AA system, detection limits at the detector for tributylethyltin, dibutylethyltin and monobutylethyltin were found to be 1.2 ng, 1.4 ng and 1.8 ng absolute respectively. For the GC MS system, detection limits based on tributylethyltin were approximately 1.5 ng absolute.

To demonstrate the ability of the system to detect a range of phenyltin compounds, a series of mass spectrum traces (Figs 1, 6, 7) are presented.

Attempted ethylation *on the column* for the analysis of methyl- and butyl-tin is now described. Following the success of on-column hydridization[10] using sodium borohydride, attempts were made to achieve on-column ethylation using sodium tetraethylborate. Doping was achieved by injecting six 10-μl volumes of a 2% solution of sodium tetraethylborate in ethanol onto the column. It was found that best results (GC AA) were achieved when the injector temperature was kept low (i.e. under 100°C). Monomethyltin trichloride, dimethyltin dichloride and trimethyltin chloride in water (at a concentration of approximtely 2 μg g^{-1}) were all successfully ethylated and detected on-column. Limited practical success was achieved with the ethylation of tributyltin chloride and tripropyltin chloride after doping with a solution of sodium tetraethylborate in ethanol injected into the GC at 100°C. The main difficulty appeared to be the necessity for a high temperature in the injector for volatilization of the butyltins after ethylation. The sodium tetraethylborate was not stable at these temperatures and ethylation was achieved for only 4–5 injections before the ethylating agent was destroyed. Use of a column insert (Fig. 8) with butyl species was no more successful, with the white sodium tetraethylborate in the insert becoming discoloured and ineffective after about an hour at the high temperatures needed in the injector. This in-column insert had been previously successful for on-column hydride generation.[27]

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