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## APPLICATION OF STATIONARY PHASES IN PREPARATIVE-SCALE GAS CHROMATOGRAPHY

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### SUMMARY

Fluorosiloxane and arylsiloxane polymers have been investigated as high-temperature siloxane phases in preparative gas chromatography. Their sorption capacities have been determined. Problems related to the vaporization of the sample and trapping of the separated fractions have also been investigated; these are of importance in high-temperature preparative chromatography. Examples are given of the use of siloxane rubbers as stationary phases for separating some mixtures on a preparative scale.

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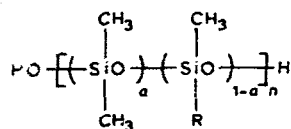
### INTRODUCTION

One of the objects of preparative-scale gas chromatography is the separation or purification of small amounts of valuable mixtures. The diversity of problems of this kind necessitates the use of stationary phases that differ in polarity, selectivity and useful temperature range.

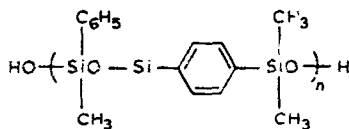
However, because of the large volumes of the preparative columns involved and the deficiency of many stationary phases, the necessary range of sorbents is not always available. The choice of a relatively versatile stationary phase that is stable at high temperatures and amenable to preparative work would greatly facilitate the solution of many practical problems.

It is recommended that siloxane rubber with various groups could be used as sufficiently versatile stationary phases because such phases permit the polarity to be varied over a wide range and they can be used at high temperatures. This is of great importance in preparative gas chromatography, in which the products of the column bleed not only impede the operation of the detector but, even more important, detract from the purity of the fractions obtained. In a number of instances it is necessary to remove trace amounts of the products of stationary phase losses from the substances obtained after separating the mixtures by gas-liquid chromatography (GLC). The use of siloxane rubbers, which can be used at high temperatures, increases the upper temperature limit of preparative-scale gas-liquid chromatography.

Fluorosiloxane (I) and arylsiloxane (II) polymers, which are linear polymers with the following general formulae, have been investigated:



(I)



(II)

where  $\text{R} = \text{CH}_2\text{CH}_2\text{CF}_3$  and  $n = 1000-5000$ .

One of the most important advantages of these siloxane polymers is their good thermal stability, as this determines their upper temperature limit and hence their applicable temperature range when used as high-temperature stationary phases.

#### EXPERIMENTAL AND RESULTS

The thermal properties of polysiloxanes were determined by thermal gravimetric analysis (TGA) and chromatography. The investigations of the thermal stability of the phases were conducted on a Paulik-Paulik-Erdey derivatograph. The measurements were made in an inert gas (helium) and the polymer was coated on to the solid support so as to make the conditions of the analysis similar to the operating conditions of a chromatographic column. It should be noted that the polymers used as stationary phases were stabilized, that is, volatile impurities and trace amounts of the catalyst were removed in order to raise the thermal stability before coating the solid support.

For a comparative estimation of the potential of thermal gravimetric analysis as a method for investigating the thermal stability of stationary phases in GLC we used SE-30 as stationary phase (the upper temperature limit of which is  $\sim 350^\circ$ ). The initial volatilization of SE-30 coated on Celite-545 was observed at  $350^\circ$ . The results were in good agreement with conventional chromatographic results, and the above method is sufficiently reliable for the determination of the thermal stabilities of stationary phases.

The results on the thermal stability of stationary phases obtained by different procedures are given in Table I.

