

# Chromatographic Properties of Different Methyl–Phenyl (1:1) Substituted Silicone Stationary Phases for Open-Tubular Gas Chromatography

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## Abstract

The influence of different configurations of silicones having 50% methyl and 50% phenyl substitution on chromatographic properties, such as polarity and thermal stability, has been systematically investigated. Polysiloxanes composed of dimethyl and diphenyl units show very low levels of column bleed at temperatures up to 370°C, while polymers having methyl–phenyl substitution show severe bleeding at this temperature. The polarity of the latter polymers, as reflected by Kováts indices, is higher than for the polymers composed by dimethyl–diphenyl units.

## Introduction

*Phenyl-substituted polysiloxanes.* Phenyl-substituted silicones have been used extensively as stationary phases for gas chromatography ever since the pioneering work of James and Martin (1). Several oils of this type have been used for packed-column GC (2), the most well known being OV-17, produced by Ohio Valley Specialty Chemicals. The composition of this phase has been reported to be inconsistent. OV-17 is supposed to have 50% phenyl and 50% methyl substitution in the elementary unit (3), but phenyl contents of 41 (4), 35 (5), and 42% (6) have been reported. OV-17 has a low molecular weight: an average of 2300 was found for one batch (7). Trimethylsilyl terminated polymers having such a low molecular weight will have a content of polar substituents that is significantly lower than the elementary unit composition, the reason for this being the diluting effect of the terminal methyl groups. Further, OV-17 is composed by a mixture of cyclic and linear chains (7,8). A similar composition was reported for DC-710 (9). Differences in the proportions of cyclics and linears from batch to batch may thus account for the variation between batches. It should be noted that for high molecular weight stationary phases, the polar group content virtually coincides with their actual composition.

The first generation of phases was found to be unsuitable for application in open-tubular columns. For the formation of stable films of stationary phase in such columns, the use of silicone

gums rather than silicone oils was desirable. A gum of OV-17-type is now commercially available (Supelco). A further stabilization of the stationary phase film is achieved by immobilization. Here, two different approaches can be distinguished; thermal immobilization of silanol-terminated silicones (10–13) and radical initiated immobilization of end-capped silicones (14–17). The former approach is considered to result in the highest thermal stability (18).

A silanol-terminated methyl–phenyl silicone, OV-17-OH, is commercially available from the Ohio Valley Company (3). This polymer has, however, a low viscosity. Its viscosity can be increased simply by heating in an aluminum pan (13). The reproducibility of such a procedure may, however, be questioned. Thermal immobilization of the viscous OV-17-OH was attempted by Blum (13). An upper temperature limit of 330°C for columns prepared in this way was indicated. Verzele et al. (12) immobilized a silanol-terminated methyl–phenyl silicone by in situ heat curing. Thermogravimetric analysis of this phase, RSL-300, showed weight loss at temperatures above 370°C (19).

A vinylated methyl–phenyl silicone oil, OV-17-Vi, has also been introduced. The polymer OV-1701 was introduced as a substitute for OV-17. In this silicone, 14% of the silicon atoms have cyanopropyl–phenyl substitution and 86% have dimethyl substitution. As may have been expected, the selectivity of this phase is significantly different from that of OV-17 (20).

The phenyl groups in methyl–phenyl silicones may occur as diphenyl or methyl–phenyl. In their studies of phenyl-containing silylating reagents, Rijks et al. (21,22) noted that phenyl groups started to be cleaved off at 250°C when occurring as methyl–phenyl substituents, but only at 350°C when occurring as diphenyl units. Obviously, such a difference should also be present between differently substituted methyl–phenyl stationary phases. Further, it has been speculated that methyl–phenyl and diphenyl-substituted silicones may result in different retention volumes (23). Accumulation of bulky phenyl groups on the same silicon atom would thus hamper interaction with the solutes (7).

*Reproducibility of Kováts index.* It is well known that the reproducibility of the retention properties of polar–polarizable stationary phases between batches is lower than for nonpolar phases. Typically, variations in Kováts indices between laboratories are within one index unit when nonpolar phases are being used, while variations in the range of  $\pm 20$  units are sometimes observed for polar–polarizable phases (24). Knowledge of the grounds for this difference is a premise for improvements. Two

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factors affecting the precision in the Kováts index will be discussed.

