

THE APPLICATION OF GAS CHROMATOGRAPHY TO THE DETERMINATION OF RETENTION DATA OF SOME TRIMETHYL-SILYL ETHERS AND TRIMETHYL-SILYL THIOETHERS

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INTRODUCTION

It has been realised for some time that gas chromatography can be applied to the determination of some physical constants of some compounds, and its use in the analytical field for the analysis of complex mixtures of organo-metallic compounds is ever widening. Following the preliminary recommendations of the International Union of Pure and Applied Chemistry¹ as to the systematised nomenclature for retention data, standard apparatus, control and experimental procedures, specific retention volumes are measured for a homologous series of trimethyl-silyl ethers, and trimethyl-silyl thioethers.

The particular problems encountered in the gas chromatography of these compounds include the tendency to hydrolyse and breakdown on some stationary phases and under some conditions. To overcome these difficulties, high column temperatures are needed to produce reasonable retention volumes for the thioethers. The accuracy and reproducibility of retention volumes is estimated.

EXPERIMENTAL

Preparation of trimethyl-silyl ethers and thioethers

With the exception of the ethyl ether which was available commercially, the methyl, *n*-propyl, isopropyl, *n*-butyl, and *tert.*-butyl ethers were prepared from redistilled trimethylchlorosilane, and the appropriate alcohol². Ammonia was passed into the reaction mixture to remove hydrogen chloride—as ammonium chloride. Samples obtained during fractional distillation of the products were analysed by gas chromatography to estimate their purity.

In contrast the thioethers were prepared by the interaction of trimethylchlorosilane and the corresponding lead mercaptide³ since no reaction occurs between the chlorosilane and the thiol. Ethyl, *n*-propyl, isopropyl, *n*-butyl and *tert.*-butyl thioethers were prepared in this way. Hexamethyldisilthiane was prepared³ by the reaction between trimethylchlorosilane and anhydrous sodium sulphide in pressure vessels at 250°.

Apparatus

The gas-liquid chromatographic apparatus used was a Burrell "Kromo-Tog" Mk. 1

instrument. The standard column used was a 2.5 m U-column of 0.5 cm internal diameter glass tubing, the exterior being wound with a heating coil giving a continuous variation of column temperature up to 300°. The temperature was measured by a thermocouple inserted into the top of one leg of the column. The carrier gas used was B.O.C. oxygen-free nitrogen, whose flow-rate was measured at the end of the flow system by a soap-bubble flowmeter. The pressure of the gas after passing through silica gel and Linde "Molecular Sieve" Type 5A drying columns was measured to within 1 mm of mercury using a mercury manometer. All connecting tubes in the gas-system were carefully checked to ensure no possible entry for moisture. Liquid samples were introduced with an error of less than 2%, using Hamilton 10 or 100 μ l syringes through a puncture-type silicone-rubber seal directly on to the top of the column. The detector was a 4-filament type, situated directly at the end of the column. The detector temperature was kept constant at 150° (this was sufficient to prevent any condensation of samples in the detector), and the filament current was 120 mA. The output from the detector was recorded directly by a Honeywell-Brown 1 mV F.S.D. potentiometric recorder.

Stationary phases

The stationary phases used were present to 20% w/w extent on acid-washed Silocel C-22 firebrick 60-85 mesh; the liquids used were (i) polyethylene glycol 400, (ii) dinonyl phthalate, (iii) tritolyl phosphate, (iv) squalane and (v) Apiezon L grease. Great care was taken to ensure that no moisture was present on the liquid phase or support.

Retention volume

The specific retention volume V_g , is defined as V_R^0 , the retention volume fully corrected for dead volume, pressure drop across the column and measured at the column temperature, divided by the weight of the solvent; it is a precise physical property for any substance, a minimum set of conditions for its measurement have been proposed¹. These recommendations were followed as closely as possible with the apparatus available, and the specifications concerning measurements at different inlet/outlet pressure ratios and column temperatures were observed.

