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OZONE-INITIATED *IN SITU* CROSS-LINKING OF NON-POLAR AND MEDIUM-POLAR SILICONE STATIONARY PHASES FOR CAPILLARY GAS CHROMATOGRAPHY

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SUMMARY

Non-polar and medium-polar stationary phases have been immobilized by an ozone-curing method in fused-silica capillaries. Phases such as SE-33, SE-54, OV-215 and methyl(tolyl)siloxanes (33% and 50% tolyl, respectively) could be cross-linked at room temperature. However, SE-30, SE-52, OV-1701, bis(cyanopropyl)methyltolylsiloxane (33% CN and 33% tolyl) and the methyl(phenyl)tolylsiloxanes (25% phenyl and 25% tolyl) required a higher temperature to obtain suitable immobilization. Tests made with columns coated with these ozone-immobilized silicones showed that non-polar and moderately polar phases were of high quality, and that the thermal stability was very good. Infra-red spectra of the silicone phases showed no or a very weak absorption band in the region of $1700-1770$ cm^{-1}.

INTRODUCTION

The general durability of capillary columns may be greatly improved by immobilization of the stationary phase. The immobilization is currently achieved by the formation of cross-links of the C–C type, initiated by a free radical reaction, for which several methods have recently been described. Stationary phase immobilization can, for instance, be initiated by the action of: (a) peroxides[1–4], (b) azo compounds[5,6], (c) gamma radiation from a ^{60}Co source[7–9], (d) accelerated electrons from a Van der Graaf generator[10] and (e) ozone[11].

Dicumyl peroxide is presently the initiator most often used, and is considered to give decomposition products that do not negatively influence column stability. For curing phenyl- and cyanopropyl-substituted silicones, the amount of peroxide required is, however, relatively high, up to 5%, which may result in some column adsorptive activity. Furthermore, under rigorous column conditions, such as high temperatures, also small amounts of peroxide may have a slightly negative effect on stability. Some types of azo compounds seem to be less harmful[5,6].

Curing by high energy radiation involves some advantages, the most important being that no foreign materials, which could be harmful to the stationary phase, are introduced. Further, it is possible to test the columns before curing, thus lowering

the number of columns which must be discarded. One disadvantage, however, is that most laboratories do not have access to the necessary equipment.

It is known that the curing of polysiloxanes may be initiated by ozone[12,13], but due to the relatively slow diffusion of ozone in silicones the method is restricted to the curing of thin sheets. The presence of vinyl or tolyl groups on the silicon increases the cross-linking efficiency, whereas phenyl and cyano groups have the opposite effect (free radical sinks). We have previously described a method for *in situ* curing of non-polar silicone stationary phases with ozone. The ozonization method has similar advantages to radiation curing, and in addition, is more readily available, since it requires only ordinary laboratory equipment.

In this paper, the ozone-initiated cross-linking of some non-polar and medium-polar stationary phases for capillary gas chromatography (GC) is described.

EXPERIMENTAL

Fused-silica capillaries (Hewlett-Packard, Avondale, PA, U.S.A., or SpecTran, Sturbridge, MA, U.S.A.), 10 m × 0.25 mm I.D., were used. Capillaries to be silylated with bis(cyanopropyl)cyclotetrasiloxane were first treated with 18% hydrochloric acid solution at 160°C for 60 h. High temperature silylation with other types of siloxanes was performed without pre-treatment. The silylation reagents were chosen so as to give a surface modification suitable for coating with the different types of stationary phases used[14]. Summary of the column preparation procedures is given in Table I.

Octamethylcyclotetrasiloxane was obtained from Ohio Valley Spec. Chem. (Marietta, OH, U.S.A.); mixed trifluoropropyl cyclics, F_3/F_4, can be obtained from Petrarch Systems (Bristol, PA, U.S.A.), but are easily synthesized[15,16]. Methyl-(phenyl)cyclosiloxanes were prepared by acidic hydrolysis of methyl(phenyl)dichlorosilane (Petrarch). The silane, 10 ml, was dissolved in methylene chloride, 40 ml, and this solution was added dropwise, with vigorous stirring to 150 ml water (0°C) during 2 h. The siloxanes were washed with water until neutral and then separated from the water phase. After solvent evaporation, the siloxanes were freeze dried. The mixture of cyclosiloxanes thus obtained comprised *ca.* 95% of tri-, tetra- and pentamers.

Cyanopropyl(methyl)cyclotetrasiloxane was synthesized by acidic hydrolysis of cyanopropyl(methyl)dichlorosilane as described earlier[17]. Some stationary phases, *e.g.,* methyltolyl, methyl(phenyl)vinyl and methyl(phenyl)tolyl pre-polymers were prepared in our laboratory according to ref. 18 and the cyanosilicones according to refs. 10 and 19. Methyl(phenyl)tolyl pre-polymer was prepared by refluxing 0.2 mol methyl(phenyl)dichlorosilane and 0.2 mol methyl(tolyl)dichlorosilane in 1 mol *n*-butanol until evolution of HCl gas ceased. The mixture was added to 2 mol distilled water and refluxed for 6 h. The washed pre-polymer was further polymerized according to ref. 18.

