

CHROM. 11,231

## SEPARATION AND PURIFICATION OF ORGANOTIN HALIDES

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(Received June 7th, 1978)

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### SUMMARY

High-performance liquid chromatography of tin tetrachloride and methylated derivatives of tin tetrachloride has been examined on silanized silica, pyrocarbon silica and styrene-divinylbenzene polymers of different pore sizes. A satisfactory separation of the methylated tin halides and their purification from tin tetrachloride have been achieved by adsorption chromatography on Styragels. These adsorbents have been shown to be of value also for other organotin compounds, and may also be used in studies of redistribution reactions.

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### INTRODUCTION

In the preparation of organotin compounds, tin tetrahalides are the most commonly used starting materials, and organotin halides are important intermediates in these processes. Organotin halides prepared by the normal routes usually give equilibrium mixtures of compounds having similar chemical properties and which are therefore difficult to separate and purify by standard methods. High-purity organotin compounds of low molecular weight can sometimes be obtained by preparative gas-liquid chromatography (GLC). However, there are problems in the use of the halides in GLC, such as redistribution, hydrolysis, reaction with the column support and stationary phase and corrosion of detectors and other instrument parts<sup>1-3</sup>.

In order to avoid the problems of elevated temperatures, as used in gas chromatography, some kind of liquid chromatography would be preferable. Figge and Bieber<sup>4</sup> have shown that methyl- and octyl-tin chlorides can be separated on silanized silica. The more reactive components were, however, strongly retained with excessive tailing, indicating the occurrence of reactions between the sample and adsorbent.

According to our previous experience, alumina and silica, as well as the more lipophilic adsorbent Sephadex LH-20, reacted with the active halides. With more inert adsorbents, such as graphite and active carbon, reactions with the adsorbent were less of a problem, although still seen, probably due to impurities. Tailing and low resolution indicated that different adsorbents would be needed in order to obtain a satisfactory purification.

In this paper we present the results from a series of experiments with high-performance liquid chromatography (HPLC).

## EXPERIMENTAL

### *Solvents*

Tin tetrachloride and some other tin halides react with water, alcohols, acids, esters, ethers, ketones and nitrogen- and sulphur-containing compounds. A high solvent purity is essential in order to avoid reactions resulting in plugged filters and tubing, as well as corroded valves, tubing, columns and detectors. Acetonitrile (zur synthese, Merck, Darmstadt, G.F.R.; Cat. No. 800015) was purified on a glass column (50 × 2.5 cm) filled with Woelm (Eschwege, G.F.R.) aluminium oxide (neutral, activity grade 1). Benzene (puriss p.a. Fluka, Buchs, Switzerland; No. 12552 and zur analyse Merck 1783), carbon tetrachloride (puriss p.a. Fluka 87031 and zur analyse Merck AH 2222) and toluene (puriss p.a. Koch-Light, Colnbrook, Great Britain; No. 5303-52) were all purified on a glass column (50 × 2.5 cm) filled with Woelm aluminium oxide (basic, activity grade 1).

### *Chemicals*

Tetramethyltin (I), trimethyltin chloride (II), dimethyltin dichloride (III) and methyltin trichloride (IV) were synthesized by a Grignard reaction<sup>5</sup> with tin tetrachloride (V) (anhydrous, pure Koch-Light 6592 c), and by redistribution reactions. Tributyltin methoxide (VI) was synthesized from tributyltin chloride (VII) and sodium methoxide.

### *Chromatography*

A Waters Model 6000 A pump was connected to a home-made on-column septum injector (or alternatively a Waters UK 6 valve-loop injector) and a Waters Model R-401 refractive index detector.

*Columns.* A = Perkin-Elmer ODS-SIL-X-1 (13  $\mu\text{m}$ , 50 cm × 2.6 mm I.D.); B = Waters  $\mu$ Bondapak CN (10  $\mu\text{m}$ , 30 cm × 3.9 mm I.D.); C = Spherosil XOB 75 + Pyrocarbon (20–31.5  $\mu\text{m}$ , 50 cm × 2.6 mm I.D.), slurry-packed in bromobenzene; D = Waters Styragel 60 A (<37  $\mu\text{m}$ , 50 cm × 7.8 mm I.D.), slurry-packed in benzene; E = Styragel 100 A (<37  $\mu\text{m}$ , 50 cm × 7.8 mm I.D.), packed as in D; F = Styragel 500 A (<37  $\mu\text{m}$ , 50 cm × 7.8 mm I.D.), packed as in D; G = Styragel 100 A (10  $\mu\text{m}$ , 30 cm × 7.8 mm I.D.).

## RESULTS

### *Silica-based adsorbents*

Tin tetrachloride was totally adsorbed on the octadecylsilyl (ODS) column (column A). After a series of injections, the column efficiency was strongly reduced, indicating irreversible reactions between the sample and adsorbent. The cyanoalkyl-silica (CN) column (column B) also gave strong adsorption of tin tetrachloride. After "saturation" with tin tetrachloride, the column was able to separate some methylated tin halides, but extended use resulted in irreversible damage to the packing, as for the ODS column.

### *Pyrolytic carbon black on silica*

The tin derivatives I–IV were chromatographed in benzene, toluene, carbon tetrachloride and acetonitrile on the pyrocarbon column (column C). No reaction

with the adsorbent was noticed, but the retention and the resolution were too low to achieve sufficient separation of the components of the mixture.

