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## Preparation of Pentylated Organotin Standards for Use in Trace Analysis with Gas Chromatography

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**Abstract.** A method for the preparation and purification of pentylated derivatives is described for nine organotin compounds that are relevant in environmental analysis (tributyltin acetate, dibutyltin dichloride, butyltin trichloride, triphenyltin chloride, diphenyltin dichloride, phenyltin trichloride, tricyclohexyltin hydroxide (cyhexatin), dicyclohexyltin dibromide and bis (trineophyltin) oxide (fenbutatinoxide)). The compounds are synthesized on a 100 mg scale and purified by column chromatography. Purity checks were performed with gas chromatography with mass selective detection. The mass spectrum of pentyltrineophyltin is presented.

**Key words:** organotin, alkylation, environmental, fentin, fenbutatinoxide.

In environmental organotin analysis, extraction of the analyte followed by alkylation and capillary gas chromatography (GC) is a commonly applied technique [1, 2]. Pentylation is often used because it yields derivatives which are not too volatile. As a result, losses due to evaporation during work up, are prevented, while the derivatives can still be determined easily by GC.

Procedural standards of pentylated derivatives are necessary to calculate derivatization efficiencies, to evaluate detector performance and to accurately determine concentrations in real samples. Such pentylated standards are not commercially available and must therefore be synthesized in one's own laboratory.

A common approach is to derivatize diluted organotin standards. In most reports it is assumed that the derivatization reaction goes to completion, and only in some cases the purity of the derivatized standards is checked, for instance by destruction of the organotin compound to inorganic tin and subsequent analysis by standard AAS procedures [3].

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The approach used in this study is to synthesize the derivatives on a preparative scale. It is then possible to further purify the pentylated organotin compounds, e.g. by column chromatography. The yield can be determined gravimetrically and calibration standards based on this product can be prepared. A similar approach as described here was published recently by Fehrer and Walters [4] who used high performance liquid chromatography (HPLC) as a purification step. The advantage of the present method is that it involves no recrystallization and while not using HPLC, it gives comparable results in less time.

## Experimental

### Materials

*Organotin compounds:* Butyltin trichloride ( $\text{BuSnCl}_3$ ) 90% purity (Janssen Chemicals, Geel, Belgium); dibutyltin dichloride ( $\text{Bu}_2\text{SnCl}_2$ ) (Aldrich, Steinheim, Germany); tributyltin acetate ( $\text{Bu}_3\text{SnOAc}$ ); gift from the Community Bureau for Reference (BCR) of the CEC, Brussels, Belgium; phenyltin trichloride ( $\text{PhSnCl}_3$ ) 98% purity (Aldrich, Steinheim, Germany); diphenyltin dichloride ( $\text{Ph}_2\text{SnCl}_2$ ) 96% purity (Aldrich, Steinheim, Germany); triphenyltin chloride ( $\text{Ph}_3\text{SnCl}$ ) 95% purity (Aldrich, Steinheim, Germany); dicyclohexyltin dibromide ( $\text{Cy}_2\text{SnBr}_2$ ) (Johnson Matthey Alfa Karlsruhe, Germany); cyhexatin (tricyclohexyltin hydroxide,  $\text{Cy}_3\text{SnOH}$ ) 99% purity (Dr. Ehrenstorfer, Augsburg, Germany); fenbutatin oxide (FBTO) (bis (trineophyltin) oxide) 99.7% purity; gift from M&T Chemicals, Vissingen, the Netherlands.

*Other chemicals:* Grignard reagent: pentyl magnesium bromide ( $\text{PeMgBr}$ ), 2 M solution in diethylether; Aldrich, Milwaukee, Wisconsin, USA. Alumina oxide: (Alumina B—super I, basic form, for column chromatography); ICN Biomedicals, Eschwege, Germany, activated before use at 200°C for 24 h. n-Hexane, diethylether, acetic acid and anhydrous sodium sulphate were analytical grade purchased from Baker, Deventer, the Netherlands.

### Apparatus

All measurements were carried out on a Hewlett Packard 5890 II GC equipped with a 25 m  $\times$  0.2 mm I.D. (film thickness 0.2  $\mu\text{m}$ ) CP-Sil 8CB fused silica column, Chrompack, Middelburg, the Netherlands. The temperature programme was 80°C for 1 min, next at 20°C/min to 210°C, and then at 10°C/min to 270°C. The final temperature was maintained for 8 min. The injection port and the detector were both set at 280°C. For injection the splitless injection port was used, using a splitless time of 2 min.