Silylation procedure

Ten per cent of the capillary was filled with deactivation solution and the plug of solution thus formed was transported through the capillary by a stream of nitrogen at a speed of 3 cm/sec; during this procedure a buffer capillary was connected to the

TABLE I

SILYLATION PROCEDURES AND OZONE-CURING CONDITIONS USED FOR THE PREPARATION OF CAPILLARY COLUMNS

Deactivation reagent	Concentration and solvent	Silylation conditions	Curing conditions	Stationary phase
(a) Methyl(phenyl)-cyclosiloxanes (50% Ph)	3% (w/v) in toluene	5°C/min to 430°C, 430°C for 2 h NH₃ gas	20°C *150°C, 15 min *150°C, 15 min *150°C, 15 min	Me-Tol (33% tolyl), Me-Tol (50% Me-Ph-V₅** (50% Ph, 3.5% V₅) Me-Ph-Tol (25% Ph, 25% Tol) OV-1701
(b) Trifluoropropyl-cyclosiloxanes F₃/F₄	10% (w/v) in ethyl acetate	As (a)	20°C	OV-215
(c) Cyanopropyl-methylcyclotetra-siloxanes	5% (w/v) in toluene	5°C/min to 400°C, 400°C for 2 h	150°C, 15 min	Me-CN-Tol (33% CN, 33% tolyl)
(d) Octamethyl-cyclotetra-siloxane, D₄	Pure	As (a)	20°C 150°C, 15 min	SE-33, SE-54 SE-30, SE-52
(e) As (d)	As (d)	As (a)	Oxygen 150°C, 30 min	SE-33, SE-54

* Heating step performed twice.
** V₅ = penta(methylvinyl)cyclopentasiloxane.

capillary. After thorough solvent evaporation (overnight with dry nitrogen), the capillaries were further heat-treated. The different silylation procedures, a–e, are listed in Table I. Those capillaries to be modified according to procedure a were filled with dry ammonia and flame sealed. They were then heated in an oven to 430°C at a rate of 5°C/min, maintained at 430°C for 2 h and allowed to cool slowly. In order to protect the polyimide, the outer covering of the capillaries, the oven was purged with nitrogen. Capillaries to be modified according to procedure b were sealed directly after solvent evaporation, heated to 430°C and kept at this temperature for 2 h. Capillaries to be modified with reagent c were evacuated after solvent evaporation and heated at a rate of 5°C/min to 400°C, then isothermal for 2 h, after which they were allowed to cool slowly. Capillaries to be modified with reagents d and e were, after the solution plug had left the capillaries, directly sealed, heated to 430°C at a rate of 5°C/min and maintained at this temperature for 2 h. After deactivation the capillaries were rinsed with 3 ml of solvent and then statically coated with a solution of 0.4% (w/v) stationary phase in methylene chloride; for OV-215 a solution of 0.6% (w/v) in ethyl acetate–diethyl ether (1:4) was used. After coating and flushing with dry nitrogen for 3 h, the columns were conditioned by heating at a rate of 2°C/min to 200°C, then isothermal for 5 h.

Curing procedure

After making various tests, the columns were disconnected from the gas chro-

matograph and filled with ozone (3% ozone in oxygen) by suction of the ozone–oxygen mixture through them for 15 min at room temperature. Ozone was produced in an ozonizator, neon transformer, Type 4045 (SEM, Sweden); an oxygen inlet of 100 ml/min was used.

Immediately after ozonization, columns coated with methyltolylsiloxanes, 33% and 50% tolyl respectively, OV-215, SE-33 and SE-54, were flushed with dry nitrogen for 3 h. Columns coated with SE-30, SE-52 and cyanotolyl stationary phases were sealed after ozone-treatment and rapidly heated to 150°C for 15 min, then flushed with dry nitrogen at room temperature for 3 h. Columns coated with OV-1701, methyl(phenyl)-V_5 siloxane and methyl(phenyl)tolylsiloxane, after ozonization at 150°C, were flushed with dry nitrogen for 5 min, and the ozone treatment described above was repeated. The columns were then flushed for 3 h with dry nitrogen at room temperature and conditioned by heating to 200°C at a rate of 2°C/min. Both before and after the ozone treatment, the columns were subjected to preliminary tests to determine whether any changes had occurred. Finally, they were slowly rinsed overnight with 5 ml of methylene chloride or ethyl acetate (for OV-215). After rinsing, the columns were conditioned at a rate of 2°C/min to 300°C, then isothermally overnight; OV-215 and the cyanosilicones were conditioned to 275°C.
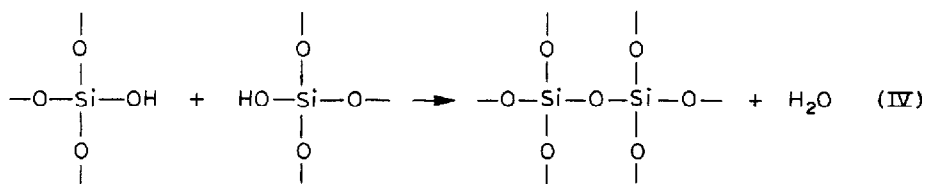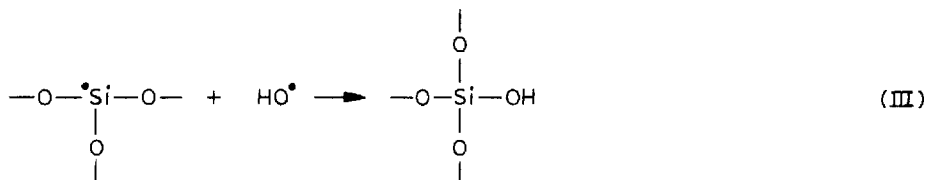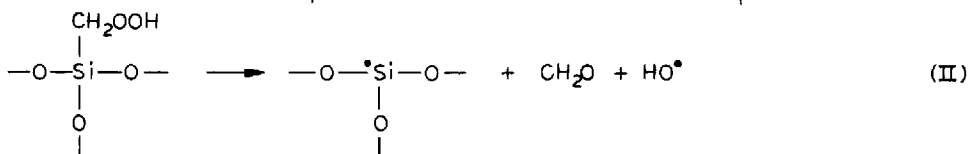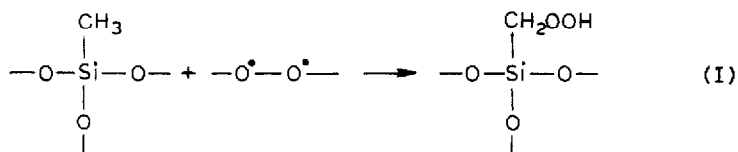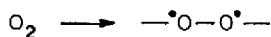
Column testing