### Styragels

Compounds I-V were examined in benzene, toluene, carbon tetrachloride, acetonitrile, and mixtures of benzene and carbon tetrachloride on Styragel columns with pore sizes of 60 A (column D), 100 A (column E) and 500 A (column F). The best separation was obtained with carbon tetrachloride as a solvent. The components were eluted in order of increasing molecular weight (Fig. 1) in all solvents except acetonitrile, which gave the opposite order of elution. Of the different pore sizes of Styragel ( $<37 \mu\text{m}$ ) in carbon tetrachloride, the highest retention of I, II and III was obtained on the 60 A packing (Table I). The 500 A packing gave the strongest retention of IV and V.

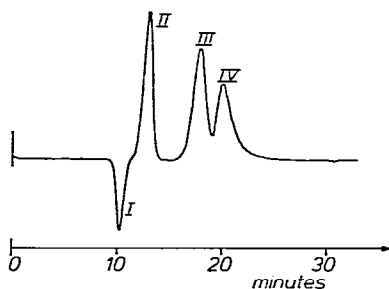


Fig. 1. Separation of methyltin chlorides on column D; eluent, carbon tetrachloride at 1 ml/min. Refractive index detector. Peaks: I =  $\text{Me}_4\text{Sn}$ ; II =  $\text{Me}_3\text{SnCl}$ ; III =  $\text{Me}_2\text{SnCl}_2$ ; IV =  $\text{MeSnCl}_3$ .

TABLE I

CAPACITY FACTORS ( $k'$ ) OF TIN DERIVATIVES IN CARBON TETRACHLORIDE ON THE STYRAGEL COLUMNS D, E AND F

Sample	D (60 A)	E 100 A)	F (500 A)
$\text{Me}_4\text{Sn}$	1.00	1.00	1.00
$\text{Me}_3\text{SnCl}$	1.30	1.21	1.18
$\text{Me}_2\text{SnCl}_2$	1.84	1.60	1.53
$\text{MeSnCl}_3$	2.02	1.72	4.46
$\text{SnCl}_4$	2.20*	3.80*	**

\* Broad tailing peaks.

\*\* Strongly retained, slowly bleeding out.

When tetramethyltin (I) was added to a mixture of II, III and IV, redistribution occurred, resulting in increasing peaks of I and III and decreasing peaks of II and IV (Fig. 2).

The micro-particle Styragel (column G) was tested for its performance on less reactive organotin compounds. Thus a mixture of VI and VII was easily separated in benzene (Fig. 3).

### DISCUSSION

The silica-based ODS and CN columns were not sufficiently inert towards the highly reactive tin halides. This may be due to the presence of unreacted silanol hydroxyl groups.

The silica column covered pyrolytically with carbon black was sufficiently

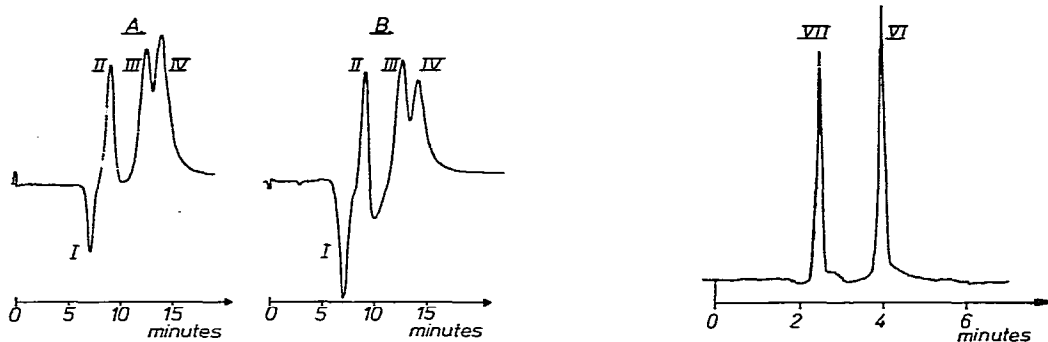


Fig. 2. Redistribution of methyltin chlorides on column D; eluent, carbon tetrachloride at 2 ml/min. Refractive index detector. Samples: A = 25  $\mu$ l, 10% each of I-IV in  $\text{CCl}_4$ ; B = as A, but injected 1 min after addition of 5% more of I. Peaks as in Fig. 1.

Fig. 3. Separation of tributyltin methoxide (VI) and tributyltin chloride (VII) on column G; eluent, benzene at 3 ml/min. Refractive index detector.

inert, but gave too low a resolution of the methylated derivatives. Organometallic compounds with larger alkyl groups would be expected to have higher retention, and for such purposes the pyrocarbon column could be valuable, especially when a packing with smaller particle diameter is available.

Providing extensive precautions are taken in purifying the solvents and keeping the system absolutely free from moisture, mixtures of the more reactive organotin halides may be separated on Styragel columns. For most routine purposes, the relatively cheap, larger particle size, Styragels combined with a simple on-column injector are recommended. For less reactive organometallic compounds, micro Styragel columns and valve-loop injectors could be used.

The elution pattern was generally opposite to what is expected from size separation on a gel-permeation packing. Thus, the separation was apparently obtained by adsorption and not by exclusion effects. In acetonitrile, where the opposite elution order was observed, exclusion chromatography may be operating on complexes formed between the tin derivatives and the solvent. The resolution was, however, much better in carbon tetrachloride than in acetonitrile.

In conclusion, the best purification of methyltin chlorides was obtained with carbon tetrachloride. Other tin derivatives may, however, be well separated in different solvents, as in the case of tributyltin methoxide and tributyltin chloride in benzene. As seen from Fig. 2, HPLC can also provide an additional (to NMR) way of studying redistribution effects in equilibrium mixtures of organotin halides.

#### ACKNOWLEDGEMENT

We thank Dr. H. Cotin, Ecole Polytechnique, Palaiseau, France, for his gift of the adsorbent used in column C.

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