RESULTS

The two stationary phases chosen for systematic measurements of the oxygen ethers were Apiezon L, and tritolyl phosphate, neither of which caused any appreciable hydrolysis of the samples injected on to the column. Investigations showed an increasing amount of hydrolysis of the oxygen ethers to hexamethyldisiloxane when using squalane (2,6,10,15,19,23-hexamethyltetracosane) as a stationary phase as the column temperature was raised from 75° to 110°. Breakdown being almost complete above 120°. Similar results were obtained with polyethylene glycol 400 except the hydrolysis was greater at low temperatures; this must be due to the presence of hydroxyl groups present on the phase which become active at these temperatures. Dionyl phthalate was investigated but rejected because its great selectivity caused retention volumes and volumes which were too large to measure accurately when the recommended specifications were followed.

TABLE I
SPECIFIC RETENTION VOLUMES ON APIEZON L

Solvent	Apiezon L					
	Temperature °C	58°	80°	100°	120°	140°
(CH ₃) ₃ Si-O-R						
R = CH ₃		16.3 ± 0.5	6.73 ± 0.03	4.28 ± 0.08	2.57 ± 0.06	1.50 ± 0.01
C ₂ H ₅		26.2 ± 1.1	10.07 ± 0.26	6.22 ± 0.07	3.72 ± 0.07	2.03 ± 0.06
iso-C ₃ H ₇		33.9 ± 0.4	12.8 ± 0.54	7.93 ± 0.16	4.71 ± 0.09	2.69 ± 0.03
n-C ₃ H ₇		53.7 ± 1.3	19.1 ± 0.7	11.56 ± 0.13	6.96 ± 0.06	3.83 ± 0.08
n-C ₄ H ₉		116.0 ± 0.8	38.8 ± 1.0	22.1 ± 0.7	12.42 ± 0.12	6.64 ± 0.14
Si(CH ₃) ₃		33.7 ± 1.5	12.7 ± 0.5	7.74 ± 0.12	4.65 ± 0.06	2.59 ± 0.04

TABLE II
SPECIFIC RETENTION VOLUMES ON TRITOLYL PHOSPHATE

Solvent	Tritolyl phosphate			
	Temperature °C	80°	90°	100°
(CH ₃) ₃ Si-O-R				
R = CH ₃		5.65 ± 0.03	3.70 ± 0.03	2.69 ± 0.04
C ₂ H ₅		7.88 ± 0.11	5.14 ± 0.08	3.64 ± 0.04
iso-C ₃ H ₇		8.76 ± 0.06	6.18 ± 0.04	4.30 ± 0.05
n-C ₃ H ₇		13.70 ± 0.27	9.10 ± 0.13	6.40 ± 0.09
tert.-C ₄ H ₉		12.02 ± 0.07	7.99 ± 0.04	5.65 ± 0.01
n-C ₄ H ₉		26.52 ± 0.53	16.75 ± 0.20	11.19 ± 0.23
Si(CH ₃) ₃		6.57 ± 0.80	4.36 ± 0.08	3.03 ± 0.04

TABLE III
SPECIFIC RETENTION ON VOLUMES ON APIEZON L

Solvent	Apiezon L			
	Temperature °C	160°	180°	200°
(CH ₃) ₃ Si-S-R				
R = C ₂ H ₅		4.33 ± 0.08	2.89 ± 0.03	2.10 ± 0.04
iso-C ₃ H ₇		5.31 ± 0.08	3.43 ± 0.11	2.48 ± 0.07
n-C ₃ H ₇		6.53 ± 0.09	4.25 ± 0.07	3.07 ± 0.05
tert.-C ₃ H ₇		7.65 ± 0.03	5.18 ± 0.14	3.70 ± 0.02
n-C ₄ H ₉		9.95 ± 0.08	6.52 ± 0.08	4.49 ± 0.03
Si(CH ₃) ₃		7.16 ± 0.09	4.80 ± 0.11	3.31 ± 0.04

The only phase found suitable for the gas chromatography of the silyl thioethers was Apiezon L. Complete breakdown of the ethers was noted on phases, e.g. tritolyl phosphate even at 80°.