The first factor involves the surface adsorption of *n*-alkanes on polar-polarizable phases. This type of adsorption normally has only a small influence on the retention, but its relative importance increases as film thickness decreases. The magnitude of such an adsorption is proportional to the stationary phase surface area, and this area is largely maintained as constant when film thickness is being decreased; the relative contribution of surface adsorption to the retention is thus increased (25–27). Kováts indices on polar-polarizable phases will thus decrease with decreasing film thicknesses. The effect might be appreciable when thin films are being applied. It is sometimes considered that a constant polarity can be maintained even on bleeding columns, provided the silicone stationary phase is composed by one single monomer, e.g., methyl-phenyl units. The bleeding should, in such a case, have a more or less constant composition, and thus not affect polarity according to Kováts. Taking surface adsorption of *n*-alkanes into consideration, such a reasoning cannot be correct for thin films of stationary phase. In order to preserve Kováts indices on this type of column, conditions have to be selected so that only slight column bleeding may occur.

The second factor involves the synthesis of the stationary phase. The retention in gas chromatography is highly dependent on stationary phase properties. Even small irregularities in a silicone stationary phase can be detected. With nonpolar silicones, retention is basically dependent on dispersion forces, and then polymer configuration is of minor importance. When selectively acting forces are operating, however, polymer configuration and composition becomes of highest importance for the retention.

For a given polymer gross composition, the retention properties vary with the manner by which the substituents are attached, e.g., a polymer having biscyanopropyl-substitution gives different retention than when the cyano-groups occur as cyanopropyl(methyl)-substituents (28). In this paper, the difference in retention between polymers composed by diphenyl and methyl-phenyl units will be demonstrated.

Polysiloxanes are oftentimes prepared by copolymerization of different cyclics. A random distribution of different siloxane units can be achieved by equilibration. Such a process may, however, lead to decreased molecular weights (29). The molecular weight can be increased by addition of a cross-linker (14,30,31). Moreover, molecular weight could be controlled by the addition of an end-blocker to the reaction mix. This is, however, not possible when the synthesis concerns silanol-terminated silicones.

In practice, copolymerization of different cyclics is also applied when one single monomer, e.g., methyl-phenylsilane, is being used for the synthesis. Hydrolysis of dichloromethylphenylsilane thus leads to the formation of two stereoisomeric trimers (29). Such cyclics have quite different reactivities. Further, there is a possibility that the configuration of the cyclics may be retained when being converted to long chain polymers, which may thus incorporate a certain degree of stereoregularity. Andrianov (32,33) presented evidence that such stereoregularity can be achieved. It may be speculated that such a stereoregularity can affect retention behavior in GC. Polymerization may also proceed via so called mixed cyclics. That is, cyclics in which differently substituted silicon moieties have been incorporated, e.g., dimethyl and diphenyl. Such cyclics may occur in several different stereoisomeric forms having widely differing reactivities (34). It is, however, considered that long equilibration times

will lead to a randomization of phenyl- and methyl-containing moieties along the chain (35).

Other factors of importance for a high degree of batch-to-batch reproducibility involve the use of pure and defined starting products for the synthesis. Further, compounds that may be harmful to substituent groups should not be liberated during the synthesis.

Although methyl-phenyl silicones have been extensively used as stationary phases in GC, the properties that are of fundamental importance for high performance in GC are still not known. This concerns chromatographic properties, such as polarity and thermal stability, of different polymer configurations. These issues are addressed in this work.

## Experimental

A series of silanol-terminated silicones having 50% methyl and 50% phenyl substitution have been evaluated for use as stationary phases. Two of these were composed of dimethyl and diphenyl units. Diphenyl 1, the repetitive unit, consists in principle of two consecutive diphenyl units followed by two consecutive dimethyl units. Diphenyl 2, the diphenyl units were spaced by a dimethyl unit. These polymers have been prepared according to Grassie et al. (34,36). A well stirred mixture of water (50 mL) and diethylether (75 mL) was added to a mixture of dichlorodimethylsilane (65 g) and dichlorodiphenylsilane (62.5 g). The ether was evaporated after washing to neutrality. Several fractions were obtained by distillation, and these were characterized by nuclear magnetic resonance (NMR). The fraction containing  $D_2D_2$  was mixed with light petroleum ether and stored at  $-30^\circ C$ ;  $1,3-D_2D_2$  and  $1,2-D_2D_2$  could be obtained by successive precipitation. Polymerization of each cyclic was done by adding 0.1% w/w tetramethylammonium hydroxide (TMAH) and heating at  $100^\circ C$  for 2 h. Finally, the polymers were purified by precipitation with a mixture of dichloromethane and methanol.