A Hewlett Packard 5971A mass selective detector (MSD) was used for detection. Scan mode was used, with scanning from  $m/z = 105$  to  $m/z = 522$ . Column chromatography was done on a homemade glass column with a bed volume of 16 cm  $\times$  7 mm I.D. packed with activated Alumina B, Alumina oxide.

### Procedure

About 100 mg of organotin compound were weighed and dissolved in 10 ml hexane/toluene (50/50) in a scintillation bottle and cooled in an ice bath. FBTO was dissolved in hexane/glacial acetic acid (0.25%) one hour before reaction in order to obtain the free acetate form. Grignard reagent (0.7 ml) was added and the bottle was closed. After the initial, slightly violent reaction (1 min) the bottle was removed from the ice bath, and transferred to a waterbath of 30°C and shaken occasionally. After 40 min, 5 ml of 2 M sulphuric acid were added to destroy the excess Grignard reagent. The organic layer was separated and dried over anhydrous sodium sulphate. The solvent was evaporated under a mild

flow of nitrogen on a 60°C waterbath until only an oily residue remained and no further decrease in weight was observed.

For further purification by means of column chromatography the product was dissolved in 1 ml hexane and applied to the top of a glass column containing 6 g of Alumina B. Elution was done with 12 ml of n-hexane and next, 35 ml of n-hexane/diethylether (9/1). Fractions of 2 ml were collected and the presence of the pentylated organotins was checked by GC/MSD. The eluates were gently evaporated under nitrogen until constant weight.

The final products were dissolved in hexane to obtain stock solutions of about 10 mg/ml, which were kept in the dark.

## Results and Discussion

GC analysis of the various series of collected fractions showed that the pentyl derivatives of the alkyltin compounds, i.e. the tetra-alkyl organotins, all elute within the first 10 ml of eluent. The aromatic organotin derivatives elute considerably later. Typical elution ranges are included in Table 1. Despite the standardization attempted in the present study, these fractions should be considered as indicative rather than as highly accurate values: they obviously need re-checking for every individual set-up.

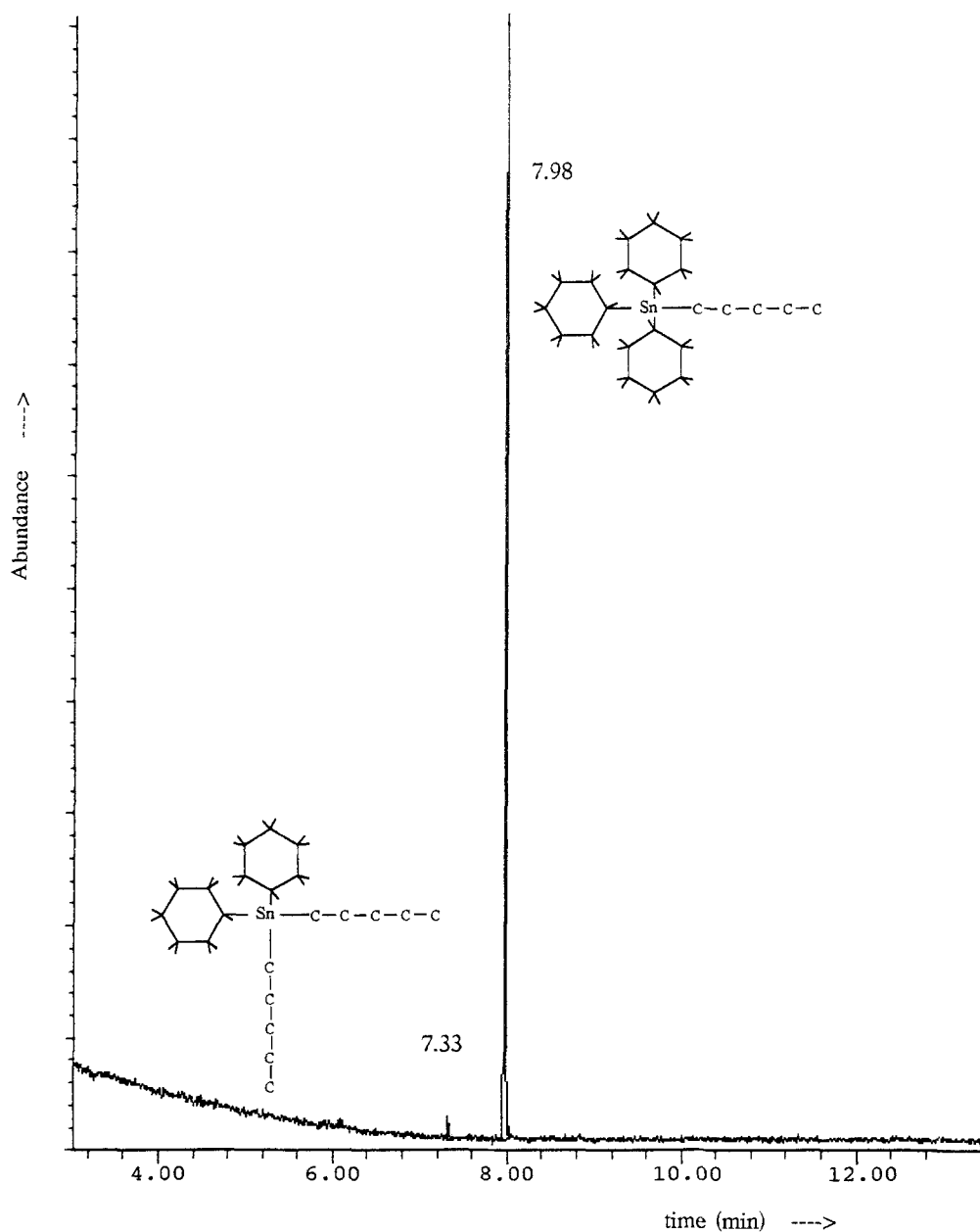
Column chromatography over alumina allowed the removal of two types of contaminants. Firstly, an unidentified band showed up with all preparations; it eluted much later than even the slowly eluting  $\text{Ph}_3\text{SnPe}$  i.e. starting only after the passage of 70 ml of n-hexane/diethylether (9/1). This contaminant evidently has to be removed because otherwise the calculation of the concentration of the pentylated standards will be invalidated. Secondly, with all phenyltins, minor quantities of tetrapentyltin were found to be present after reaction. It could easily be separated from the main reaction product because, being a tetra-alkyltin, it elutes in an earlier fraction than do the aromatic organotins. The 10 mg/ml stock solutions of the various purified pentylated organotins which were finally obtained were diluted to approx. 20  $\mu\text{g/ml}$  and determined by GC/MSD. In some cases minor amounts of other organotin derivatives were still present. Most probably they are the result of