The columns were tested in Hewlett-Packard Model 5790, Carlo Erba Models 2350 and 4160 gas chromatographs equipped with a flame ionization detector and with hydrogen as carrier gas (50 cm/sec). The results were computed on a Hewlett-Packard integrator, Model 3391 A. The test mixtures were: (i) the Grobs test mixture and (ii) a polarity mixture, containing dodecane, *n*-octanol and naphthalene. The concentrations of the different compounds were about 100 ng/μl; the split was adjusted to give *ca.* 1 ng per peak.

RESULTS AND DISCUSSION

Some aspects of silicone oxidation

Silicones show relatively good resistance towards oxidation. For methylsilicone rubber, the oxidative processes were found to be insignificant at temperatures below 200°C. Cleavage of network cross-links by oxidative processes was detectable only above 250°C[20]. Thermo-oxidative degradation begins with attack of oxygen on the organic group, the nature of the latter influencing the stability to oxidation. Ethyl substituents are thus less stable then methyl groups. Phenyl groups, on the other hand, due to their resonance stabilization are more stable to oxidation than are methyl groups. Tolyl groups are more easily oxidized than phenyl groups[6]. Further, oxidative degradation is a function of surface area, the internal mobility of the molecules and their capacity for diffusion to the surface[21]. Linear polyorganosiloxanes are more susceptible to thermo-oxidative degradation than are cross-linked molecules[22].

Volatile products of the thermal oxidation of polymethylsiloxanes comprise mainly carbon monoxide and water, small amounts of carbon dioxide, formaldehyde, methanol and traces of formic acid. A reaction scheme has been proposed by Andrianov[22]:

$$O_2 \longrightarrow -{}^\bullet O-O^\bullet-$$

$$\underset{\underset{O}{\overset{CH_3}{|}}}{-O-\overset{|}{\underset{|}{Si}}-O-} + -O^\bullet-O^\bullet- \longrightarrow \underset{\underset{O}{\overset{CH_2OOH}{|}}}{-O-\overset{|}{\underset{|}{Si}}-O-} \qquad (I)$$

$$\underset{\underset{O}{\overset{CH_2OOH}{|}}}{-O-\overset{|}{\underset{|}{Si}}-O-} \longrightarrow \underset{\underset{O}{|}}{-O-{}^\bullet\overset{|}{\underset{|}{Si}}-O-} + CH_2O + HO^\bullet \qquad (II)$$

$$\underset{\underset{O}{|}}{-O-{}^\bullet\overset{|}{\underset{|}{Si}}-O-} + HO^\bullet \longrightarrow \underset{\underset{O}{\overset{O}{|}}}{-O-\overset{|}{\underset{|}{Si}}-OH} \qquad (III)$$

$$\underset{\underset{O}{\overset{O}{|}}}{-O-\overset{|}{\underset{|}{Si}}-OH} + \underset{\underset{O}{\overset{O}{|}}}{HO-\overset{|}{\underset{|}{Si}}-O-} \longrightarrow \underset{\underset{O}{\overset{O}{|}}}{-O-\overset{|}{\underset{|}{Si}}-O-\overset{|}{\underset{|}{Si}}-O-} + H_2O \qquad (IV)$$

Thermal decomposition of formaldehyde gives:

$$CH_2O \rightarrow CO + H_2 \qquad (V)$$

Some of the formaldehyde is oxidized:

$$2CH_2O + O_2 \rightarrow 2HCOOH$$
$$CH_2O + O_2 \rightarrow CO_2 + H_2O \qquad (VI)$$
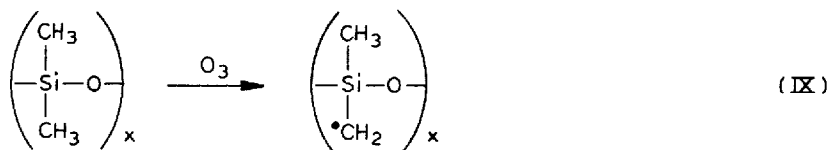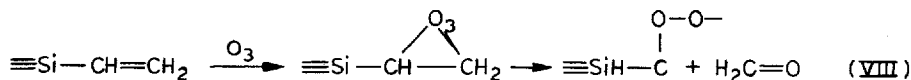
The thermo-oxidative degradation of polyorganosiloxanes is reviewed by Balykova and Rode[23].