The polymer Methyl-phenyl 1 was composed of methyl-phenyl units. The methods presented by Grassie and coworkers (37) were, with some modifications, applied for the synthesis of this polymer. Methylphenyldichlorosilane was thus hydrolyzed and the resulting mixture was distilled. The fraction obtained at  $160-190^\circ C/0.5$  mm Hg was collected and characterized by NMR. Polymerization of the collected fraction was attempted with TMAH as above.

Two commercially available polymers, OV-17 (Alltech) and OV-17-OH (Ohio Valley Specialty Chemicals), have been tested. Fused-silica capillary tubing, i.d. 0.25 mm (Chrompack) was used as column material in lengths of 10 m. Before coating, the capillaries were flushed with hydrogen for 2 h at  $250^\circ C$ . Further, a batch of fused-silica capillary tubing having low silanol content, < 5 ppm, (Chrompack) has been used. Some capillaries, intended for coating with an OV-17 type of stationary phase, were pretreated with OV-17-OH (Ohio Valley Chemicals) for 2 h at  $370^\circ C$  in an inert atmosphere (38). Some capillaries were acid treated (39). Coating and column evaluation were executed as described earlier (39,40). Prior to making a preliminary test, the columns were conditioned at  $200^\circ C$  for 20 min, programming rate  $5^\circ/min$ . Heat curing was performed under a slow flow of hydrogen at  $370^\circ C$  for 10 h, heating rate  $5^\circ/min$ . A slower temperature programming rate,  $0.1^\circ/min$ , has also been evaluated.

The coating solution for some columns contained OV-17-OH at 1% (w/w) of the stationary phase amount. Tailing factors were calculated according to McNair (41). The degree of immobilization was calculated from the capacity factor of 2-methylnaphthalene. The capacity factor was measured after the first conditioning and after rinsing with solvent. The % decrease in film thickness was calculated from these data.

## Results and Discussion

The molecular weights of the newly synthesized polymers were measured by means of GPC. Average molecular weights

around 200,000 were found. A low glass-transition temperature,  $T_g$ , indicates that the polymer will also show good chromatographic performance also at moderate temperatures. The  $T_g$  of Diphenyl 1 was  $-40^\circ\text{C}$ .

*Polarity and immobilization.* Kováts indices for 2-methylnaphthalene and biphenyl have been measured in order to observe small differences in chromatographic properties. This concerns possible differences between different types of methylphenyl-substituted silicones, as well as changes that might have been introduced during the different steps of the column manufacturing. The test substances chosen here are quite sensitive towards small shifts in column properties. As a consequence of the high sensitivity, testing must be executed with great care. For 2-methylnaphthalene, an increase in temperature from 90 to  $100^\circ\text{C}$

