CHROM. 14,593

PEROXIDE-INITIATED *IN SITU* CURING OF SILICONE GUMS FOR CAPILLARY COLUMN GAS CHROMATOGRAPHY

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SUMMARY

The combination of leaching, silanization with cyclic siloxanes and peroxide-initiated *in situ* vulcanization of silicone stationary phases for gas chromatography gives capillary columns that show very high efficiencies, very low adsorptivity as reflected by stringent tests and very high stability, *e.g.*, low bleeding rates. Such columns have been prepared using AR-glass and fused silica as the supports and SE-30, SE-52, SE-54 and polar OV-215 as stationary phases. The versatility of these columns is demonstrated by the analysis of underivatized drugs, barbiturates and tricyclic antidepressants. The separation of aqueous solutions is also described.

INTRODUCTION

The *in situ* preparation of bonded silicone stationary phases applied to capillary columns for gas chromatography (GC) was first described by Rigaud *et al.*[1], and since then several papers dealing with refinements of the method have been published[2–5]. The preparation of columns coated with bonded silicone phases was also investigated in our laboratory when we attempted instead to combine bonding with the introduction of a slight degree of cross-linking in the polymer[6–10]. The cross-linking was accomplished by addition of tri- or tetrachlorosilanes to the so-called pre-polymer. Madani and co-workers[1–5] prepared polymers from dichlorosilanes only, which makes cross-linking impossible unless some siloxanes able to undergo tri- or tetrafunctional reaction were formed during the *in situ* polymerization.

Earlier endeavours to combine experimentally bonding and cross-linking of the stationary phase in capillary columns were made by Grob[11] with polybutadiene phases and by Bossart[12] with silicones.

When a stationary phase film has been fixed by cross-linking, it can withstand various strains. The column thus retains its good chromatographic properties also at elevated temperatures and there is no risk of stationary phase rearrangements or deterioration of performance due to poor wettability. Further, as the phase is insoluble in commonly used solvents, the stationary phase film is resistant to the relatively large amounts of liquid solvent passing the first column coils upon on-column injection. Moreover, the insolubility of the phase makes possible the rinsing out of

non-volatile material from a used column, thus regenerating the column[10]. Another advantage is that an immobilized phase can withstand water[13], the analysis of aqueous solutions thus being feasible. A further application would be that with a supercritical fluid as carrier[14].

Cross-linking of a stationary phase would in general result in impaired chromatographic performance[15]. Our silicones probably contain relatively few cross-links, and according to our experience these do not seem to have an adverse effect on the chromatographic properties[10].

In our earlier work, cross-linking was obtained through Si–O–Si bonds[6–10]. Recently, immobilization of stationary phases by means of Si–C–C–Si bonds has been described by Grob and co-workers[16,17], Sandra *et al.*[13] and the present authors[18]. This type of cross-linking is a radical reaction, the radicals being formed by decomposition of organic peroxides[19]. Peroxide curing of silicones was first reported in 1948[20], and the method has since been used extensively in the rubber industry[21]. Several types of peroxides are useful, see *e.g.* refs 22 and 23, but we chose to use dicumyl peroxide, which has proved to be effective in the rubber industry, especially when the polymer contains some vinyl groups[21]. Further, relatively inactive ketones are formed on decomposition of dicumyl peroxide[24]. Some peroxides, *e.g.*, benzoyl peroxide, form organic acids on decomposition, which might be a drawback, as the hydrolysis of siloxanes is catalysed by acids[24].

Radical-initiated cross-linking can also be effected by other methods, *e.g.*, with high-energy radiation[19]. For glass capillary columns, a low-temperature plasma has been used[25]. Air-curing of SE-52 columns has been reported to result in increased column stability; such an effect can also be attributed to cross-linking[26].

Compared with our earlier methods, the peroxide-initiated cross-linking is simpler to perform and, in addition, the necessary chemicals are readily available. The columns prepared according to the two methods have, however, different properties.

In this paper, we describe the preparation of capillaries coated with *in situ* cured stationary phases. AR-glass and fused silica capillaries have been used as supports and SE-30, SE-52, SE-54 and OV-215 as stationary phases. Further, some properties of peroxide-cured columns and SiCl$_4$-cured columns are compared.

