

CHROM. 13,134

Note

Comparative assessment of gas-liquid chromatography and high-performance liquid chromatography for the separation of tin tetraalkyls and alkyltin halides

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(First received April 14th, 1980; revised manuscript received July 10th, 1980)

Alkyl- and aryltin compounds are extensively used as fungicides, in anti-fouling paints and as poly(vinyl chloride) stabilisers¹. The toxicity of these compounds varies with the nature and the number of organic groups covalently bonded to tin^{2,3}. Precise speciation is thus important in the manufacture of products and in considering their dispersion and sequential degradation in the environment⁴. Gas-liquid chromatography (GLC) with a flame ionization detector (FID) has been extensively applied to the separation and determination of organotin compounds in the past decade⁵ although selective fluorimetric assay is possible for certain compounds⁶.

Two problems arise in the GLC of alkyltin compounds using FIDs: (a) the occurrence of on-column redistribution reactions at the operating temperatures for reasonable elution times and peak shapes⁷ and (b) drift in detector sensitivity due to build up of SnO₂ in the FID^{8,9}. Both effects were confirmed, the latter was closely associated with detector design: Pye FIDs showed less rapid drift than Perkin-Elmer detectors. A katharometer detector is more suitable for quantitative studies of the on-column distribution reactions, but is not suitable for trace analysis because of poor detection limits.

Traditional laminar and column chromatography techniques for organotin compounds have been reviewed⁵; recently high-performance liquid chromatography (HPLC) has been applied to some organotins^{10,11} and to other organometallic compounds with varying success^{12–14}. Excellent isocratic HPLC separations are reported herein for each series of compounds. Detection is a problem for lower alkyl compounds which have virtually no absorption in the near UV and also give low refractive index response.

EXPERIMENTAL

Samples, reagents and solutions

Synthesis of organotin chlorides. Tetra-, tri-, di- and mono-, methyl and ethyltin chlorides were prepared by Grignard reaction¹⁵ and purified, by crystallisation or distillation under nitrogen as appropriate, until their elemental analyses agreed to within 0.3% of the theoretical values for each element.

Reagents. All reagents were of analytical grade unless otherwise stated.

Solvents. Acetone (laboratory grade) and pentane (spectroscopic grade).

Solutions. Samples of each alkyltin compound, containing 100–400 mg of tin, were weighed, transferred into standard flasks (10 cm³), then dissolved and made up to volume with acetone.

Apparatus. (a) Perkin-Elmer F17 gas chromatograph equipped with katharometer detector. (b) Liquid chromatograph, equipped with a constant-flow pump (Pye-Unicam Model LC3), a differential refractometer (Waters Assoc. Model R-400), circulating-water thermostat (Grant Instruments, Model SB401), injection head (Pye-Unicam component) used with a 50- μ l high-pressure microsyringe (Hamilton, V. A. Howe & Co.).

Chromatographic conditions

GLC. Column, stainless steel 2 m \times 8.0 mm O.D.; stationary phase, 3% silicone rubber SE-30 (E301) on 80–100 mesh Chromosorb G AW DMCS support; column temperature, 90°C for tetra-, tri-, di- and monomethyltin chloride and 150°C for tetra-, tri-, di- and monoethyltin chloride; carrier gas, helium; flow-rates, 16 cm³ min⁻¹ for the methyltin chlorides and 50 cm³ min⁻¹ for the ethyltin chlorides; detector, katharometer, filament 225°C, block 200°C; chart speed 0.2 cm min⁻¹.

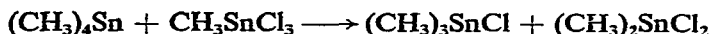
HPLC. Column, 250 \times 3.0 mm I.D.; stationary phase, ODS Spherisorb S5W (Phase Separations, Queensferry, Great Britain). Mobile phase, acetone–pentane (60:40), for the methyltin chlorides and acetone–pentane (70:30) for the ethyltin chlorides; temperature, 23°C \pm 0.1°C; chart speed, 0.3 cm min⁻¹.

RESULTS AND DISCUSSION

GLC

A series of non-polar columns were examined and silicone rubber SE-30 selected for detailed studies. Samples of 5 μ l of each methyl- and each ethyltin chloride solution were chromatographed and conditions sought to produce resolution within each set of compounds. Using a 2-m column it was not possible to resolve CH₃SnCl₃ and (CH₃)₂SnCl₂.

Mixtures of tin tetraalkyl and its halide derivatives react slowly at room temperature to form an equilibrium mixture. For the ethyltin series the redistribution reactions, on-column, are so slow that, at 150°C, relative peak areas for each component correlated well with the initial sample composition. This was not the case for the methyltin series. By chromatographically examining all possible pairs of compounds it was established that the only forward reaction to occur significantly, under the conditions examined, was



Hence it is not possible to examine all four methyltin compounds in admixture and either CH₃SnCl₃ or (CH₃)₄Sn must be absent to avoid redistribution. The retention times (t_R), numbers of plates (N), capacity ratios (k'), and resolution data (R), under optimised conditions, are given in Table I. Quantitative studies showed linear response curves up to 400 μ g tin for each compound, with slight variation in response between compounds, these factors and twice baseline noise detection limits are also in Table I.