Oxidation of methylsilicones with ozone at elevated temperatures results in volatile products different from those produced by oxidation with oxygen[12]:

$$6 \equiv SiCH_3 + 8 O_3 \rightarrow 3 \equiv SiOSi \equiv + 9 H_2O + 6 CO_2 \qquad (VII)$$
$$2 \equiv SiCH_3 + 2 O_2 \rightarrow \equiv SiOSi \equiv + H_2O + 2 CH_2O \qquad (VIIa)$$
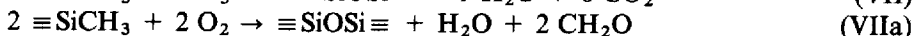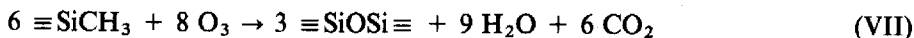
Ozone, which reacts much more readily with siloxanes than does oxygen, reacts with

vinylsiloxanes even at $-55°C$. Further, silanes are generally more reactive towards ozone than are the corresponding carbon compounds. In a silicone, ozone cleaves Si–C bonds more readily than C–C bonds[24]. Although the mechanism of ozone-initiated curing is not known, the following schemes have been suggested by Barry and Beck[12]:

$$\equiv Si-CH=CH_2 \xrightarrow{O_3} \equiv Si-\overset{\overset{\displaystyle O_3}{\diagup\diagdown}}{CH}-CH_2 \longrightarrow \equiv SiH-\overset{\overset{\displaystyle O-O-}{|}}{C} + H_2C=O \qquad (VIII)$$

$$\begin{pmatrix} CH_3 \\ | \\ -Si-O- \\ | \\ CH_3 \end{pmatrix}_x \xrightarrow{O_3} \begin{pmatrix} CH_3 \\ | \\ -Si-O- \\ | \\ {}^{\bullet}CH_2 \end{pmatrix}_x \qquad (IX)$$

Curing with ozone

As with other radical-initiated curing methods, ozone-curing is greatly facilitated by the presence of some vinyl substituents in the silicone. The vinyl-containing methylsilicone gum SE-33 could thus be ozone-cured at room temperature, while the corresponding methylsilicone gum SE-30 had to be heated with ozone to obtain vulcanization. Such a difference was also observed for SE-54 and SE-52 silicone gums[11]. Tolyl substitution in a silicone has been shown to facilitate cross-linking when peroxides[18,19], azo compounds[5,6] or radiation are used as initiators[10]. Simi-
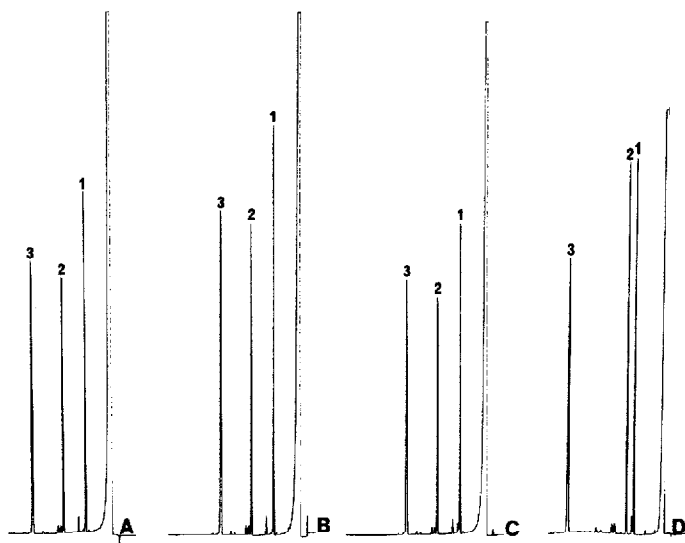