EXPERIMENTAL

AR-glass (Glaswerk Wertheim, Wertheim am Main, G.F.R.) capillaries were drawn on a Brechbühler (Schlieren, Switzerland) glass-drawing machine. Fused silica capillaries were obtained from Hewlett-Packard (Avondale, PA, U.S.A.).

The AR-glass capillaries were leached with 18 % hydrochloric acid, principally according to Grob *et al.*[27], *i.e.*, heat treatment overnight at 140°C. The hydrochloric acid was then displaced by two capillary lengths of dilute hydrochloric acid solution (pH 3), this solution being in turn displaced by two capillary lengths of methanol. The methanol was flushed out and the capillary placed in an oven, the temperature of which was programmed from 60 to 250°C at 10°C/min, then held at 250°C for 2 h. This dehydration step was accomplished under a low carrier gas flow. Dehydration could also be carried out by heating for 30 min at 230°C. Both ends of the capillary were then connected to a vacuum.

Some fused silica capillaries were treated with hydrochloric acid in the same

way as AR-glass capillaries, with the exception that they were heated at 100°C and then rinsed with several capillary lengths of hydrochloric acid of pH 3, followed by methanol.

Silanization was performed with octamethylcyclotetrasiloxane[28,29] and 3,3,3-trifluoropropyl(methyl)cyclosiloxane[30]. For AR-glass, reaction was effected by heating at 400°C for 15 h, and for fused silica, at 350°C for 15 h. During the heat treatment, the polyimide of the fused silica capillary was protected by an atmosphere of nitrogen.

Curing procedure

Solutions for static coating of capillaries were prepared using methylene chloride as solvent for all phases except OV-125, for which diethyl ether–ethyl acetate (4:1) was used. For phases containing vinyl groups, the amount of dicumyl peroxide (Merck, Darmstadt, G.F.R.) added to the solution was 0.1–0.5% (w/w) of the amount of stationary phase; for other phases 0.5–1.0% was used. The solutions were dried over calcium sulphate and, when stored in the dark, remained stable for at least 1 week. Before use, the solutions were centrifuged.

Capillaries were statically coated using the prepared solutions. After coating, the capillaries were flushed with dry nitrogen for 1 h at room temperature. The capillary was then evacuated by attaching both ends to vacuum and sealing with a micro-flame. To seal fused silica capillaries, a micro-flame gas-welding torch was used. The closed capillary was placed in the oven of a gas chromatograph, the temperature of which was rapidly raised to 140°C and maintained at this temperature for 30 min (for OV-215 only for 5 min). The oven was then rapidly cooled, and the column flushed with dry nitrogen at room temperature. Finally, the columns were rinsed with 5 ml of methylene chloride. The rinsing should be performed slowly; 5–6 h are suitable. Before testing, the columns were conditioned at 300°C (270°C for OV-215) for 1 h.

Testing procedure

The columns were tested by injection of a Grob text mixture[31] and also by test mixtures suggested by Schomburg et al.[32]. The amount of each test substance injected on the column was ca. 1 ng.

RESULTS AND DISCUSSION

The leaching of AR-glass has four purposes. First, metal ions, especially sodium ions, are removed from the glass surface. Second, a dense layer of silica xerogel is formed, which is presumed to counteract further diffusion of sodium ions from the bulk to the surface. The properties of such a layer are, however, dependent on how the gel has been formed. Silica hydrogel shrinks upon drying and is converted to a silica xerogel. The degree of shrinkage is, however, reduced if the gel water is displaced by an organic liquid before drying[33]. Third, the number of surface silanol groups is increased, and thus the surface is prepared for the following silanization. Fourth, leaching might level off differences between different glass batches.

Some fused silica capillaries were "leached" in order to increase the number of surface silanol groups. For the silanizing agents used here, however, such "leaching"

had little effect on silanization. We think that "leaching" of fused silica deserves to be further investigated.

Cyclic siloxanes were used for the silylation of AR-glass and fused silica capillaries. The reagents were chosen to give properties to the glass that facilitate wetting with stationary phases. For this purpose, a silylating agent was selected that contained the same functional side-groups as the phase to be coated, *e.g.*, for coating with silicone gum OV-215, the glass surface was silanized with cyclic siloxanes having (methyl)trifluoropropyl side-groups. The silylation procedure thus provides both deactivation and wettability[29,30].