**Table 1.** Yields and purities of organotin standards

Compound	Eluent*	Fraction (ml)	Yield/%	Purity/%	Contaminations
$\text{BuSnPe}_3$	h	0–5.0	87	>99	
$\text{Bu}_2\text{SnPe}_2$	h	2.5–4.5	87	95.6	$\text{Bu}_1\text{SnPe}_3$ 1.9% $\text{OcBuSnPe}_2^1$ 2.4%
$\text{Bu}_3\text{SnPe}$	h	4.0–6.0	72	>99	
$\text{PhSnPe}_3$	h	5.0–8.5	56	>99	
$\text{Ph}_2\text{SnPe}_2$	h/d	5.0–14	65	>99	
$\text{Ph}_3\text{SnPe}$	h/d	17–35	77	>99	
$\text{Cy}_2\text{SnPe}_2$	h	4.5–7.5	73	91.1	$\text{Cy}_3\text{SnPe}$ 8.9%
$\text{Cy}_3\text{SnPe}$	h	2.0–9.0	74	97.1	$\text{Cy}_2\text{SnPe}_2$ 1.8%
FBT-Pe	h/d	5.0–10	69	>99	

\* The eluent was 12 ml hexane (h) followed with 35 ml hexane/diethylether (9/1) (h/d). The eluate fraction in which the analyte was recovered is given in the next column.

<sup>1</sup>  $\text{OcBuSnPe}_2$  octylbutyldipentyltin.



**Fig. 1.** Total ion chromatogram of the  $\text{Cy}_3\text{SnPe}$  standard.  $\text{Cy}_3\text{SnPe}$  elutes at 7.98 min and a minor contaminant ( $\text{Cy}_2\text{SnPe}_2$ ) at 7.33 min

impurities present in the purchased standards. As an example in Fig. 1 the total ion current chromatogram of  $\text{Cy}_3\text{SnPe}$  is shown which indicates the presence of one contaminant. All compounds and contaminants were identified by hand on the generated mass spectra.

