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The Use of Sodium Tetraethylborate in the Derivatization of Octyltin Compounds*

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Octyltin trichloride ($OctSnCl_3$) and dioctyltin dichloride (Oct_2SnCl_2) have been reacted with sodium tetraethylborate ($NaBEt_4$) to yield the volatile tetraalkyltin derivatives $OctSnEt_3$ and Oct_2SnEt_2. Single and mixed solutions of the octyltin chlorides have been derivatized, separated and quantified using interfaced GC AA and GC MS methodology.

Keywords: Octyltin, derivatization, sodium tetrathylborate, analysis, GC AA, GC MS

INTRODUCTION

Sodium tetraethylborate ($NaBEt_4$) has found much use in recent years for the derivatization of metallic compounds to produce volatile alkylated species for analysis.[1] Sodium borohydride has also been much used for this purpose.[2] The ethyl borate has found some favour over sodium borohydride ($NaBH_4$) because it appears to be more robust for extractions in polluted aqueous or sediment environments[2] and because it can be used in aqueous media (unlike the analogous Grignard reagents). Sodium tetraethylborate has been used recently in the derivatization and analysis of tin,[3] lead,[1] mercury,[4] selenium[5] and arsenic[6] species. Successful results have been reported for methyl and lower-alkyl tin species (including butyltins),[3] phenyltins[7] and cyclohexyl tins.[7] We now report its use for octyltin derivatives analogous to those used in heat and light stabilizers for PVC polymers.

EXPERIMENTAL

Instruments

The interfaced GC AA and GC MS systems have been described previously.[8] For GC AA, an Analytical Instruments Model 92 GC and a Perkin–Elmer 3100AA instrument were used; for GC MS a Hewlett Packard 5890 and a VG Trio 3 instruments were used as described below. In our interfaced GC AA, the column used was a capillary which was extended through the transfer line itself, terminating immediately prior to the quartz furnace. Engineering aspects of this transfer line–capillary system have been described previously.[9] The transfer line (30 m) itself (inner to outer) consists of SE30 capillary column; 1.09 m i.d. stainless-steel tube; 1.59 m i.d. stainless-steel tube; ceramic insulating beads containing nichrome wire; fireclay outer covering.

The GC AA system was optimized as described previously, and optimized conditions were used.[9, 10] It should be pointed out that the studies leading to optimization conditions were carried out on tributyltin compounds. The quartz furnace was rinsed with 40% hydrofluoric acid for 15 min (full safety precautions were taken). This leads to a threefold increase in sensitivity for the furnace.[10]

The GC AA was operated using a tin hollow-cathode lamp at 286.6 nm with a slit width of 0.7 nm. GC conditions were: injector temperature 200 °C; GC oven temperature 100 °C, rising at 20 °C min^{-1} to a maximum of 280 °C which was held for 5 min. Transfer line temperature was 280 °C. Retention times of triethyloctyltin and diethyldioctyltin are shown in Table 1. Flow rates were as follows: nitrogen carrier and make-up gases 60 cm^3 min^{-1} (5 and 55 cm^3 min^{-1} respectively), hydrogen 250 cm^3 min^{-1}, air 13 cm^3 min^{-1}.

GC MS chromatographic conditions were: injector temperature 200 °C; GC oven initial temperature 100 °C held for 2 min, rising at

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Table 1 Retention times of derivatized octyltin compounds (min)

Compound	GC AA	GC MS
OctSnEt$_3$	8.0	7.5
Oct$_2$SnEt$_2$	11.0	10.9

Table 2 Main MS peaks for octyltin derivatives and their assoginment[a]

OctSnEt$_3$		Oct$_2$SnEt$_2$	
m/z	Fragment	*m/z*	Fragment
291	OctSnEt$_2^+$	375	Oct$_2$SnEt$^+$
207	SnEt$_3^+$	291	OctSnEt$_2$
179	SnEt$_2$H$^+$	263	OctSnEtH$^+$
149	SnEt$^+$	231	OctSn$^+$ − 2H$^+$
121	SnH$^+$	179	SnEt$_2$H$^+$
		151	SnEtH$_2^+$
		121	SnH$^+$

[a] Unassigned *m/z* 282 in Oct$_2$SnEt$_2$; peaks below *m/z* 121 isotope clusters are not listed.