TABLE I  
PRINCIPAL PROPERTIES OF SILOXANE PHASES

Polymer type	Trade name	$T_{max}$ ( $^\circ\text{C}$ )			Polarity $P$ ( $^\circ_{10}$ )	Dielectric constant, $\epsilon$
		TGA	TCD	FID		
Dimethylsiloxane polymer	SKT	350	350	300	6.8	2.31
Siloxane polymer with methyl-trifluoropropyl groups	SKTFT-25	380	305	300	15.0	6.00
	SKTFT-50	380	350	310	21.3	8.80
	SKTFT-75	380	350	310	26.5	9.30
	SKTFT-100	350	330	300	31.7	9.80
Siloxane polymer with arylene groups	SKTA	450	--	350	20.6	4.90

For successful use in preparative-scale gas chromatography, the stationary phase, in addition to general requirements, must possess a sufficient sorption capacity. It is only then that the HETP increase upon overloading will be sufficiently slow. Therefore, the resolutions and efficiencies obtained on siloxane rubber and some other phases were compared. Some problems related to the vaporization of the sample and collection of the separated fractions important for high-temperature preparative-scale gas chromatography were investigated.

The tests were performed on a Tswett-I analytical chromatograph, specially modified by us for preparative purposes<sup>1</sup>.

The separated fractions were collected in glass traps connected to the outlet ports of the distribution device by ground-glass joints<sup>2</sup>. A number of traps were used, and their designs are shown in Fig. 1. The traps were cooled with liquid nitrogen or dry ice. In some instances, substances with boiling points above 200° were condensed at room temperature.

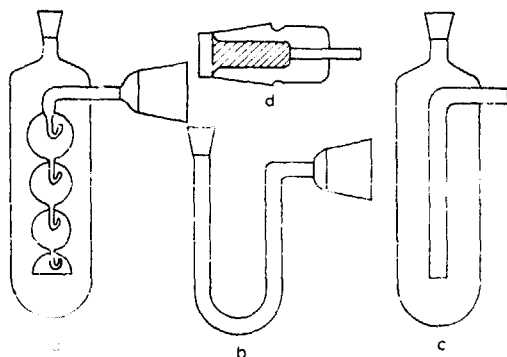


Fig. 1. Design of the traps: (a) with a separator; (b) U-tube traps; (c) "tube-in-tube"; (d) special device for trapping.

As the siloxanes used here were to be used for separations at the maximum possible temperature, the problem of trapping substances at high temperatures was investigated.

Upon condensation of substances with boiling points above 200°, aerosols are generally formed, and the amount of the substances trapped is very small. Trapping methods based on electroprecipitation, centrifugation, the use of temperature gradients, etc., are too complicated to be used in this case.

The trap used for condensation is shown schematically in Fig. 1a. The efficiency of this trap was compared with a U-tube trap and the "tube-in-tube" type (Figs. 1b and c). The condensation of the substances was carried out at room temperature. Cooling of the trap to 0° did not increase the efficiency of trapping. The trapping efficiency with filter materials was also investigated. A special device filled with a piece of fine glass wool or closed with a disc cut out of "Schott" glass filter-paper was connected to the outlet joint of the traps. The trapping efficiency was controlled in the following way. The sample of hexamethylphenylcyclotetrasiloxane was introduced into the chromatograph at a flash evaporator temperature of 300° and a column temperature of 210°. Upon a deflection of the recorder pen caused by the appearance of a peak, the trap was connected to the outlet joint of the chromatograph. The amount condensed was determined by weighing the traps.

TABLE II

EFFICIENCY OF DIFFERENT TRAPPING METHODS

Trap type	Filter material	Amount introduced (mg)	Amount trapped (mg)	Trapping efficiency (%)
a	Without filter	68	56	83
a	"Schott" filter	68	65	96
b	Without filter	68	28	42
b	"Schott" filter	68	66	97
b	Glass wool	70	64	91
c	Without filter	68	33	48

It can be seen from Table II that the traps of the simplest types (Figs. 1b and c) provide a trapping efficiency of only 40–50%, whereas the trap with the separator traps 85% of the amount introduced. The use of the filter device increases the trapping efficiency to 96%. Hence the use of a type "a" trap makes it possible to trap a large proportion of the sample introduced, and the use of the filter device enables almost the whole of the sample to be trapped.