**Table I. Column Properties**

Column no.	Stationary phase	Thermal treatment and extraction	$d_f$ ( $\mu\text{m}$ )	$k'$ ( $90^\circ\text{C}$ ) 2-Methyl-naphthalene	HETP ( $90^\circ\text{C}$ ) 2-Methyl-naphthalene	Tailing factor $C_{15}$ $90^\circ\text{C}$	Kováts retention indices			% immob.
							2-Methyl-naphthalene $90^\circ\text{C}$	2-Methyl-naphthalene $100^\circ\text{C}$	Biphenyl $125^\circ\text{C}$	
1.	Diphenyl 1	A*	0.15	12.50	0.27	0.92	1481.4	1492.0	1614.6	
	Diphenyl 1	B†	0.15	11.60	0.34	1.12	1479.1	1488.4	1612.9	
	Diphenyl 1	C‡	0.094	7.85	0.35	1.27	1478.4	1488.3	1612.1	
2.	Diphenyl 2	A	0.15	14.13	0.27	1.07	1478.1	1487.0	1611.7	
	Diphenyl 2	B	0.13	12.48	0.29	1.21	1476.0	1485.4	1609.9	
	Diphenyl 2	C	0.091	8.56	0.30	1.24	1473.9	1483.5	1607.6	
3.	Methyl-Phenyl 1	A	0.15	15.52	0.25	0.96	1484.7	1494.0	1620.1	
	Methyl-Phenyl 1	B	0.060	6.62	0.32	1.48	1478.4	1488.9	1613.5	
	Methyl-Phenyl 1	C	0.033	3.37	0.57	1.92	1470.4	1480.6	1604.9	
4.	Diphenyl 1	A	0.08	5.10	0.36	1.06	1476.2	1486.0	1609.4	
	Diphenyl 1	B	0.068	4.33	0.58	2.24	1469.4	1479.9	1602.9	
	Diphenyl 1	C	0.043	2.71	0.96	3.28	1462.0	1473.1	1599.7	
5.	Diphenyl 1	A	0.04	3.43	0.34	1.11	1474.8	1484.7	1607.4	
	Diphenyl 1	B	0.037	3.18	1.03	4.76	1461.5	1473.0	1599.8	
	Diphenyl 1	C	0.030	2.58	1.11	4.64	1455.5	1466.3	1591.6	
6.	Methyl-Phenyl 1	A	0.30	30.04	0.22	0.89	1486.8	1496.2	1621.9	
7.	Methyl-Phenyl 1	A	0.08	7.62	0.21	0.82	1482.8	1493.1	1617.5	
8.	Methyl-Phenyl 1	A	0.05	5.09	0.23	0.99	1477.7	1487.8	1612.5	
9.	Methyl-Phenyl 1	A	0.033	3.42	0.91	1.10	1473.8	1483.7	1606.8	
10.	Diphenyl 1	D§	0.15	12.80	0.28	0.98	1481.0	1490.5	1615.0	
	Diphenyl 1	E**	0.14	11.62	0.32	1.13	1479.3	1489.8	1613.2	
	Diphenyl 1	C	0.094	8.01	0.38	1.38	1477.7	1488.5	1611.1	
11.	Diphenyl 1, batch 2	A	0.15	12.11	0.31	1.03	1481.2	1490.7	1614.5	
	Diphenyl 1, batch 2	B	0.14	11.69	0.34	1.31	1477.8	1487.3	1611.9	
	Diphenyl 1, batch 2	C	0.076	6.13	0.52	1.85	1476.2	1484.3	1608.5	
12.	OV-17-OH	A	0.15	17.7	3.9	0.93	1481.6	1488.2	1608.7	
		B	0.06	7.13	4.1	1.51	1468.3	1475.6	1599.7	
		C	0.03	3.05	5.6	1.92	1459.9	1470.5	1598.6	

\* A = conditioning at  $200^\circ\text{C}$  for 20 min, programming rate,  $5^\circ/\text{min}$ .

† B = conditioning at  $370^\circ\text{C}$  for 10 h, programming rate,  $5^\circ/\text{min}$ .

‡ C = after thermal treatment B, and extraction with 5 mL dichloromethane.

§ D = conditioning at  $130^\circ\text{C}$  for 20 min, programming rate,  $5^\circ/\text{min}$ .

\*\* E = conditioning at  $370^\circ\text{C}$  for 10 h programming rate,  $0.1^\circ/\text{min}$ , and constant temperature for 6 h at  $200^\circ$  and  $300^\circ\text{C}$ .

results in an increase in Kováts index of approximately 10 units. In order to cope with this temperature dependence, all columns are tested in the same instrument, a Carlo Erba Mega GC, and temperature equilibration is carried out for a relatively long period of time before testing. For the columns described in this paper, a testing precision of  $\pm 0.5$  units is readily obtained.

The next aspect to evaluate is the column-to-column reproducibility. The precision observed here was  $\pm 1.5$  index units. Five columns were involved in this evaluation.

Thermal immobilization of phenyl-containing silicones may lead to shifts in retention index. First, heat treatment of such silicones in an inert atmosphere results in scission of a fraction of the phenyl groups. Benzene and branched structures are thereby formed (37,36,34), and a small decrease in the Kováts index and capacity factors can be observed. The formation of benzene on thermal treatment of columns coated with silanol-terminated methyl-phenyl silicones has been reported by Welsch et al. (42). Second, film thickness has an influence on the Kováts index on

this type of column. The film thickness will decrease drastically if the column is bleeding at the temperatures necessary for the immobilization. Further, if the degree of immobilization is low, polarity will be decreased after rinsing with solvent.