TABLE I
GLC DATA FOR METHYL- AND ETHYLTIN CHLORIDES

Compound	t_R (min)	N	k'	R	Relative response factor	Detection limits ($\mu\text{g tin}$)
$(\text{CH}_3)_4\text{Sn}$	1.6	1024	1.13	6.3	1.0	8.25
$(\text{CH}_3)_3\text{SnCl}$	3.7	1369	3.93	5.2	0.9	8.25
$(\text{CH}_3)_2\text{SnCl}_2$	6.5	1201	7.66		1.0	8.25
$(\text{C}_2\text{H}_5)_4\text{Sn}$	1.9	1296	2.25	2.0	1.0	8.25
$(\text{C}_2\text{H}_5)_3\text{SnCl}$	2.7	1444	3.62	3.1	1.0	8.25
$(\text{C}_2\text{H}_5)_2\text{SnCl}_2$	4.5	2024	6.71	3.0	1.2	12.37
$\text{C}_2\text{H}_5\text{SnCl}_3$	6.3	2540	9.80		1.4	16.50

HPLC

Reversed-phase chromatography was selected by the nature of the solutes. Solvents ranging from *n*-pentane to methanol, with different polarities¹⁶ having refractive indices compatible with the detector (refractive index, 1.3–1.4) were examined using a bonded ODS column.

The best performance in terms of peak shape, plate numbers and relative separations was achieved with mobile phases of acetone–*n*-pentane (60:40) for the methyltin compounds and acetone–*n*-pentane (70:30) for the ethyltin compounds. No decomposition or redistribution reactions were observed for either set of compounds. The chromatographic data, response and detection limits, are given in Table II, response curves were linear for up to 30 mg tin for each compound. A typical chromatogram from a mixture of methyltin chlorides is shown in Fig. 1. Results for the quantitative elemental and HPLC analysis of a commercial, nominal 4:1, mixture of di- and monomethyltin chlorides agree well and are given in Table III.

TABLE II
HPLC DATA FOR METHYL- AND ETHYLTIN CHLORIDES

Compound	t_R (min)	N	k'	R	Relative response factor	Detection limits ($\mu\text{g tin}$)
$(\text{CH}_3)_4\text{Sn}$	1.1	2116	0.70	2.0	1.0	50
$(\text{CH}_3)_3\text{SnCl}$	1.3	2704	1.05	2.0	1.1	80
$(\text{CH}_3)_2\text{SnCl}_2$	1.5	2567	1.31	2.0	1.2	90
CH_3SnCl_3	1.7	2736	1.58		1.3	100
$(\text{C}_2\text{H}_5)_4\text{Sn}$	1.2	2304	0.78	3.0	1.0	50
$(\text{C}_2\text{H}_5)_3\text{SnCl}$	1.5	3600	1.27	2.6	1.1	80
$(\text{C}_2\text{H}_5)_2\text{SnCl}_2$	1.8	3067	1.72	3.0	1.2	90
$\text{C}_2\text{H}_5\text{SnCl}_3$	2.2	3441	2.29		1.3	100

Previous HPLC studies using organotin compounds have been directed at detection rather than separation. The electrochemical properties of di- and trimethyltin cations in an ammonium acetate buffer in methanol water were determined, but chromatograms were not reported¹⁰ as was the case for certain other organometallic compounds studied. The present work shows the clear advantage of HPLC over GLC

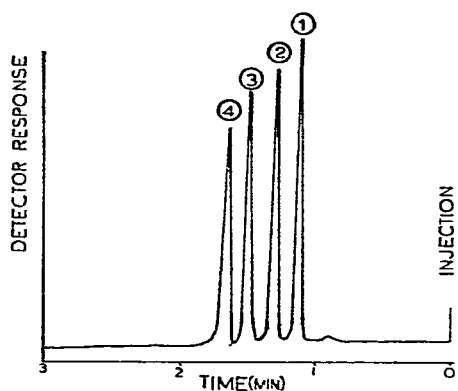


Fig. 1. Chromatogram of admixture of (1) $(\text{CH}_3)_4\text{Sn}$, (2) $(\text{CH}_3)_3\text{SnCl}$, (3) $(\text{CH}_3)_2\text{SnCl}_2$ and (4) $\text{CH}_3\text{-SnCl}_3$.

TABLE III

ANALYSIS OF DI- AND MONOMETHYLTIN CHLORIDE MIXTURE

	Elemental analysis		HPLC	
	Theor. 4:1 mixture (%)	Obs. (%)	Dimethyltin chloride	Monomethyltin chloride
Tin	53.0	53.0	Mean (%) 80.2	20.1
Chlorine	34.9	35.5	S.D. (%) ± 0.3	± 0.3
Carbon	9.7	9.3	(Five results)	(Five results)
Hydrogen	2.4	2.3		

for the separation of mixtures of methyltin chlorides, in the latter case redistribution reactions require the absence of either CH_3SnCl_3 or $(\text{CH}_3)_4\text{Sn}$ from samples. For mixtures of ethyltin chloride both GLC and HPLC are satisfactory for identification or for quantitative applications.

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