When large amounts of the substance are present, it can be extracted from the traps by means of a capillary. With samples of 50–100 mg, the substance is spread over the walls of the trap, and the following procedure was used to extract it. The trap and the filter material were washed three times with 5–10-ml portions of distilled ether and poured into a 35-ml flask. The ether was allowed to volatilize and then pumped out for 2 h, after which the flask was warmed to 50–60°. Under these conditions, samples with boiling points above 300° did not volatilize. The transfer of the substance from the traps into the flask was almost quantitative. Upon evaporation of the ether, however, substances of high boiling points were volatilized with the ether vapour, and droplets of these substances condensed on the flask joint. Hence the flask should be filled to within 2–3 cm of its upper rim. Substances with lower boiling points can be transferred from the traps into ampoules by precooled condensation in a vacuum.

The preparative column was filled with SKTFT-50 siloxane rubber, which has been used before for analytical purposes<sup>3</sup>. The inert support, type C-22, was coated with the previously stabilized polymer from an acetone solution, the weight of the polymer being 20% of that of the support. The columns were filled by using a magnetic vibrator<sup>4</sup>. The efficiency of the packed column was determined by using *n*-heptane. The calculated height equivalent to a theoretical plate (HETP) was 2 mm.

The suitability of the phase for preparative separations was checked by introducing increasing volumes of different mixtures of hydrocarbons and chloro-hydrocarbons into the column (length 2.1 m, I.D. 1.4 mm). With an increase in the sample size, the peak width is known to increase in proportion to the volume of the sample. The plots for chloroform and dichloroethane are shown in Fig. 2.

Fig. 2 also shows similar plots for dinonyl phthalate (DNP). The peak width for SKTFT-50 increases more slowly than that for DNP, *i.e.*, the overloading of the column takes place more slowly. The slope of the straight lines is 7 for DNP and 4.3 for SKTFT-50. Plots of the dependence of  $K_1$  for a chloroform–dichloroethane

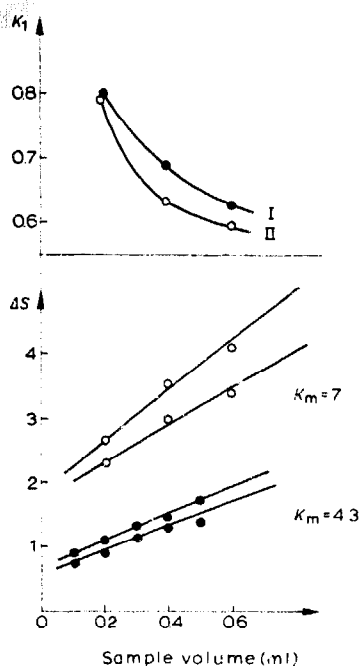


Fig. 2. Dependence of peak width and  $K_1$  upon sample volume on different phases for chloroform and dichloroethane: (I) SKTFT-50; (II) DNP.

mixture on the sample volume using SKTFT-50 and DNP are also given in Fig. 2. For these phases, the separation factor  $\alpha$  was the same (1.4). For the small sample on these phases  $K_1$  is almost the same, but as the sample on SKTFT-50 increases,  $K_1$  decreases much more slowly. Similar results were obtained for other mixtures of hydrocarbons and chlorohydrocarbons.

Hence, the sorption capacity of SKTFT-50 is not inferior to that of DNP, and this phase can be used successfully for the separation of large volumes of mixtures.

#### APPLICATIONS

Some applications of siloxane rubbers as stationary phases for the separation of mixtures on a preparative scale are described below.

##### *Separation of hexahydroindane isomers*

The initial mixture contained 90% of the *cis*-isomer and 10% of the *trans*-isomer. A 15-ml volume of the mixture was separated (Fig. 3). The analysis of the separated fractions on a Griffin chromatograph (column length 2.7 m, I.D. 6 mm) using the above phase showed that *cis*- and *trans*-isomers with purities of 99.99% and 99.90%, respectively, were obtained.