Fig. 1. Gas chromatograms with flame ionization detection (FID) of a polarity test mixture on 10-m fused-silica capillary columns coated with immobilized methyl(tolyl)silicones. Isothermal at 90°C. A, Column coated with 33% tolyl phase before curing; B, the same column after ozone-curing; C, the same column after rinsing with methylene chloride, D, column coated with 50% tolyl phase, cured and rinsed. Peaks: 1 = *n*-octanol; 2 = dodecane; 3 = naphthalene.
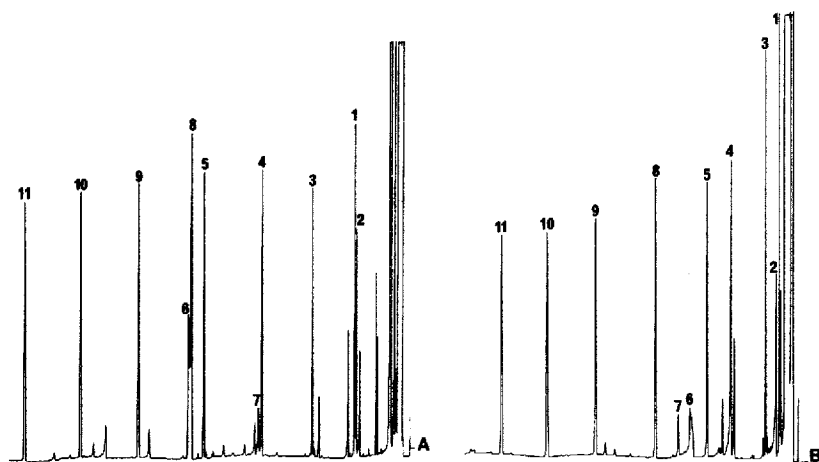
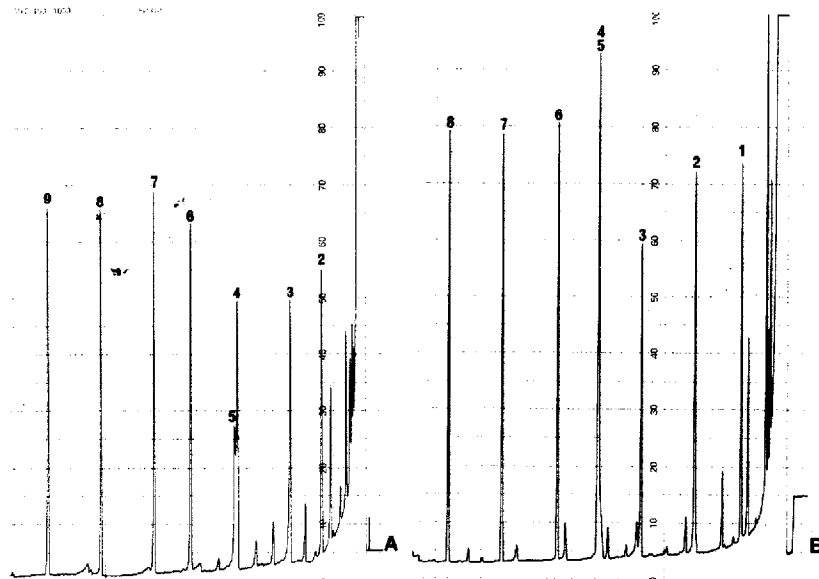Fig. 2. Gas chromatograms with FID of a Grob test mixture on 10-m fused-silica capillary columns coated with immobilized silicones. A, OV-1701; B, OV-215. Injection at 50°C, programmed at 5°C/min. Peaks: 1 = decane; 2 = butanediols; 3 = undecane; 4 = n-octanol; 5 = 2,6-dimethylphenol; 6 = 2-ethylhexanoic acid; 7 = n-nonanal; 8 = 2,6-dimethylaniline; 9, 10, 11 = C_{10}, C_{11}, C_{12} fatty acid methyl esters. Dicyclohexylamine was not eluted.

Fig. 3. Gas chromatograms with FID of a Grob test mixture on 10-m fused-silica capillary columns coated with immobilized silicones. A, Methyl(phenyl)tolylsilicone; B, methyl(phenyl)-V_5 silicone. Injected at 50°C, programmed at 5°C/min. Peaks: 1 = decane; 2 = undecane; 3 = n-octanol; 4 = 2,6-dimethylphenol; 5 = 2-ethylhexanoic acid; 6 = 2,6-dimethylaniline; 7, 8, 9 = C_{10}, C_{11}, C_{12} fatty acid methyl esters. Dicyclohexylamine was not eluted.

TABLE II

CHARACTERISTICS OF FUSED-SILICA CAPILLARY COLUMNS COATED WITH DIFFERENT STATIONARY PHASES, TREATED WITH OZONE AND AFTER RINSING

Columns: 10 m × 0.25 mm, $n = 5$.

Column	Coating efficiency (%)	HETP for naphthalene at 90°C (mm)	% decrease in k' (naphthalene) at 90°C	Kováts retention index at 90°C		Change in retention index	
				n-Octanol	Naphthalene	n-Octanol	Naphthalene
OV-215	96.1	0.23	2	1242.7	1440.1	+0.6	−0.8
50% Tolyl	88.7	0.26	7	1154.0	1328.1	+1.8	+0.1
33% Tolyl	108.5	0.21	1	1114.1	1273.2	−0.4	+0.5
Me-Ph-V$_5$	88.0	0.26	10	1174.5	1377.0	+1.1	+1.6
OV-1701	122.1	0.18	9	1185.5	1286.6	−1.0	−0.6
Me-Ph-Tol	89.0	0.26	11	1159.3	1357.5	+1.4	−1.3
33% CN	82.0	0.28	0	1396	1560	($n = 2$)	
SE-30	83.3	0.26	4	1054.1	1150.0	+0.9	−2.1
SE-33	87.9	0.25	8.2	1052.6	1150.3	−0.8	+1.1
SE-54	86.3	0.25	25.0	1071	1182	(oxygen-cured)	($n = 2$)

larly, the presence of tolyl groups facilitates ozone-curing, and thus silicone gums containing 33% and 50% tolyl could be cured at room temperature (Table II, Fig. 1). Also silicone gums that have trifluoropropyl substitution are known to be easily curable[22]; the silicone gum OV-215 (50% trifluoropropyl) could thus be cured with ozone at room temperature (Table II, Fig. 2B).

Higher temperatures were required for curing of phases containing phenyl groups. Curing of these silicones could be accomplished by heating with ozone–oxygen for 15 min at 150°C, which resulted in a *ca.* 50% immobilization of the stationary phase. In order to increase the percentage of phase immobilization, the curing procedure can be performed twice, when a 75–95% immobilization could be achieved. The relatively moderate curing temperature was chosen in order to avoid any undesirable side-reactions between silicone and ozone–oxygen. Further, the reaction time was chosen by taking into consideration the rapidity of ozone decomposition. Several types of phenyl- and one cyanopropyl-containing silicone gums could be successfully ozone-heat cured (Table II and Figs. 2A, 3 and 4A). Columns coated with room temperature ozone-cured stationary phases and high temperature ozone-cured SE-30, SE-52 and OV-1701 showed excellent results. For more polar phases, however, some adsorptive activity could be observed.

