

CHROMATOGRAPHIC STUDIES ON ORGANO-TIN COMPOUNDS

PART I. THE GAS CHROMATOGRAPHY OF ALKYL-TIN COMPOUNDS

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Although much study of organo-tin compounds has been made¹, little data is available concerning the chromatographic behaviour of organo-tin compounds. KAESZ *et al.*^{2,3} have observed the possibility of eluting perfluoroalkyl, and perfluorovinyl tin compounds on polyethylene glycol column. ABEL, NICKLESS AND POLLARD⁴ have published separations of the tetra-methyls of the Group IV B elements, using Apiezon L columns. Gas chromatography studies on organo-tin compounds have also been reported by MATSUDA AND MATSUDA⁵, while FRANC, WURST AND MAUNDRY⁶ have studied these compounds using paper and gas chromatography.

The two factors which render the gas chromatography of σ - and π -bonded organo-metallic compounds difficult as compared to organic compounds are:

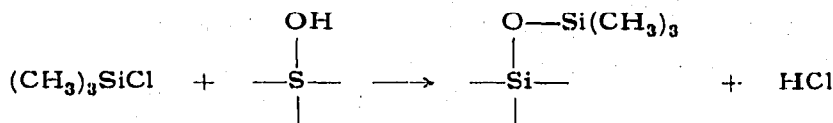
- (i) chemical reactivity, *e.g.* instability towards oxygen or moisture, and
- (ii) thermal instability.

The column support used in gas-liquid chromatography, should be solid-particles which are inert; but often this is not the case. If a support is insufficiently covered by the stationary liquid phase, *e.g.* 2-5 %, adsorption on the exposed siliceous sites becomes significant with polar solutes, and trailing occurs. As a consequence, retention volumes are no longer just directly proportional to the weight of solvent, and hence specific retention volumes can only be measured with columns containing a high proportion of stationary phase. Where organo-metallic solutes are involved, this adsorption becomes very important, the bond spreading is so bad that squalane columns can hardly be used for analysis of mixtures of such materials⁷.

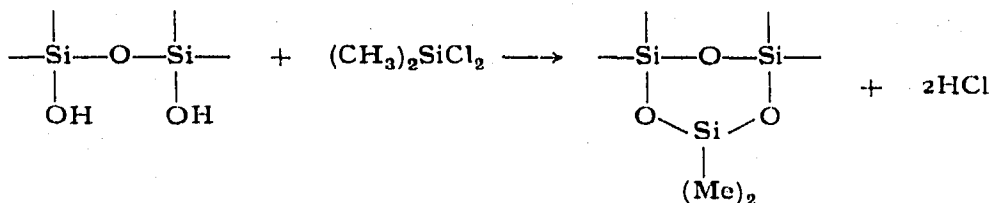
Chemical instability gives rise to chemical change as the compound passes through the chromatographic column. This usually occurs through formation of bonds between the compound and reactive groups either on the column support (*e.g.* acid sites), or the stationary phase (*e.g.* hydroxy-groups as in polyethylene glycol). This phenomenon is termed trans-esterification⁸, and was observed in the organo-tin hydrides, chloro-silanes, and amino-compounds, *e.g.* hexamethyldisilazane.

The initial approaches to pre-treatment of support to remove this activity was to add small amounts of highly polar and involatile liquids to the support^{8,9}, or to acid and then alkali wash the support¹⁰⁻¹². More recently there have been attempts to deposit solids such as silver on the support surface¹³, but unfortunately, this method cannot be used in the presence of thio-compounds, *e.g.* silyl thioethers⁷. The alternative method is to treat the active sites of the support, (which are presumed to be hydroxyl groups (-Si-O-H)), and replace these by groups which should yield at least a weakly

adsorbing site. Both trimethylchlorosilane^{14,15} and dimethyldichlorosilane^{16,17}, have now been used successfully to reduce the activity, the surface reaction is presumed to be of the type:



or:



When the hydroxyl groups are not adjacent, then a chlorosilyl ether $\geq\text{SiOSi(CH}_3)_2\text{Cl}$ may be left, which is not beneficial since it will be as reactive as the grouping replaced, because of the chlorine grouping.