Impurity concentrations were calculated on the basis of peak areas and the final concentrations of the pentylated standards were recalculated. The electron impact mass spectra of most pentylated organotin compounds studied have been published before [4, 5]. In this paper, the mass spectrum of pentyltrineophyltin is presented for the first

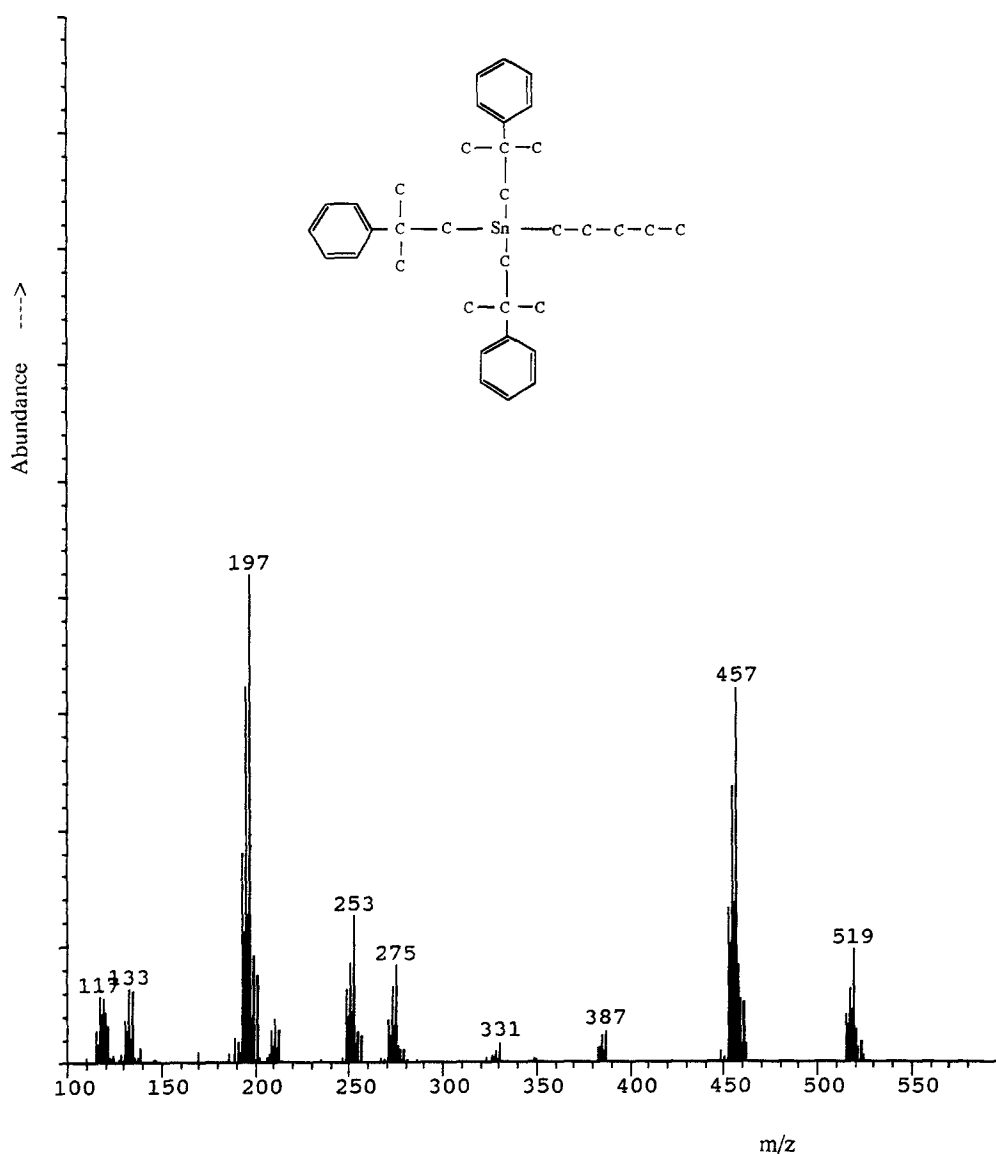


Fig. 2. Electron impact mass spectrum of pentyltrineophyltin

time (Fig. 2). As is expected on the basis of data for the other pentylated compounds the molecular ion is not visible and typical tin isotope patterns are seen on loss of the pentyl group ( $m/z$  519) or one neophyl group ( $m/z$  457). At  $m/z$  197 the fragment where only one phenyl group remains on the tin atom is present.

## Conclusions

Pentylated standards of nine environmentally important organotin compounds can be obtained using a straightforward Grignard procedure. With a subsequent clean-up over an alumina column, in six instances their purity is over 99%. With the other three pentylated standards, minor contaminations by other organotin derivatives are observed. These probably arise from impurities present in the

organotin compounds. No further purification of these three pentylated compounds was deemed necessary, since in real practice concentrations can easily be calculated introducing the appropriate correction factor.

*Acknowledgements.* This work is part of a Ph.D. thesis and is supported by a grant from the University Stimulation Fund of the Free University (USF Grant 89-27). The GC/MSD facilities were kindly provided by the Rhine Basin Program (Waldbronn, Germany/Amsterdam, the Netherlands).

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