In this work, we have used methyl(phenyl)cyclosiloxanes as silylating reagents for the capillaries to be coated with phenylsilicone type stationary phases. This gave surfaces suitable for coating with silicones having 50% phenyl substitution. For higher phenyl contents, the necessary wettability is achieved by silylation with hexaphenylcyclotrisiloxane[18,25]. Bis(phenyl) cyclics are however less reactive than the corresponding methylphenylcyclotrisiloxane on the batches of fused silica used in this work.
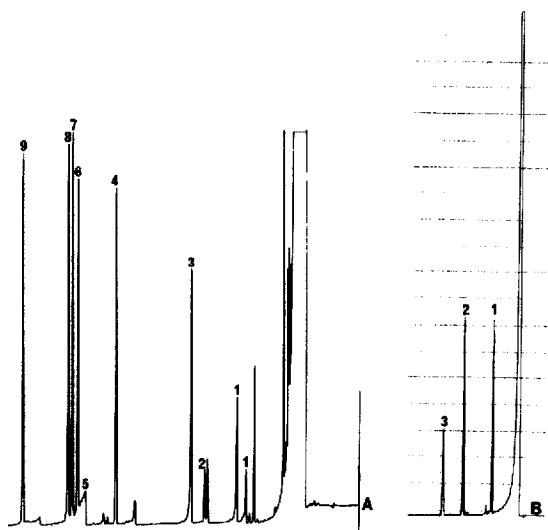

Fig. 4. Gas chromatograms with FID of test mixtures on 10-m fused-silica capillary columns coated with immobilized silicones. A, Grob test mixture on a 33% CN phase, injected at 50°C, programmed at 5°C/min. Peaks: 1 = 2,3-butanediols; 2 = *n*-nonanal; 3 = *n*-octanol; 4 = C_{10} fatty acid methyl ester; 5 = dicyclohexylamine; 6 = 2,6-dimethylphenol; 7 = 2,6-dimethylaniline; 8 and 9 = C_{11} and C_{12} fatty acid methyl esters. B, Polarity mixture on a column coated with SE-54, immobilized by reaction with O_2. Peaks: 1 = *n*-octanol; 2 = naphthalene; 3 = dodecane.

For curing thin sheets of polysiloxane, it was proposed that the sheets first be exposed to ozone at room temperature and then heated in an ozone-free atmosphere[13]. The small amounts of ozone that diffuse into the sheets should be sufficient for vulcanization. This method was also applied to capillary columns, which were thus exposed to ozone at room temperature, rapidly flushed with nitrogen, sealed and heated to 100°C for 3 h. These columns showed properties similar to those of corresponding columns that had been heat-cured in an atmosphere of ozone–oxygen. The degree of immobilization of SE-30 was, however, low, only 40–60%. When this procedure was repeated the immobilization increased to 60–70%.

It was of interest to determine whether curing could be initiated by oxygen alone. Vinyl-containing silicone gums, SE-33 and SE-54, could be heat-cured at 150°C for 30 min which resulted in an immobilization degree of 75% (Table II, Fig. 4B), but corresponding gums without vinyl substituents, SE-30 and SE-52, remained soluble after such a heat treatment with oxygen.

Oxidation of substituent groups

When flushing the columns with nitrogen after ozone-heat curing, it was observed in a few cases that a pH-paper could be coloured weakly red, possibly by formic acid, *cf.*, eqn. VI. Such an effect was never observed with SE-30, SE-33 and OV-215. Phenyl groups are relatively easily attacked by ozone[24], and it may be speculated that the acidity emanates *inter alia* from oxidized phenyl groups. The acid–base nature of ozone-cured columns after conditioning was, however, similar to that obtained on curing with dicumyl peroxide (DCP). A certain acidity is evident, which seems to stem from the fused-silica surface; all columns prepared from the batch of fused silica used in this work were slightly acidic, Fig. 5B. Other batches have given better results in this respect, Fig. 5A.

Richter *et al.*[6] have recently studied the oxidation of methyl(tolyl)polysiloxanes. It was found that heating a tolylsilicone, doped with 5% DCP, in an oxygen-
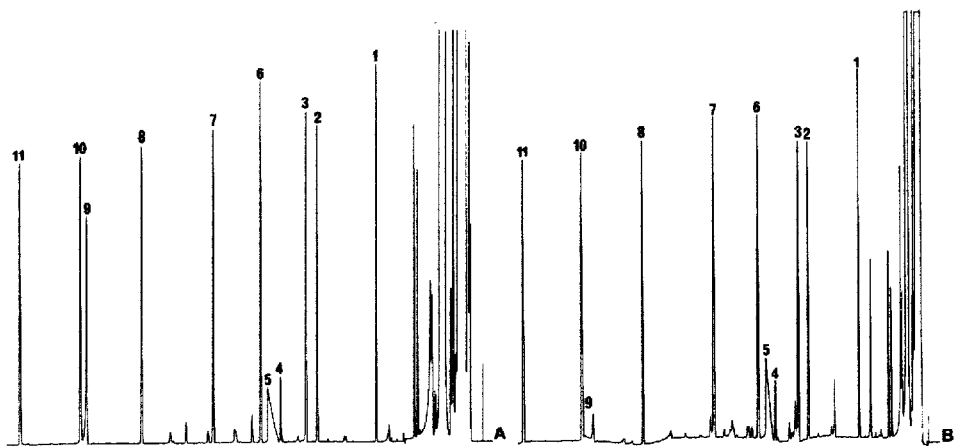