In our opinion, it is very important that the stationary phase is deposited as an even film upon coating. This film is fixed in position on cross-linking, and no improvement of the film can be obtained after fixation. The pre-treatment of the capillaries gives the necessary wettability, and a carefully performed static coating results in the formation of even films. High column efficiencies were obtained (Table I).

TABLE I

CHARACTERISTICS OF SOME TYPICAL CAPILLARY COLUMNS

Column No.	Column diameter (mm)	Type of capillary	Stationary phase	d_f (μm)	Coating efficiency (%)	HETP for naphthalene (mm)	Kováts retention index at 90°C	
							Octanol	Naphthalene
1	0.28	AR-glass	SE-30	0.34	107	0.25	1051	1153
2	0.20	Fused silica	SE-30	0.25	93	0.19	1054	1156
3	0.28	AR-glass	SE-52	0.34	99	0.24	1066	1184
4	0.26	AR-glass	SE-54	0.32	90	0.25	1069	1191
5	0.20	Fused silica	SE-54	0.25	96	0.19	1069	1184
6	0.26	AR-glass	OV-215	0.32	86	0.28	1244	1436
7	0.26	AR-glass	OV-215*	0.32	87	0.25	1242	1429

* Not cross-linked.

Peroxide concentration, reaction time and temperature are inter-related, the peroxide decomposition rate increasing rapidly with increase in temperature. At 140°C, the half-life of dicumyl peroxide in benzene is 30 min and at 160°C it is 3 min[34]. We have found that for the preparation of non-polar columns, the reaction conditions are not particularly critical, and highly inert columns are obtained [Figs. 1, 2(2) and 2(3)] (peaks in all figures represent an amount of sample of *ca.