The values of V_g given in Tables I–III are the mean values at each temperature of determinations at inlet/outlet pressure ratios of 1.2, 1.4 and 1.6.

Errors given are on the mean of several determinations and are in almost every case less than 2%.

DISCUSSION

Chromatography of the trimethyl-silyl ethers

Fig. 1 shows the graphical relationship between $\log V_g$ and column temperature for the trimethyl-silyl ethers on Apiezon L and tritolyl phosphate. The relationship is approximately linear for both phases, tritolyl phosphate showing a slight curvature,

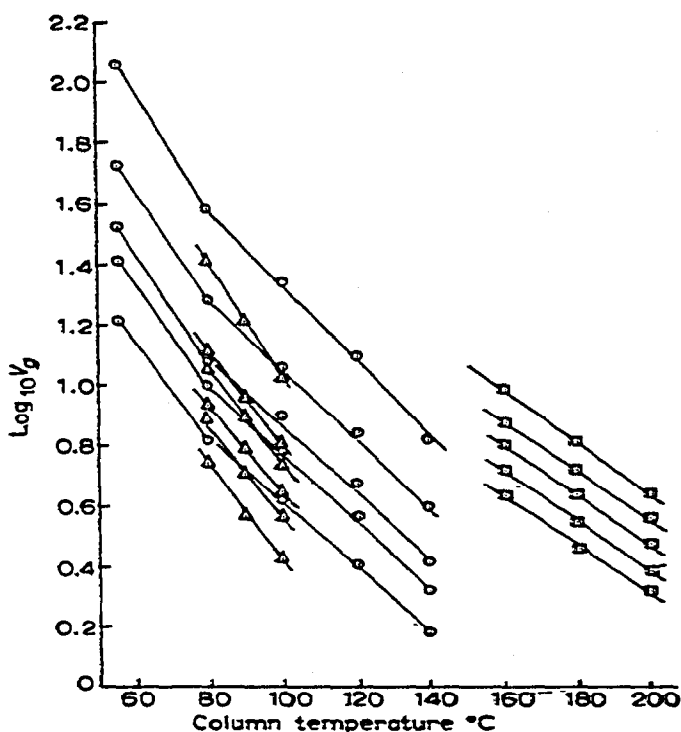


Fig. 1. Mean values for $\log_{10} V_g$ (at inlet/outlet pressure ratios 1.2, 1.4, 1.6) against column temperature, for the series. ○ $\text{Me}_3\text{Si-O-R}$ on Apiezon L; △ $\text{Me}_3\text{Si-O-R}$ on tritolyl phosphate; □ $\text{Me}_3\text{Si-S-R}$ on Apiezon L.

with the exception of $\log V_g$ values measured at 58° on Apiezon L. The discrepancy is attributed to Apiezon L not being fully liquid at this temperature, thus giving rise to distinct retention characteristics.

Figs. 2 and 3 relate $\log V_g$ to the number of carbon atoms in the alkoxy group, for different column temperatures on Apiezon L and tritolyl phosphate respectively. As may be predicted from theoretical considerations, approximately linear plots for the straight chain members were obtained. The exception was the methyl ether (having a greater V_g value than expected) which may be due to some interaction with the stationary phase since other considerations such as "dead time errors" can be