Fig. 5. Gas chromatogram with FID of a Grob mixture on 10-m fused-silica capillary columns coated with immobilized 33% tolylsilicone. A and B, fused silica from different batches. Injection at 50°C, programmed at 5°C/min. Peaks: 1 = decane; 2 = undecane; 3 = *n*-octanol; 4 = *n*-nonanal; 5 = 2-ethylhexanoic acid; 6 = 2,6-dimethylphenol; 7 = 2,6-dimethylaniline; 8 = C_{10} fatty acid methyl ester; 9 = dicyclohexylamine; 10 and 11 = C_{11} and C_{12} fatty acid methyl esters.

free atmosphere at 175°C for 1 h resulted in the appearance in the IR spectrum of the phase of a carbonyl band at 1700 cm^{-1}. It was thus of interest to investigate whether ozone treatment would result in chemical modifications detectable by IR spectroscopy. Ozone treatment of vinyl- and tolyl-containing phases, under the conditions tested, resulted in the appearance of a very weak absorption band in the region 1770–1700 cm^{-1}. A weak absorption band at 1750 cm^{-1} was noted with OV-17-Vi (Ohio Valley) and the home-made Me-Ph-V$_5$ siloxane after 30-min ozone treatment at 20°C. Similarly, treatment of the 67% methyl, 33% tolyl phase gave no indication of absorption at 1750 cm^{-1} and the 50% methyl, 50% tolyl phase showed a very weak absorption. No absorption bands in this region were detected for the home-made phases 50% methyl, 25% phenyl, 25% tolyl or 25% methyl, 50% phenyl, 25% tolyl even after heating to 150°C in ozone for 15 min, Fig. 6. The cyanopropyl- and trifluoropropylsilicones did not give any new absorption bands between 1700 and 1770 cm^{-1} after ozone treatment, at room temperature. Eventual changes in the
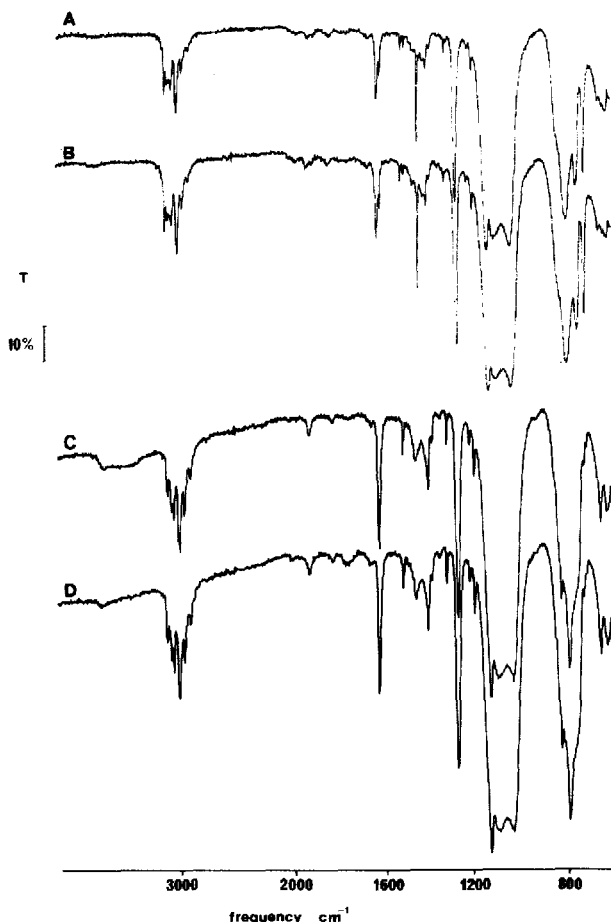