* 1 ng). The curing is performed in a closed system at a relatively low temperature, which we believe, facilitates control of the reaction, and thereby reproducibility. One can, of course, use higher temperatures combined with smaller amounts of peroxide, but too intense curing leads to stationary phase films that are unsuitable for chromatographic purposes, *e.g.*, adsorption of hydrocarbons occurs. Dicumyl peroxide shows a higher reactivity with vinyl groups than with methyl groups, and therefore a smaller amount of peroxide can be used for vinyl-containing siloxanes than for methylsiloxanes[24]. With polar phases, column adsorptivitiy is a problem, but when using short curing times (5 min) for OV-215, well deactivated columns are obtained also with this phase [Fig. 2(1)]; a certain amount of amine adsorption is evident, however.
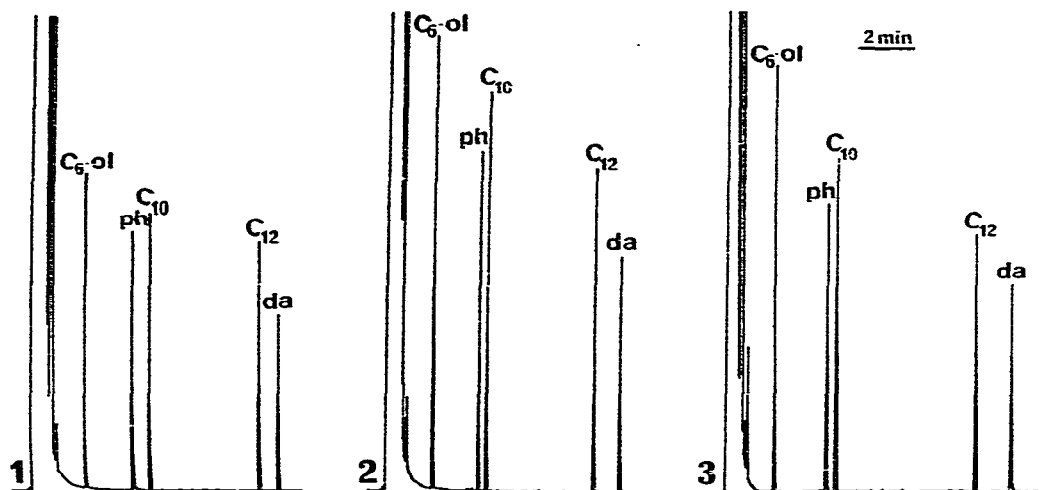
Fig. 1. Gas chromatograms [with flame-ionization detector (FID)] of a test mixture on different AR-glass capillary columns, D_4-deactivated and dicumyl peroxide cured. Initial temperature, 40°C for chromatograms 1 and 2, programmed at 7°C/min; 50°C for chromatogram 3, programmed at 5°C/min. Stationary phases: (1) SE-30; (2) SE-52; (3) SE-54. Peaks: C_6-ol = cyclohexanol; ph = phenol; C_{10} = decane; C_{12} = dodecane; da = decylamine.
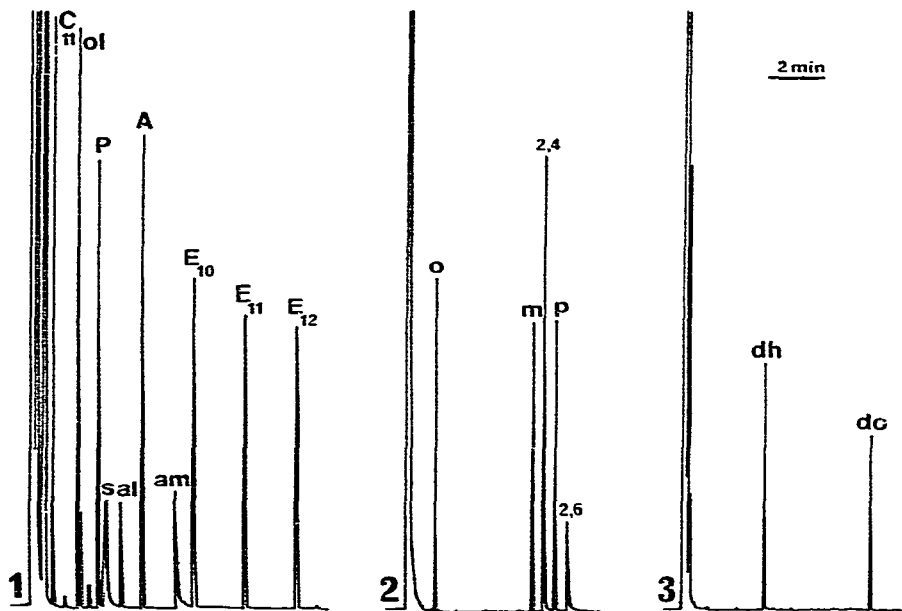