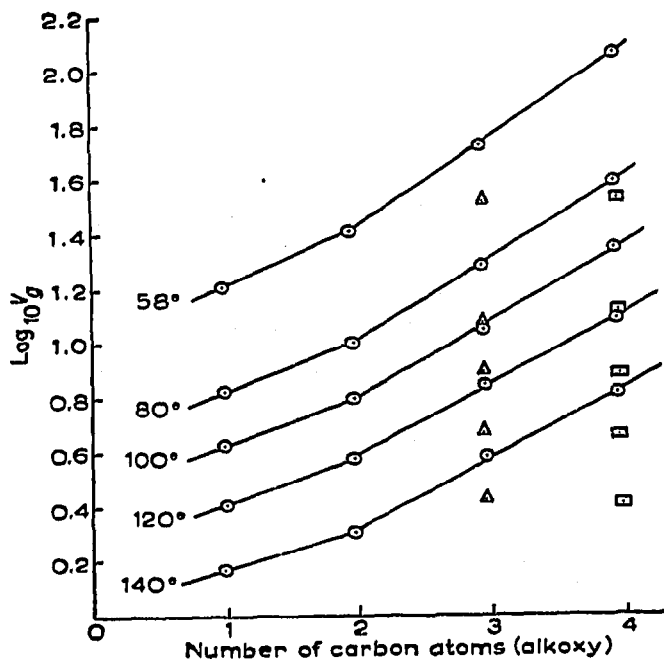


Fig. 2. Mean values for $\log_{10} V_g$ (pressure ratios 1.2, 1.4, 1.6) against number of alkoxy carbon atoms [counting one silicon as carbon in $(\text{CH}_3)_3\text{SiOSi}(\text{CH}_3)_3$], for different column temperatures. 20% Apiezon L stationary phase. \odot Normal alkoxy series; \triangle $R = \cdot\text{CH}(\text{CH}_3)_2$; \square $=(\text{CH}_3)_3\text{SiOSi}(\text{CH}_3)_3$.

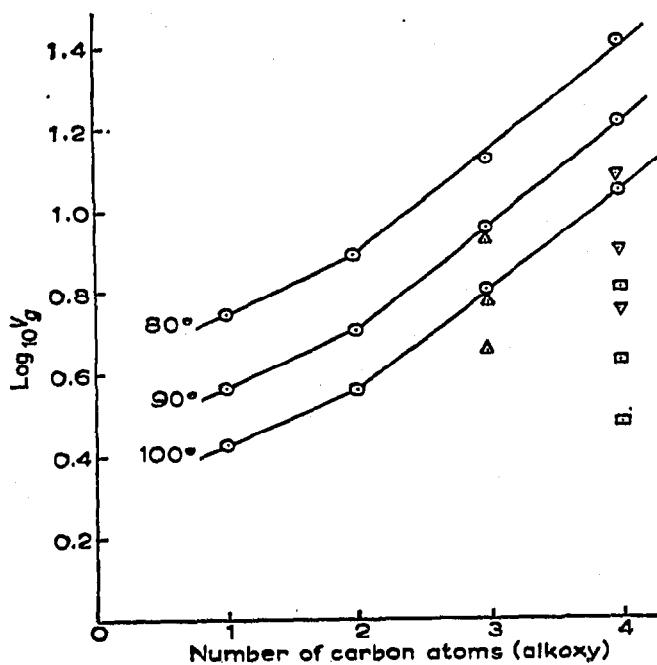


Fig. 3. As Fig. 2 except for 20% tritolyl phosphate stationary phase. \odot Normal alkoxy series; \triangle $R = -\text{CH}(\text{CH}_3)_2$; ∇ $R = -\text{C}(\text{CH}_3)_3$; \square $=(\text{CH}_3)_3\text{SiOSi}(\text{CH}_3)_3$.

ignored because of the standard procedures adopted. The branched chain isomers show correspondingly smaller retention volumes, although these are not exactly paralleled by their boiling points (see Fig. 4) which shows the mean values of $\log V_g$ against boiling point on 20% Apiezon L at 100°. Here, straight and branched chain isomers are seen to be linear, with the exception of the *tert.*-butyl ether and hexamethyldisilox-