*Diphenyl-substituted silicones.* Thermal treatment resulted in a small decrease in retention index of biphenyl and 2-methyl naphthalene, which may be interpreted as a consequence of decreased phenyl content, column 1, Table I. The degree of immobilization for columns having a film thickness of  $0.15 \mu\text{m}$  was ca. 60%. The rinsing of such columns resulted in a small decrease in the index, cf. column 1, Table I. Thinner films,  $d_f = 0.04 \mu\text{m}$ , could be immobilized to 75%, column 5, Table I.

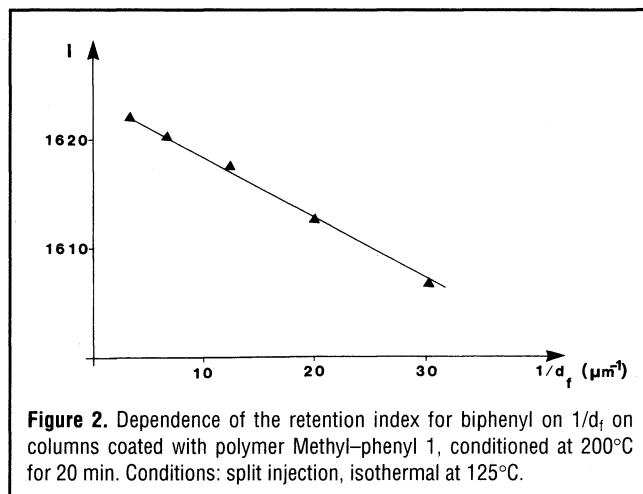
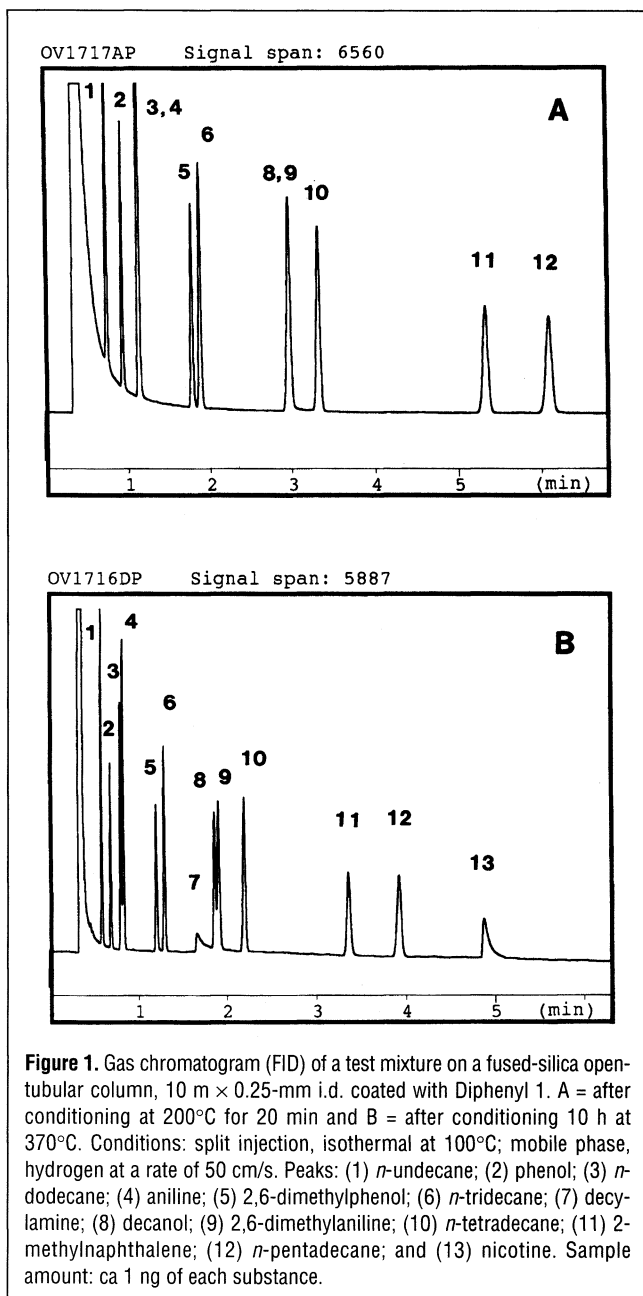
Column 11 was coated with a second batch of the polymer Diphenyl 1. A good agreement of the polarities was observed, and the index for biphenyl was thus 1614.6 on batch one and 1614.5 on batch two (Table I). Batch two gave a somewhat lower degree of immobilization and therefore had a slightly lower polarity after rinsing.