##### *Purification of phenylcyclopentane*

The initial product was a mixture containing 81.5% phenylcyclopentane (b.p. 217°). The separation was carried out on a column of length 4.8 m and I.D.

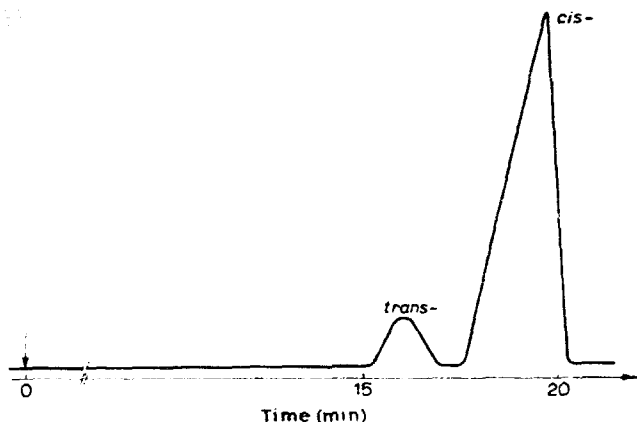


Fig. 3. Chromatogram of the preparative separation of the isomers of hexahydroindane (column length 4.8 m, I.D. 17 mm, column temperature 115°).

17 mm at an oven temperature as high as 178° and a flash heater temperature as high as 230°. The purity of the separated phenylcyclopentane, as determined on this analytical chromatograph, was 99.0%; the remainder was water transferred from the trap into the ampoule during pre-condensation of the substance (Fig. 4).

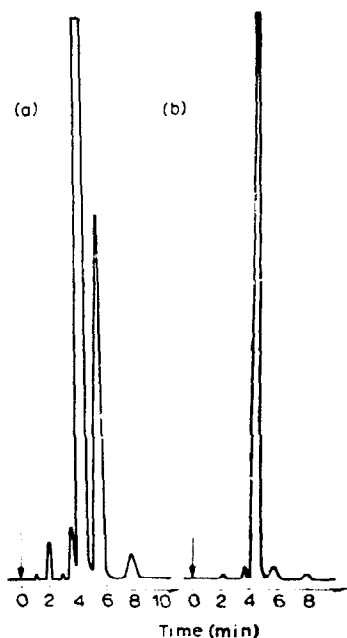


Fig. 4. Chromatogram of phenylcyclopentane on the analytical chromatograph (column length 2.7 m, column temperature 179°) (a) Initial mixture; (b) purified mixture.

#### *The isolation of siloxanes from reaction mixtures<sup>5</sup>*

The isolation of siloxanes was carried out on the column described above. The flow-rate of the nitrogen carrier gas was 0.75 l/min, and the flow split through the detector was 4%; the bridge current was 150 mA; the column outlet pressure was

1 atm. The analysis of the products obtained was also carried out on the Griffin chromatograph.

As chlorosiloxanes are strongly hydrolyzed, a special trap with FP tissue cooled with liquid nitrogen was added to the system involving standard columns with calcium chloride and silica gel. Moreover, some brass parts of the distribution tap were replaced by parts made of stainless steel. However, hydrogen chloride formed as a result of hydrolysis, owing to high local concentration, causes corrosion even of stainless steel parts when chlorides are evolved. After the separation of 100 ml of the initial mixtures, the outlet tubes were covered with a dark film, and the purity of the resulting product was gradually reduced from 99.9% to 96.3%.

The products of separation were collected in glass traps connected to the distribution tap. When these traps were disconnected, their inlets were closed with glass wool and the outlets with a plastic tube with a clamp.