As an alternative to this treatment, hexamethyldisilazane has been used since it reacts quantitatively with hydroxyl groups^{18,19}, and was used by BOHEMEN, LANGER, PERRETT AND PURNELL⁸, and has now been used to treat all the common solid supports²⁰. Many advantages have been claimed for hexamethyldisilazane, but it is expensive and gives a surface similar to the trimethylchlorosilane.

Much thought must be given to the detector and its design since often when a compound is eluted from a column, decomposition occurs in the detector, invalidating the elution process.

When such decomposition occurs, the metal is deposited on the wires or filaments of the katharometer, or on the collector plates of a flame ionization gauge. Recently the formation of tarry, and finally carbonaceous deposits which foul the katharometer filaments, has been reported²¹, when operating columns containing polar materials such as polyesters. Recommended treatment in such cases is regular flushing of the detector block, with both polar and non-polar solvents. Although such treatment was beneficial, in the course of time, however, the tarry deposits would carbonize, leading to permanent changes in the katharometer resistance. The partial contacts of carbon deposits between helices of the coiled filament, presumably were responsible for the increase in recorder base line noise. When finely-divided powder metal is deposited in the katharometer, especially on the filaments, a similar situation arises, but the bridge becomes permanently out of balance, since unfortunately no cleaning procedure can be used. A similar situation is found with the flame ionisation detector, especially the conventional types where the collector electrode plate is vertically above the flame. A modified detector is required, and even when detection can occur, attention must be paid to saturation limits, since non-linearity of signal response, and the inversion effect as reported by NOVÁK AND JANÁK²² has been observed.

EXPERIMENTAL

Trans-esterification was overcome by treatment of the supporting phase⁸. Celite 545 (36-60 mesh B.S.S.) was baked at 300° for 5 h, acid- and alkali-washed, dried at 50°, and treated with trimethylchlorosilane.

After such treatment it was possible to chromatograph and separate the methylchlorosilanes²³ and organo-tin hydrides, but as indicated later, the choice of stationary phase is important for this type of compound.

The gas-liquid chromatography of thermally unstable organo-metallic compounds was carried out using separation techniques at normal temperatures (20–100°) followed by combustion in a conventional micro-analytical furnace, absorption of water, and detection of the carbon dioxide with a Stuvé katharometer²⁴. The metal (as oxide) deposited in the furnace gradually poisons the copper oxide furnace packing, and has to be replaced frequently.