20 °C min^{-1} to a maximum of 280 °C which was held for 5 min. Mass spectra are shown in Fig. 1. The GC was a Hewlett Packard 5890 fitted with a 12 m SE54 capillary column (Altech), interfaced to a VG Trio 3 triple quadrupole MS. Helium gas pressure was 5×10^4 N m^{-2}.

Chemicals and derivatization

Monooctyltin trichloride and dioctyltin dichloride were obtained as gifts from the University of Bordeaux and used as received. A 1000 ppm standard solution of each was prepared in spectroscopic-grade ethanol using grade A 100-cm^3 graduated flasks, and used to prepare single or mixed working solutions in the 1–10 ppm range by dilution of the original standard, again using grade A volumetric glassware.

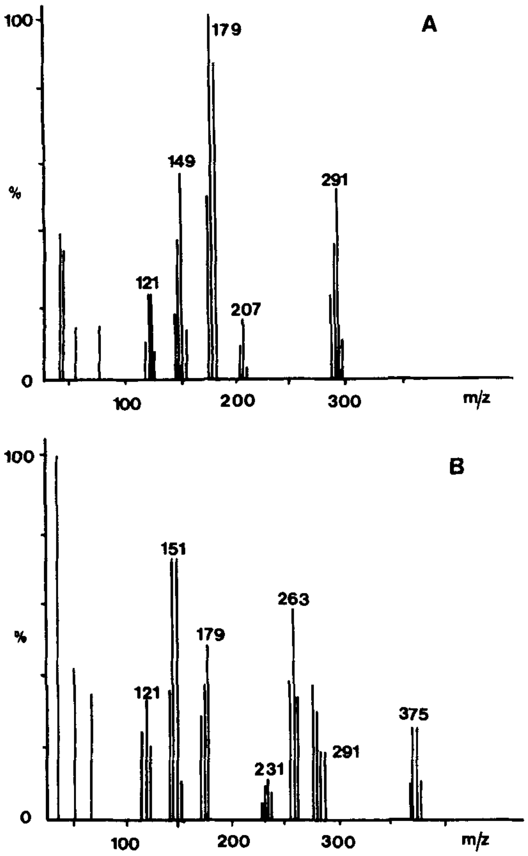

Figure 1 Mass spectra of derivatized monooctyltin (A) and dioctyltin (B) species. Numbers refer to isotopes occurring with maximum intensity in the group. There is an unassigned peak at *m/z* 282 near the cluster noted at *m/z* 291.

Sodium tetraethylborate was obtained from Strem chemicals, and was used as received to prepare, daily, fresh solutions of 1% sodium tetrathylborate in spectrocopic-grade ethanol. Derivatization of the octyltin species was achieved by the addition of a 0.1 cm^3 aliquot of the sodium tetraethylborate solution to a 1 cm^3 aliquot of the mixed organotin solution in ethanol. The derivatized solutions were left for 15 min and 1 μl of the solution was injected to GC AA or GC MS. Yields were measured by comparison with an external tin standard of tetrabutyltin injected at the same time.

RESULTS

From the GC AA and GC MS results given in Table 1 and Fig. 1 it can be seen that the octyltin chlorides both derivatize and separate following reaction with sodium tetraethylborate. From previous work with butyltin species, the yield on derivatization approached 100%;[3] using the same conditions the yield for octyltins was found to be 80%. It is likely that further optimization could increase the yields for octyltins. However, yields are consistent, based on 10 test samples, and the method is adaptable to analytical use by the involvement of a tin-containing internal standard. Detailed MS assignments are given in Table 2.

CONCLUSION

The use of sodium tetrathylborate as a derivatizing reagent for analysis has been extended to octyltin species.

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