Fig. 2. Gas chromatograms (FID) of test mixtures on AR-glass capillary columns. (1) Grob test mixture on OV-215. Initial temperature 70°C, programmed at 5°C/min. Peaks: C_{11} = undecane; ol = octanol; P = 2,6-dimethylphenol; s = 2-ethylhexanoic acid; al = nonanal; A = 2,6-dimethylaniline; am = dicyclohexylamine; E_{10}, E_{11} and E_{12} = C_{10}, C_{11} and C_{12}-acid methyl esters. (2) Nitrophenol test on SE-52. Initial temperature 100°C, programmed at 7°C/min. Peak assignment: *o, m, p* = *ortho, meta, para*-nitrophenol; 2,4, 2,6 = 2,4-dinitrophenol and 2,6-dinitrophenol. (3) Diamine test on SE-30. Initial temperature 60°C, programmed at 7°C/min. Peaks: dh = 1,6-diaminohexane; do = 1,8-diaminooctane.

For all columns listed in Table I, extraction with methylene chloride led to a decrease in k values of only *ca.* 5%, as established by comparison with columns coated with non-cured stationary phases.

Column polarity, as reflected by the Kováts retention indices for octanol and naphthalene, is not much affected by vulcanization (columns 6 and 7 in Table I).

Fused silica columns have some acidic properties[32], which lead to a certain adsorptivity for amines (Fig. 3). Substances having a slightly basic character can, however, be chromatographed; the separation of some underivatized drugs is thus equally good on fused silica and AR-glass capillaries (Fig. 4). On the other hand, AR-glass has a basic character, which can be reduced by careful leaching. The separation of some underivatized barbiturates, slightly acidic in character, is thus very similar on fused silica and AR-glass capillaries (Fig. 5). The alkaline properties of AR-glass become evident on increasing the amount of sample, AR-glass columns being thus overloaded by *ca.* 20 ng of a barbiturate. The separation of some underivatized barbiturates has been demonstrated earlier[35].

The separation of underivatized tricyclic antidepressants is a new application at our laboratory. Separations achieved on fused silica capillaries coated with cross-linked SE-54 are shown in Fig. 6. The columns are so temperature stable and inert that even high-boiling, polar compounds such as opipramol can be chromatographed [Fig. 6(3)].

Separation of aqueous solutions

The GC separation of aqueous solutions on capillary columns can in some instances be an alternative to separation by high-performance liquid chromatography
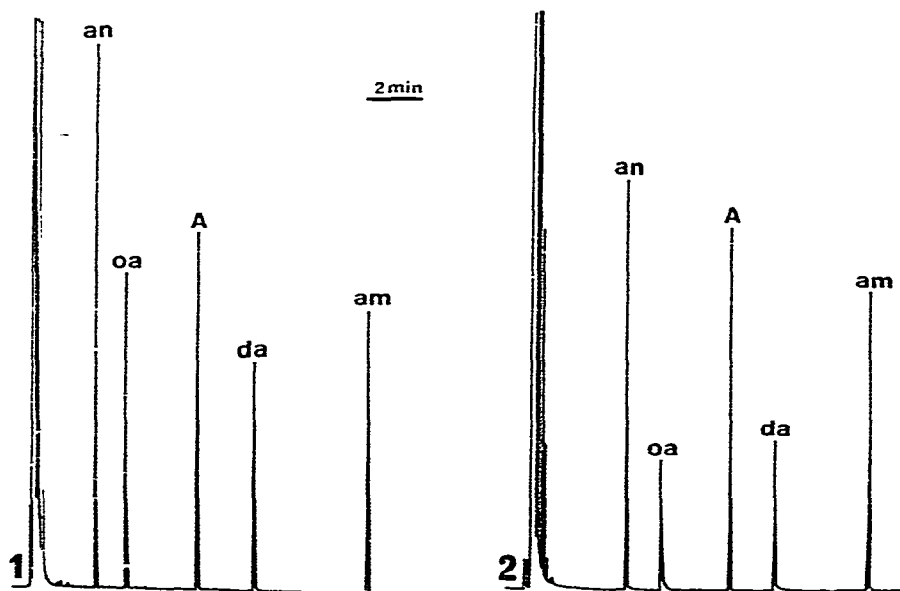