The concentration of  $\alpha,\omega$ -dichloro-octamethyltetrasiloxane in the mixture obtained by the reaction of telomerisation was as high as 42%.  $\alpha,\omega$ -Dichloro-octamethyltetrasiloxane was evolved at an oven temperature of 178°; the flash heater temperature was 230° and the temperature of the distribution tap was 180°. The volume of the sample introduced was 3 ml. The purity of the product obtained was 99.2%.

As a result of the Grignard reaction, chlorine contained in the siloxane was substituted by  $-\text{CD}_3$  and  $-\text{CH}_3$  groups. Under the conditions described above (oven temperature 154°; the volume of the sample injected was reduced to 0.5 ml because of a deficiency of the products), 1,4-bis-deuteromethyltetrasiloxane of 93% purity was isolated with a purity of 99.9% (Fig. 5).

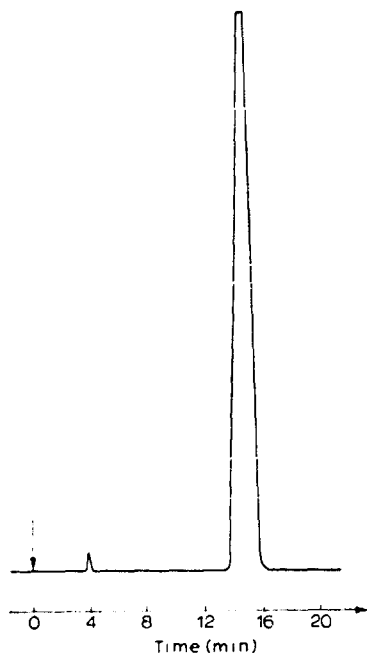


Fig. 5. Chromatogram of  $\alpha,\omega$ -di(trideuteromethyl)octamethyltetrasiloxane (purified by preparative GLC; 99.9% purity). Packing: 20% SKTFT-50 on Celite-545 (column length, 1.87 m).

*Micropreparative separation of some high-boiling compounds*

A procedure has been developed<sup>6</sup> for the preparative separation of the isomers of high-boiling organosilicone compounds (adducts of hydride of siloxane to nitro- and aminostyrenes) listed in Table III.

The difference between the isomers lies in the linear ( $-\text{CH}_2-\text{CH}_2-$ ) or branched ( $-\text{CH}-$ ) character of the  $\text{C}_2\text{H}_4$  group. As these compounds were available in small



TABLE III  
ORGANOSILICONE COMPOUNDS SEPARATED ON A PREPARATIVE-SCALE GAS CHROMATOGRAPH

No.	Formula	Boiling point (°C)	Column temperature (°C)	Impurity content (%)
1	$p\text{-NH}_2\text{C}_6\text{H}_4\text{C}_2\text{H}_4\text{Si}(\text{CH}_3)_2\text{OSi}(\text{CH}_3)_3$	90-91 (1 mm)	215	1.2 1.5
2	$m\text{-NO}_2\text{C}_6\text{H}_4\text{C}_2\text{H}_4\text{Si}(\text{CH}_3)_2\text{OSi}(\text{CH}_3)_3$	143 (3 mm)	212	0.7
3	$\begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \\   \quad   \\ m\text{-NH}_2\text{C}_6\text{H}_4\text{C}_2\text{H}_4\text{-Si-O-Si-CH}_3 \\   \quad   \\ \text{O} \quad \text{O} \\ \\ \text{H}_3\text{C-Si-O-Si-CH}_3 \\ \\ \text{CH}_3 \quad \text{CH}_3 \\   \quad   \\ \text{CH}_3 \quad \text{CH}_3 \end{array}$	142-144 (2 mm)	220	0.6 1.0
4	$\begin{array}{c} \text{O} \quad \text{O} \\   \quad   \\ m\text{-NO}_2\text{C}_6\text{H}_4\text{C}_2\text{H}_4\text{-Si-O-Si-CH}_3 \\   \quad   \\ \text{H}_3\text{C-Si-O-Si-CH}_3 \\ \\ \text{CH}_3 \quad \text{CH}_3 \end{array}$	114 (1 mm)	220	1.0
5	$o\text{-NH}_2\text{C}_6\text{H}_4\text{C}_2\text{H}_4\text{Si}(\text{CH}_3)_2\text{OSi}(\text{CH}_3)_3$	137 (3 mm)	210	1.0