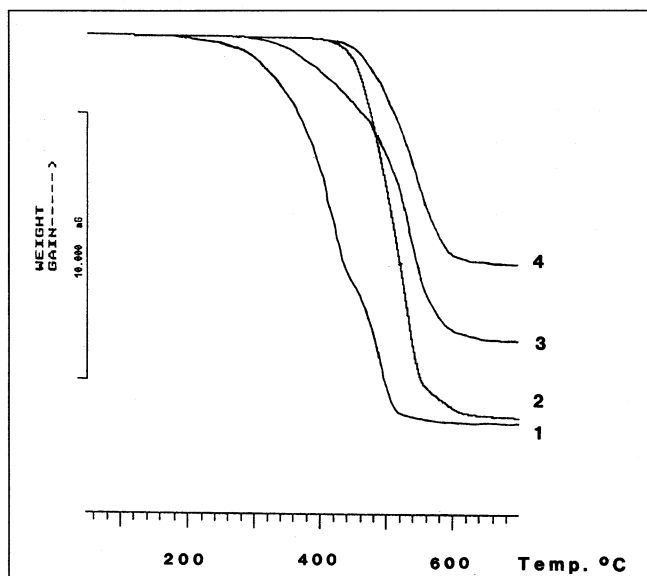
Immobilization was also attempted using a slow temperature programming rate (column 10, Table I). The immobilization however, was not improved by the application of such a procedure.

Thermal immobilization was not possible when the phases had been coated on deactivated fused silica. The importance of condensation between terminal -OH groups on the stationary phase and surface silanols for the immobilization has been emphasized by Blum and coworkers (43,44). Another mechanism for immobilization involves acid catalyzed scission of substituent groups and the subsequent formation of branched structures. It seems that both methods fail when deactivated fused silica is being used as a support. On the other hand, the use of fused-silica tubing that had been acid treated with HCl before coating gave a higher degree of immobilization. However, this was achieved at the expense of column adsorptive activity.

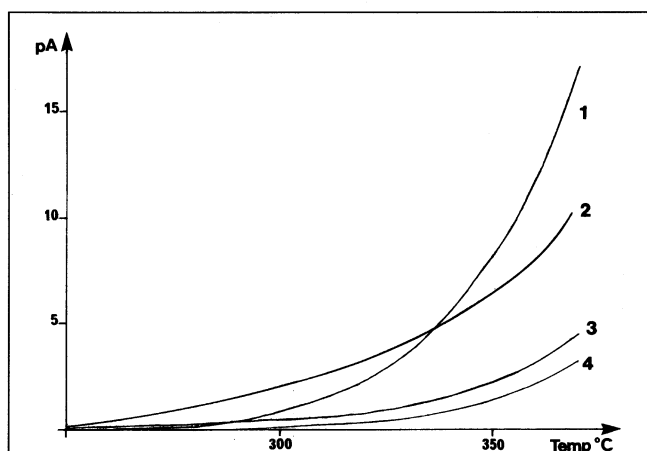
Coating on the untreated fused silica resulted in adsorptive activity (Figure 1A). This was greatly reduced after thermal treatment (Figure 1B). Elution of basic compounds was improved after the heating step, but some tailing of the peaks was still experienced.

Two configurations of diphenyl-dimethyl silicones have been compared. The polymer having a dimethyl unit between two diphenyl units, Diphenyl 2, showed a slightly lower polarity than the polymer where the diphenyl units were adjacent (columns 1 and 2, Table I). It seems that the interaction is more sterically hindered in Diphenyl 2 than in Diphenyl 1.