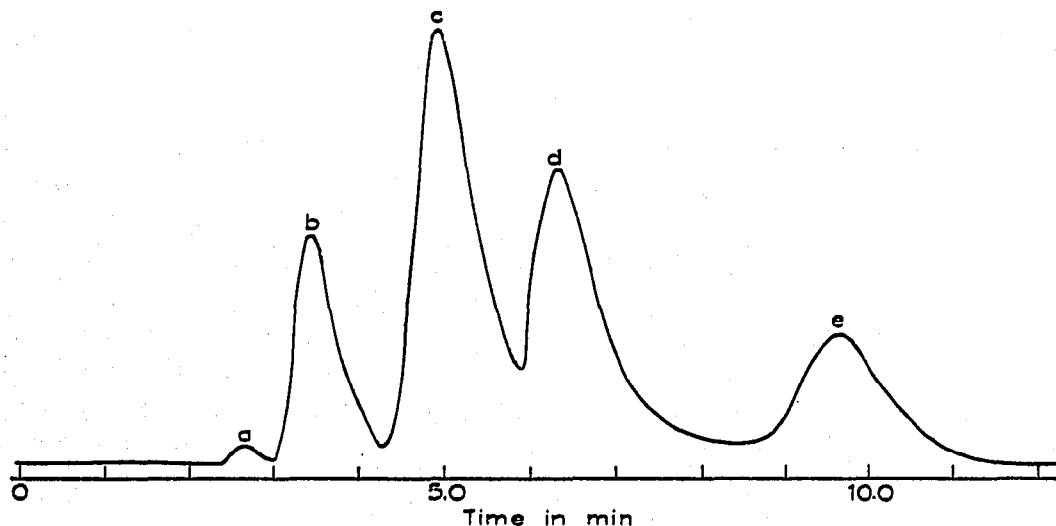


Fig. 1. Separation of alkylsiloxanes. (a) Diethyl ether; (b) trimethylsilyl methyl ether; (c) trimethylsilyl ethyl ether; (d) hexamethyldisiloxane; (e) trimethylsilyl *n*-propyl ether.

The unit gave linear calibration curves for aliphatic and aromatic hydrocarbons, ketones, and alkylsiloxanes (for separation see Fig. 1), and a separation of nickel and iron carbonyls is shown in Fig. 2. The column was 3 ft. of 25 % w/v di-2-ethylhexyl sebacate on Celite (36–60 mesh) at 56°. Carrier gas was oxygen free nitrogen at 50 ml/min.

However, it was found by subsequent work that the tin tetra-alkyls and related compounds could be detected by thermal conductivity cell, a modified flame ionization gauge²³, and a commercial gas-density balance unit²⁵ (Griffin and George D6 unit, Wembley, London). The latter unit has many advantages for such work, not

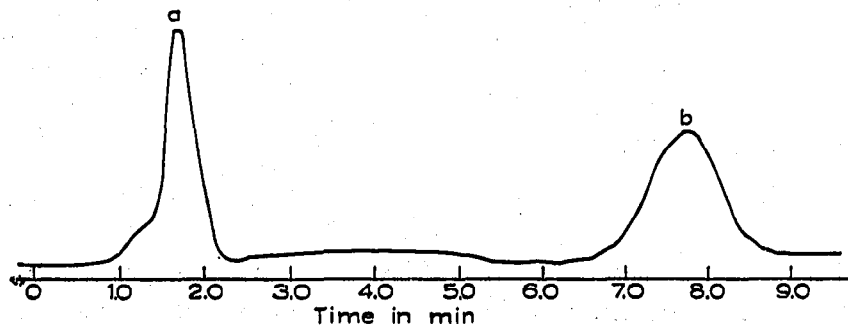


Fig. 2. Separation of metal carbonyls. (a) Nickel carbonyl; (b) iron carbonyl.

the least of these being that the sample is not subjected to a temperature greater than the column temperature; presumably a temperature at which the compound is stable. Results comparing these three detectors, with tetramethyl-tin with the appropriate conditions are given below:

Thermal conductivity detector (Fig. 3)

Column 6 ft. of 25 % w/w Apiezon M on treated Silicel 36-60 mesh.

Column temperature 140°. Detector temperature 150°.

Hydrogen carrier gas 30.0 ml per min. Recorder 5 mV F.S.D.

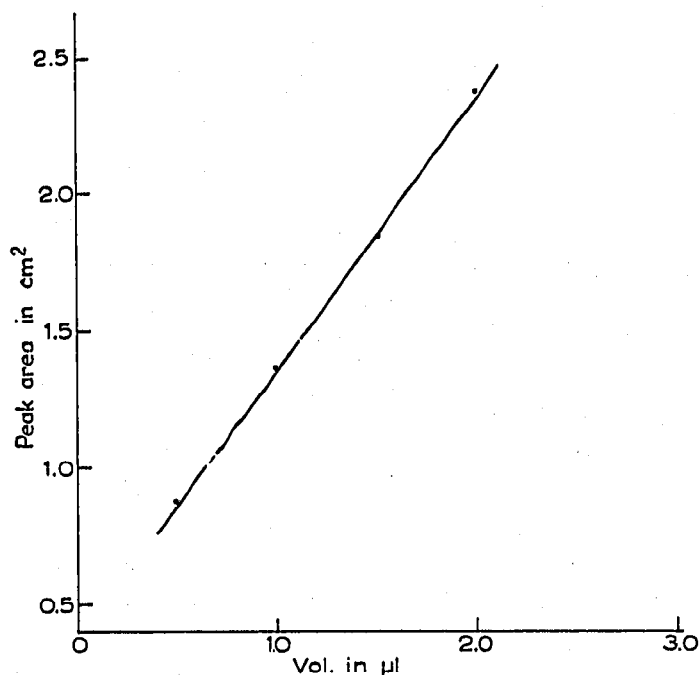


Fig. 3. Calibration graph for tetramethyltin using a thermal conductivity detector.