amounts and are expensive, a preliminary test of the procedure was made on hexamethylphenylcyclotetrasiloxane. The preparative gas chromatograph had a standard gas flow system. About 2% of the helium stream from the column was directed into the detector. The columns (length 2.1 m, I.D. 14 mm) were packed with C-22 as the inert support coated with 20% SKTFT-50. In most experiments the column temperature was 200-220°.

A study of the effect of the flash heater temperature on the separation efficiency showed that the resolution of two isomers difficult to separate was markedly improved on this phase as the flash heater temperature increased from 240° to 340°. It is recommended that the flash heater temperature is not decreased below 335°.

The above procedure was used for the separation of the isomers listed in Table III. The total amount of each substance was 200-500 mg, 70 mg of the sample being



used per injection. The condensation was carried out in the "a" type trap with glass wool as the filter material. The temperature of the separation and the purity of the fractions isolated are shown in Table III. The flow-rate of the helium carrier gas was 400 ml/min.

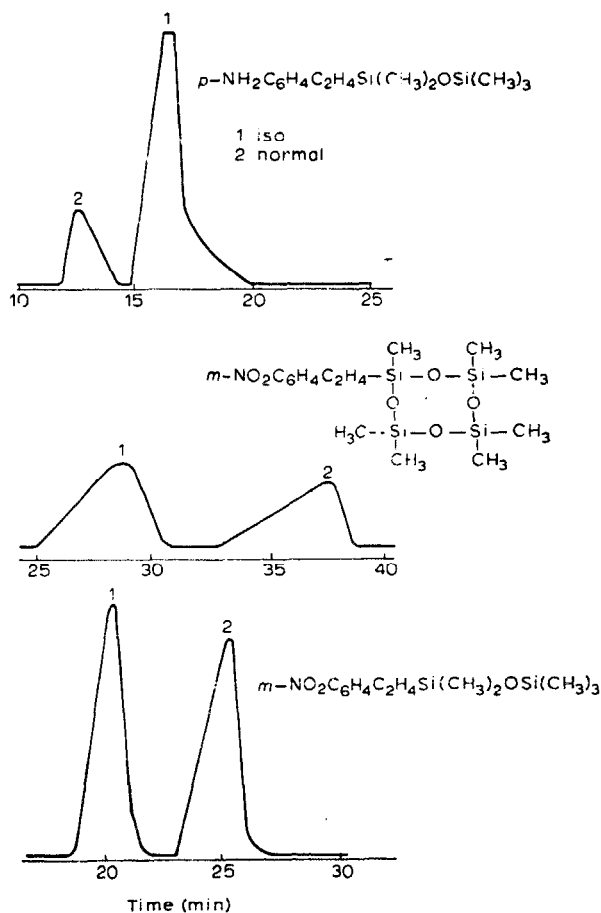


Fig. 6. Chromatograms of the separation of isomers of organosilicone compounds on the preparative gas chromatograph.

The chromatograms obtained on the preparative gas chromatograph are shown in Fig. 6. Infrared and nuclear magnetic resonance spectra<sup>7</sup> confirmed the sufficiently high purity of the fractions isolated, which was tested on a Griffin analytical chromatograph.

In addition, we have tested a siloxane stationary phase containing arylene groups (SKTA) for preparative separation. This phase, compared with SKTFT-50, has better selectivity for aromatic substances, with a similar thermal stability.

The examples of the separation of different classes of compounds given above show that the proposed siloxane phases containing trifluoropropyl groups (SKTFT) and arylene groups (SKTA) can be used in gas chromatography for preparative work at high temperatures.

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