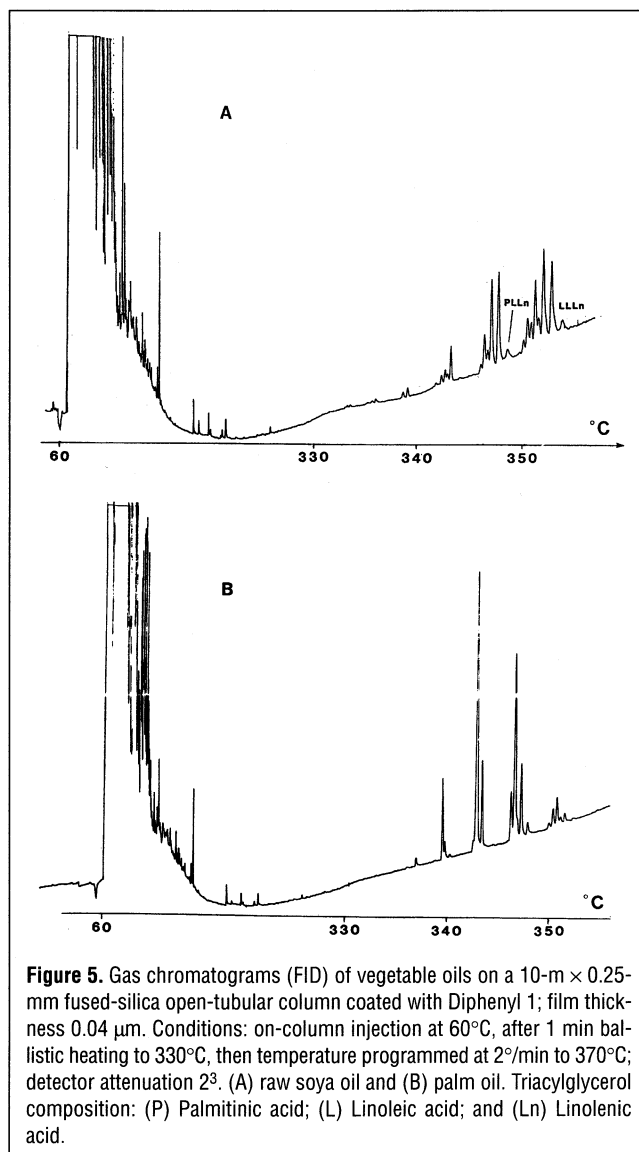
**Figure 3.** TG traces for polysiloxanes containing 50% methyl and 50% phenyl substitution. Heating rate 10°C/min under dynamic nitrogen. Curves: (1) OV-17-OH; (2) Diphenyl 1; (3) OV-17; and (4) Diphenyl 2. Start temp. (°C): (1) 175; (2) 383; (3) 260; and (4) 382. Peak temp. (°C): (1) 421 and 489; (2) 529; (3) 537; and (4) 539. Residue: (1) 5% (2) 26% (3) 39%; (4) 42%.



**Figure 4.** Relative column bleeding rates obtained with columns coated with different stationary phases. (1) Methyl-phenyl 1; (2) OV-17-OH; (3) Diphenyl 2; and (4) Diphenyl 1. Stationary phase film thicknesses: (1) 0.07  $\mu\text{m}$ ; (2) 0.06  $\mu\text{m}$ ; (3) 0.13  $\mu\text{m}$ ; and (4) 0.15  $\mu\text{m}$ .

Excessive cross-link density in polar-polarizable stationary phases may result in increased adsorption of *n*-alkanes at the gas-liquid interface. Depending on solute concentration, such an adsorption may lead to tailing peaks (45). In the range of solute concentrations normally used in open-tubular GC, adsorption of nonpolar solutes on polar stationary phases generally leads to symmetrical peaks (45); the *n*-alkane peaks obtained here were relatively symmetrical, as expressed by their tailing factors (Table I). Tailing of *n*-alkane peaks, however, was observed after thermal treatment of columns coated with thin films of stationary phase (columns 4 and 5, Table I). This effect can be attributed to adsorption at the gas-liquid interface.

**Methyl-phenyl-substituted silicones.** These polymers show a higher index for biphenyl, 1620.1, than the polymers where



**Figure 5.** Gas chromatograms (FID) of vegetable oils on a 10-m  $\times$  0.25-mm fused-silica open-tubular column coated with Diphenyl 1; film thickness 0.04  $\mu\text{m}$ . Conditions: on-column injection at 60°C, after 1 min ballistic heating to 330°C, then temperature programmed at 2°/min to 370°C; detector attenuation 2<sup>3</sup>. (A) raw soya oil and (B) palm oil. Triacylglycerol composition: (P) Palmitic acid; (L) Linoleic acid; and (Ln) Linolenic acid.