From Fig. 3, it is obvious that the graph is linear for low sample volumes, but above 2.5 μl , the thermal conductivity response is no longer linear. The relative detector responses to a number of compounds are given in Table I, using the nomenclature due to JAMIESON²⁶.

TABLE I

Compound	Response per mole relative to tetramethyltin (= 100)
Tetramethyltin	100
<i>n</i> -Hexane	98
Cyclohexane	92
<i>n</i> -Heptane	87
Benzene	116

Flame ionization detector

Column 6 ft. Apiezon M on Silocel (36-60 mesh).

Column temperature 140°. Bleed off 98 %;

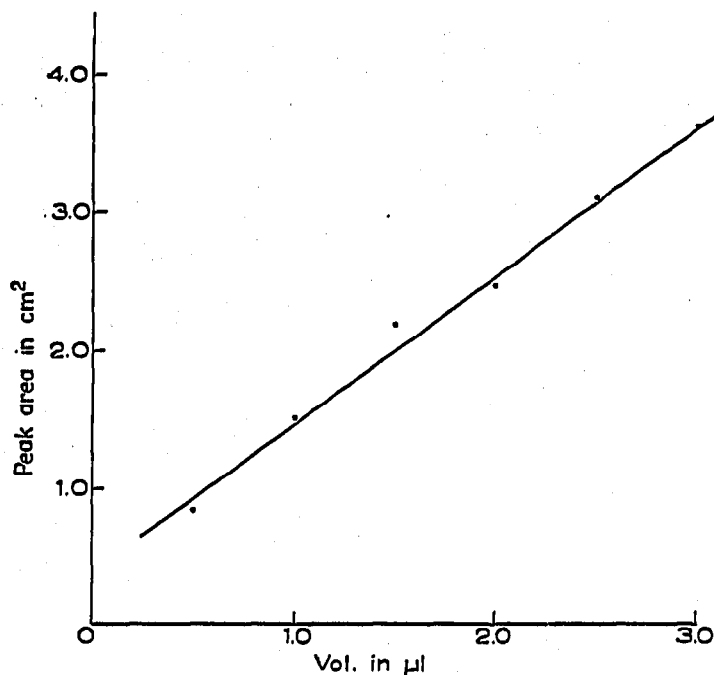


Fig. 4. Calibration graph for tetramethyltin using a flame ionization detector.

Flow rate of nitrogen through column 7 ml/min.

Hydrogen flow rate 30 ml/min.

Air flow rate 400 ml/min.

The response results are shown in Fig. 4, while it can be seen the graph is again linear over the lower ranges, while Fig. 5 shows the saturation phenomena at 4.0 μ l sample size or above, compared with the shape of the elution peak at 3.0 μ l sample size.