Fig. 6. IR spectra of siloxanes. A, A polymer with 50% methyl, 25% phenyl, 25% tolyl before ozone treatment; B, same polymer after 15 min in ozone at 150°C; C, a polymer with 50% methyl, 50% tolyl substituents before ozone treatment; D, same polymer after 30 min in ozone at 20°C.
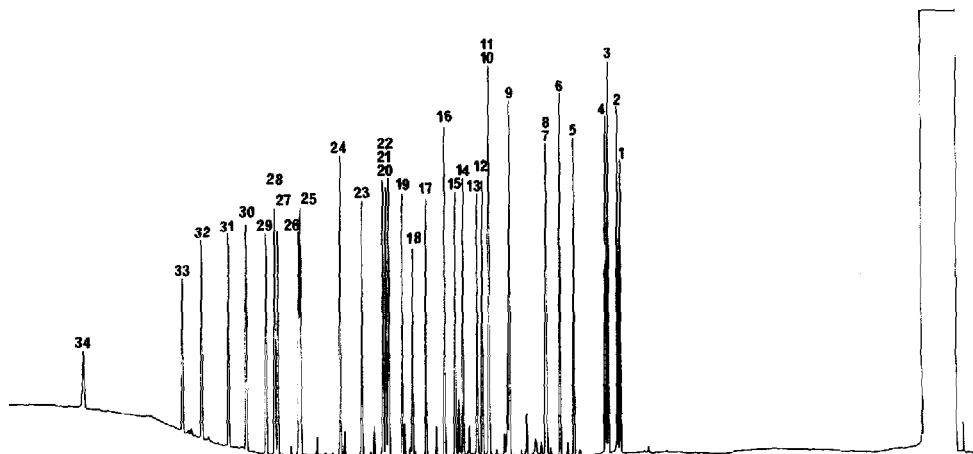
Fig. 7. Gas chromatogram with FID of polynuclear aromatic compounds (PACs) (*ca.* 5 ng/μl) on a 10-m fused-silica column coated with 0.1 μm immobilized methyl(tolyl)siloxane (50% tolyl). Splitless injection for 1.5 min at 70°C. Initial temperature 70°C for 1.5 min, then programmed at a rate of 7°C/min to 305°C. Carrier gas: hydrogen, 60 cm/sec at 150°C. Peaks: 1 = fluoren-9-one; 2 = dibenzothiophene; 3 = phenanthrene; 4 = anthracene; 5 = 3-methylphenanthrene; 6 = 1-methylphenanthrene; 7 = 9-methylanthracene; 8 = 2-phenylnaphthalene; 9 = fluoranthene; 10 = pyrene; 11 = phenanthrene-9-carbaldehyde; 12 = 9,10-dimethylanthracene; 13 = benzo[*b*]naphtho[2,3-*d*]furan; 14 = benz[*a*]fluorene; 15 = 2-methylpyrene; 16 = 1-methylpyrene; 17 = 1-ethylpyrene; 18 = 10-methylanthracene-9-carbaldehyde; 19 = 9-phenylanthracene; 20 = cyclopenteno[*c,d*]pyrene; 21 = benz[*a*]anthracene; 22 = chrysene; 23 = benzanthrone; 24 = 2,2′-binaphthyl; 25 = 4,5-epithiobenz[*a*]anthracene; 26 = benzo[*k*]fluoranthene; 27 = benz[*e*]pyrene; 28 = benz[*a*]pyrene; 29 = perylene; 30 = dinaphtho(2,1′,1′,2′)thiophene; 31 = *p*-quaterphenyl; 32 = indeno[1,2,3-*c,d*]pyrene; 33 = benzo[*g,h,i*]perylene; 34 = coronene.
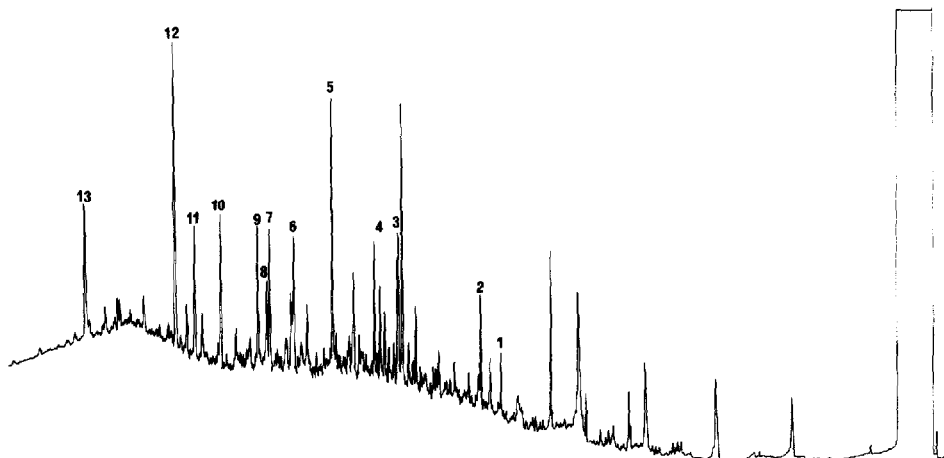

Fig. 8. Gas chromatogram with FID of a PAC sample (air sample from a heavily trafficked street in the city of Stockholm). Same column and conditions as in Fig. 7. Peaks: 1 = fluoranthene; 2 = pyrene; 3 = benzo[*g,h,i*] fluoranthene; 4 = cyclopenta[*c,d*]pyrene; benz[*a*]anthracene, chrysene; 5 = 2,2′-binaphthyl (internal standard); 6 = benzo[*j*]fluoranthene, benzo[*k*]fluoranthene, benzo[*e*]fluoranthene; 7 = benz[*e*]pyrene; 8 = benz[*a*]pyrene; 9 = 6H-benzo[*c,d*]pyren-6-one; 10 = *p*-quaterphenyl; 11 = indeno[1,2,3-*c,d*]pyrene; 12 = benzo[*g,h,i*]perylene; 13 = coronene.

character of silicone side-groups can also be easily monitored by determination of the retention index. It was found that ozone-curing led to only marginal differences in Kováts retention indices, which were not significant ($P > 0.05$) when estimated according to the Student's t-test for paired observations (Table II). The number of capillary columns tested with each stationary phase ($n = 5$) was rather low, but gives an indication of how the retention indices change before and after ozone treatment. These observations confirm further the results concerning stability obtained by IR spectroscopic analysis. The utility of an ozone-cured methyl(tolyl)siloxane (50% tolyl) column is demonstrated in Figs. 7 and 8.

A gas chromatogram of a test solution containing some polynuclear aromatic compounds separated on a 10-m fused-silica column (film thickness, $d_f = 0.1$ μm) is shown in Fig. 7. In this case a column coated with a thin phase has been used in order to obtain coronene at a relatively low temperature (305°C). With a d_f of *ca.* 0.25 μm, an upper temperature of 350°C was necessary to elute coronene. The polyimide protective covering of the fused-silica columns became brittle at this high temperature after five analyses. An air sample from a heavily trafficked street in the city of Stockholm is shown in Fig. 8.

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