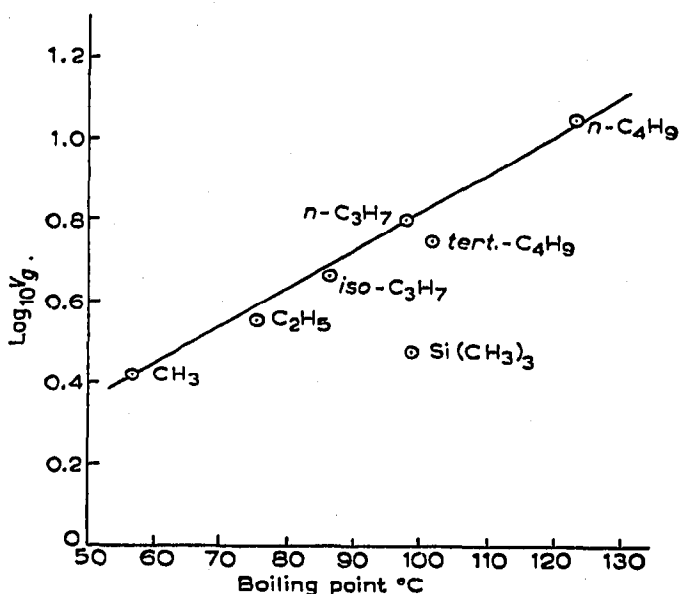


Fig. 4. Mean values of $\log_{10} V_g$ against boiling point for trimethyl-silyl alkyl ethers on 20% tritoyl phosphate at column temperature 100°.

ane. These two, especially the disiloxane, have much smaller retention volumes than anticipated from their boiling points. Thus there is some indication of selective retention of straight chain compounds over the more bulky branched isomers. Also the compound having an $\equiv \text{Si}-\text{O}-\text{Si} \equiv$ linkage is eluted much more rapidly than its $\equiv \text{Si}-\text{O}-\text{C} \equiv$ analogues.

On Apiezon L, hexamethyldisiloxane is seen to have a retention volume very close to that of the isopropyl ether, whilst on tritoyl phosphate, it has a smaller retention volume than the ethyl ether. This indicates selective retention of the disiloxane on Apiezon L as compared with tritoyl phosphate.

Chromatography of trimethyl-silyl thioethers

At the temperatures necessary to elute them, some breakdown into lower boiling components occurred, the proportion of breakdown for the majority of the thioethers increasing from 5% to 25% between 160° and 200°. An exception was the *tert.*-butyl thioether which showed a greater tendency to breakdown than the straight chain compounds, and could not be eluted even at 180° at low pressure ratios. Hexamethyldisilthiane showed less degradation than the carbon-containing compounds.

Since the preliminary breakdown products are consistent in form for each thioether under different conditions, but differ between the thioethers, there is scope for a more complete systematic study and characterisation of their decomposition, and this is under active investigation.