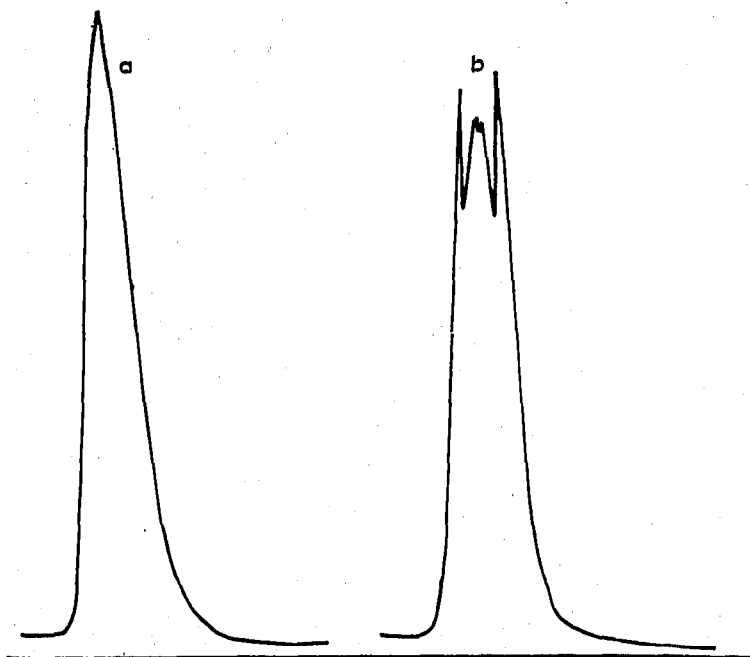


Fig. 5. Elution pattern of tetramethyltin using a flame ionization detector. (a) Normal response; (b) saturation response.

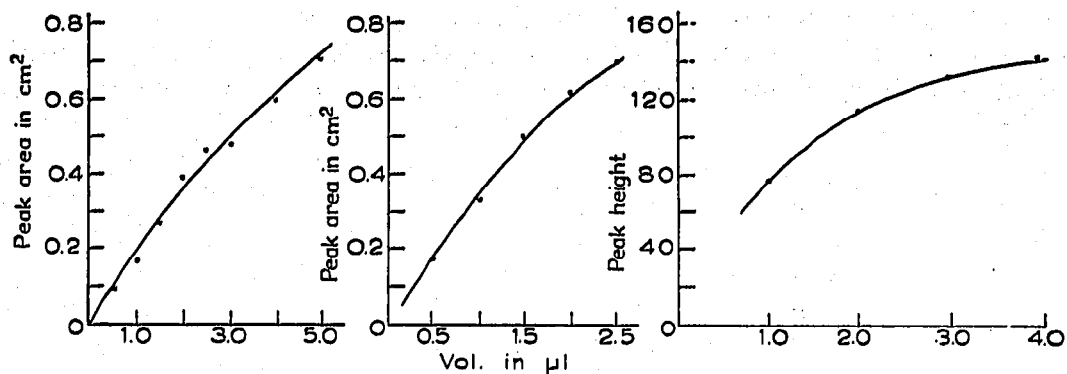


Fig. 6. Calibration graphs for tetramethyltin using a gas density detector.

Gas-density balance detector

Column 6 ft. 15% w/w silicone oil E 301 on Celite 545 (36-60 mesh).

Column and balance temperature 100°. Flow rate 30.0 ml of nitrogen per ml.

Due to non-linearity of signal response, the tetramethyltin was diluted with *n*-heptane, in the ratios 1:1, 1:5, and 1:10, and the results are shown in Fig. 6 (a), (b) and (c). Relative gas density balance responses for the compounds tested in the thermal conductivity experiments are given in Table II.:

TABLE II

Compound	Response per mole relative to tetramethyltin (= 100)
Tetramethyltin	100
<i>n</i> -Hexane	51
Cyclohexane	73
<i>n</i> -Heptane	78
Benzene	73

The relative sensitivities of the three detectors is:

Thermal conductivity: Gas-density balance: Flame ionization gauge
 1 10 1.700

During a study of the addition reactions of alkyltin mono- and dihydrides with unsaturated hydrocarbons, it was found necessary to find conditions under which such hydrides could be detected without breakdown. The gas-density balance proved to be excellent for this purpose, although the compounds were also detected using the flame ionization gauge. A separation of trimethyltin hydride, tetramethyltin and dipropyltin dihydride is given in Fig. 7. The conditions were identical for those given in Fig. 6, except the column temperature was 80°. It was possible to elute trimethyltin hydride through Silicone E 301, Apiezon L, and dinonyl phthalate phases, but when attempts to elute down a squalane (hexamethyltetracosane) column were made, decomposition occurred, and an elution pattern of the type shown in Fig. 8 was obtained. Several batches of squalane were used but all gave similar results. The shape of the peak is extremely interesting, because the negative flat portion is obviously

hydrogen formed by decomposition. The flat portion is interpreted as saturation of the gas-density balance, and the small positive peak is identified as tetramethyltin. This shows some rearrangement reaction must take place in or on the stationary phase