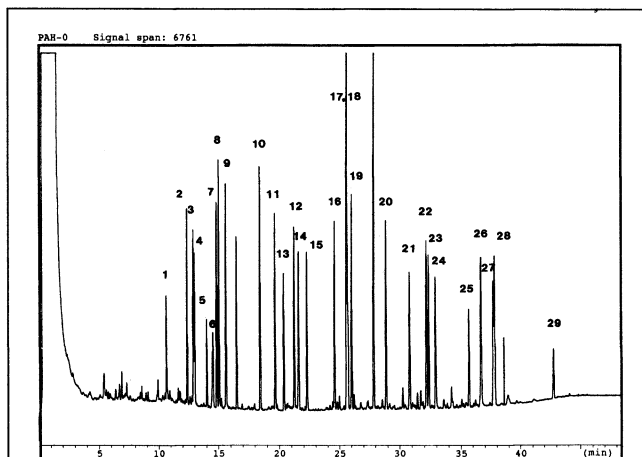
phenyl occurs as diphenyl units, 1614.6 (columns 1 and 3, Table I). Earlier hypotheses concerning the polarity of phenyl silicones are thus confirmed (23,7).

Lee and coworkers (17) reported an index value of 1619.9 for biphenyl at 125°C on vinylated OV-17. The commercial OV-17-OH evaluated in this work gave a relatively low index value, 1609 (column 12, Table I). Examination by NMR indicated that this stationary phase consisted of a mixture of cyclics and linear chains.

The commercial OV-17-OH was immobilized to 17% and the newly synthesized methyl-phenyl siloxane was immobilized to 22% (columns 12 and 3, Table I). A significant decrease in capacity factors resulted from the high column bleeding that took place during the heat treatment step. The influence of film thickness on the Kováts index is demonstrated by the indices of biphenyl on columns 3 and 6-9 of Table I and in Figure 2.

**Thermal stability.** The thermal stability of the polymers, as experienced in thermogravimetric analysis (TG), is compared in Figure 3. Diphenyl 2 showed the highest stability.

Relative column bleeding rates are shown in Figure 4. Polymers Diphenyl 1 and 2 showed moderate bleeding up 370°C (Figure 4). Methyl-phenyl-containing polymers demonstrated



**Figure 6.** Gas chromatogram (FID) of a test mixture containing polycyclic aromatic hydrocarbons on a 10-m  $\times$  0.25-mm fused-silica open-tubular column coated with immobilized Diphenyl 1; film thickness 0.04  $\mu$ m. Conditions: splitless injection at 68°C, after 1 min temperature programmed at 20°/min to 100°C, then 5°/min to 305°C; attenuation 2<sup>3</sup>. Peaks: (1) 2-methylfluorene; (2) dibenzothiophene; (3) phenanthrene; (4) anthracene; (5) 4-me-dibenzothiophene; (6) 3-me-ndibenzothiophene; (7) 3-methylphenanthrene; (8) 2-methylanthracene; (9) 1-methylphenanthrene; (10) fluoranthene; (11) pyrene; (12) benz(a)fluorene; (13) 1-methyl-7-isopropylphenanthrene; (14) 2-methylpyrene; (15) 1-methylpyrene; (16) benzo(ghi)fluoranthene; (17) cyclopenta(cd)pyrene; (18) benz(a)anthracene; (19) chrysene; (20) 2,2-binaphthyl; (21) benzo(k)fluoranthene; (22) benzo(e)pyrene; (23) benzo(a)pyrene; (24) perylene; (25) indenofluoranthene; (26) indeno(cd)pyrene; (27) picene; (28) benzo(ghi)perylene; and (29) coronene.

high bleeding. The stabilizing effect of diphenyl substitution is thus shown.

**Applications.** Silicones having 50% phenyl substitution may be quite useful for the separation of triacylglycerols (46,19,47). The utility of columns coated with Diphenyl 1 for the separation of triacylglycerols from soya oil and palm oil is demonstrated in Figures 5A and B. High temperature GC has been reported to result in relatively low recoveries of triacylglycerols containing trilinolenin (48). The linolenin containing triacylglycerols PLLn and LLLn were eluted as broad peaks (Figure 5A) which may indicate artifact formation. The separation of a standard solution of polycyclic aromatic hydrocarbons is shown in Figure 6.

## Conclusions

The chromatographic properties of methyl-phenyl-substituted silicones are influenced by the polymer composition. Thermal stability is thus greatly improved by the presence of diphenyl-containing moieties. Kováts index of biphenyl is ca. 6 units higher on methyl-phenyl-substituted silicones than on polymers having dimethyl and diphenyl substituents. Poor thermal stability was obtained with the commercially available OV-17-OH.

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