As for the oxygen analogues, graphs are drawn of (i) $\log V_g$ against column

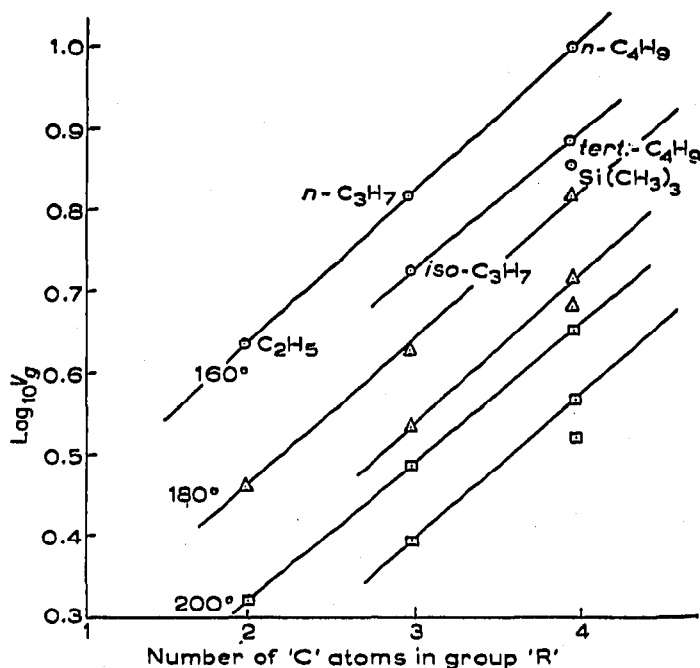


Fig. 5. Mean values for $\log_{10} V_g$ (pressure ratios 1.2, 1.4, 1.6) against number of carbon atoms in group R in thioethers for different column temperatures. 20% Apiezon L stationary phase. $\odot = 160^\circ$; $\triangle = 180^\circ$; $\square = 200^\circ$.

temperature for each thioether (Fig. 1), (ii) $\log V_g$ against the number of carbon atoms in the group R (Fig. 5). The former graph has a similar form to that for the oxygen series with some slight curvature. The latter graph also shows a similar form to that obtained for the oxygen series. The normal members of the series are again almost linear while the branched chain isomer have lower value of V_g , consistent with their boiling points. In contrast to the oxygen series on Apiezon L, where the V_g values of

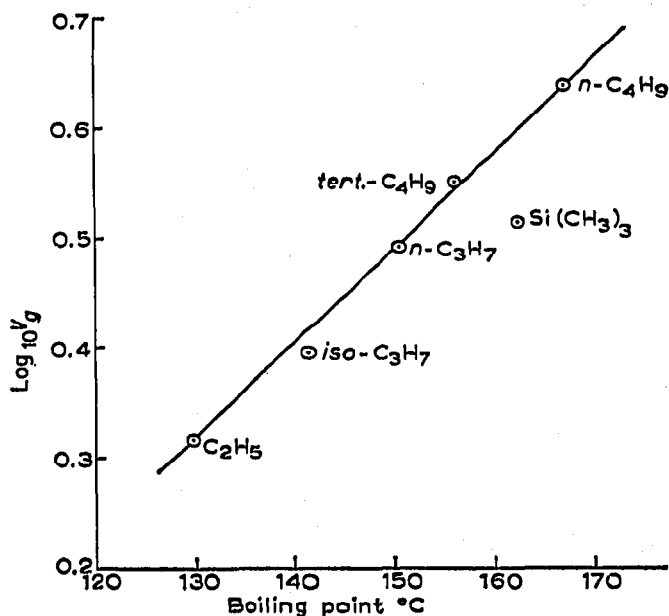


Fig. 6. Mean values of $\log_{10} V_g$ against boiling point for trimethyl-silyl alkyl thioethers on 20% Apiezon L at column temperature 200° .

hexamethylsiloxane and the isopropyl ether are almost identical. In the sulphur series, the retention volume of hexamethyldisilthiane was greater than either of the propyl thioether isomers, and only slightly smaller than that of the *tert.*-butyl thioether.

Since the respective boiling points of these compounds are:

$(\text{CH}_3)_3\text{Si-S-Si}(\text{CH}_3)_3$	163°
$(\text{CH}_3)_3\text{Si-S-CH}(\text{CH}_3)_2$	142°
$(\text{CH}_3)_3\text{Si-S-(CH}_2)_2\text{CH}_3$	151°
$(\text{CH}_3)_3\text{Si-S-C}(\text{CH}_3)_3$	157°

it can be seen that the thioethers are still retarded by the stationary phase in comparison with hexamethyldisilthiane, though not to as great an extent as in the oxygen series. These relative differences are shown in Fig. 6 which shows the graph of $\log V_R$ against boiling point (at column temperature 200°).

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SUMMARY

The conditions for the gas chromatography of the trimethyl-silyl ethers and the trimethyl-silyl thioethers and similar compounds have been investigated. Efficiencies of various stationary phases have been evaluated, and specific retention data obtained under standard conditions.

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