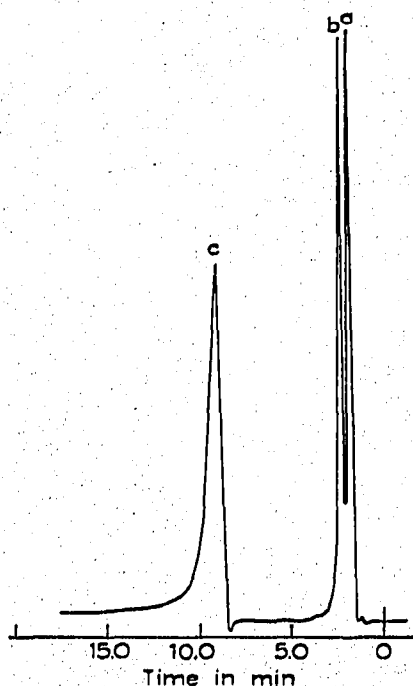


Fig. 7. Elution pattern of alkyltin hydrides. (a) Trimethyltin hydride; (b) tetramethyltin; (c) dipropyltin dihydride.

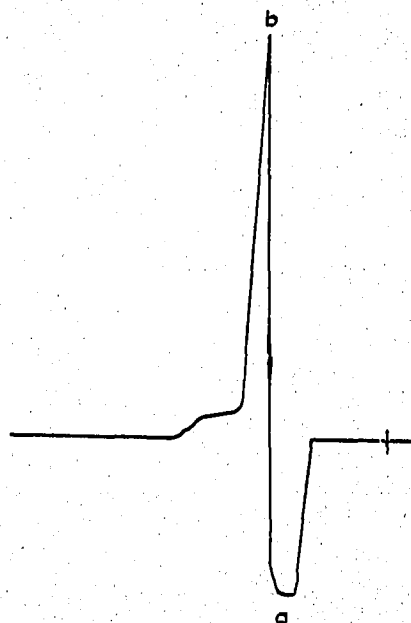
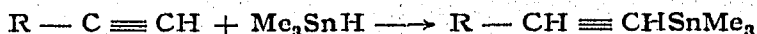
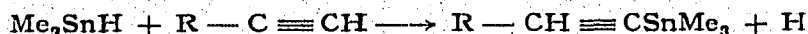


Fig. 8. Elution pattern of trimethyltin hydrides on squalane. (a) Hydrogen; (b) tetramethyltin.

because the trimethyltin hydride was identified as pure before injection on to the column. The reaction of the hydride with the phase was not unexpected, since the hydride readily adds to a triple bond²⁷, and less easily to a double bond. If some unsaturation was present in the squalane, then the reaction:



is possible. However, this reaction does not produce hydrogen, or tetramethyltin. In a radical-mechanism, which is favoured by NEUMANN, NIERMANN AND SOMMER²⁸, it is possible that a reaction of the type:



can take place. The hydrogen atom formed may then abstract hydrogen from further trimethyltin hydride forming hydrogen molecules and the radical Me_3Sn . Such a radical could again react with trimethyltin hydride, abstracting a methyl group, and so forming the tetramethyltin. Exchange reactions of this type between differing tetra-alkyl-tins are being studied, in an attempt to elucidate these points. Compounds of the type $R - CH = CHSnMe_3$ are perfectly stable and can be chromatographed without decomposition, when the molecular weight is low, *i.e.* up to $R = C_7$ (alkyl).

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SUMMARY

Conditions are given for the gas chromatographic elution of tetra-alkyl-tin, alkyl tin mono- and dihydrides, using thermal conductivity, gas density balance, and flame ionization detectors.

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