Fig. 3. Gas chromatograms (FID) of an amine test mixture on capillary columns coated with SE-54. (1) AR-glass. Initial temperature 60°C, programmed at 5°C/min. (2) Fused silica. Initial temperature 60°C, programmed at 7°C/min. Peaks: an = aniline; oa = octylamine; A = 2,6-dimethylaniline; da = decylamine; am = dicyclohexylamine.
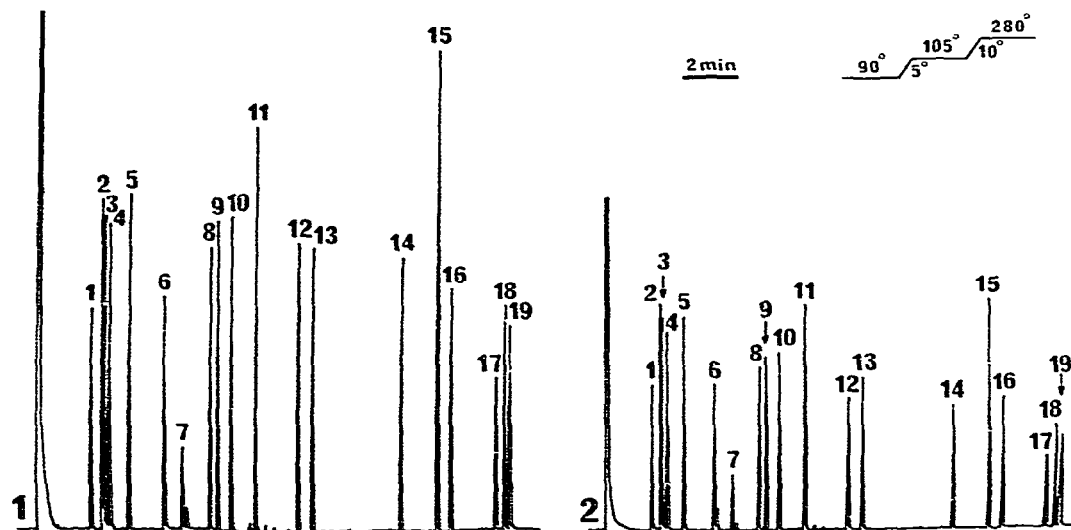
Fig. 4. Gas chromatograms (FID) of drug standard mixtures on capillary columns coated with SE-54. Temperature programme as shown. (1) AR-glass; (2) fused silica. Substances: 1 = Amphetamine; 2 = phentermine; 3 = propylhexedrine; 4 = methamphetamine; 5 = ethylamphetamine; 6 = propylamphetamine; 7 = ephedrine; 8 = phenmetrazine; 9 = phendimetrazine; 10 = amfepramone; 11 = benzocaine; 12 = phenacetin; 13 = methyl phenidate; 14 = procaine; 15 = methaqualone; 16 = cocaine; 17 = codeine; 18 = ethylmorphine; 19 = morphine.
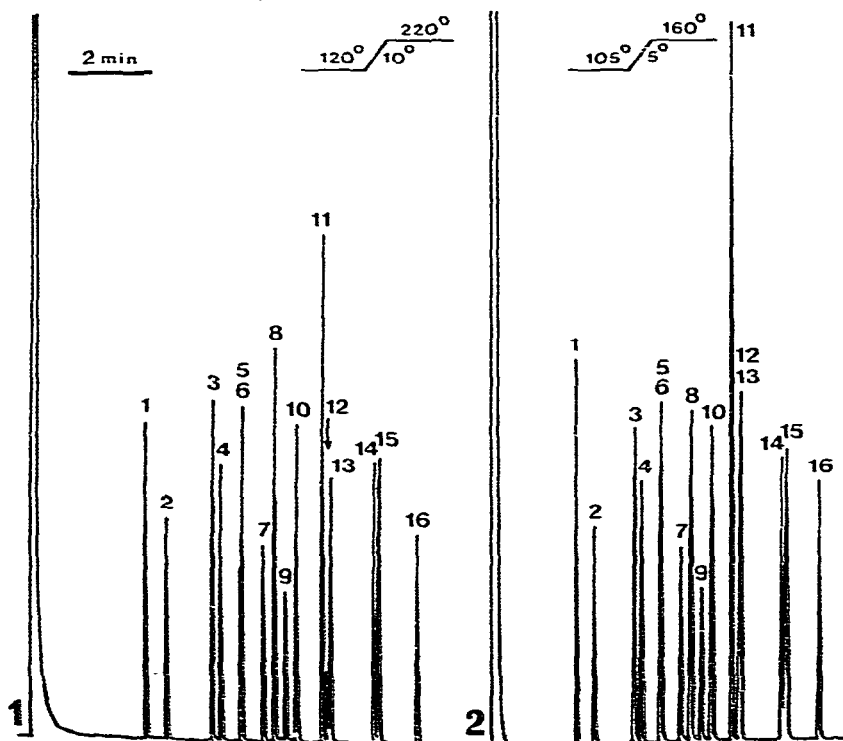

Fig. 5. Gas chromatograms (FID) of barbiturate standard mixtures on capillary columns coated with SE-54. Temperature programme as shown. (1) Fused silica; (2) AR-glass. Substances: 1 = Metharbital; 2 = barbital; 3 = allobarbital; 4 = aprobarbital; 5 = butethal; 6 = butalbital; 7 = amobarbital; 8 = pentobarbital; 9 = vinbarbital; 10 = secobarbital; 11 = glutethimide; 12 = brallobarbital; 13 = hexobarbital; 14 = phenobarbital; 15 = cyclobarbital; 16 = heptabarbital.
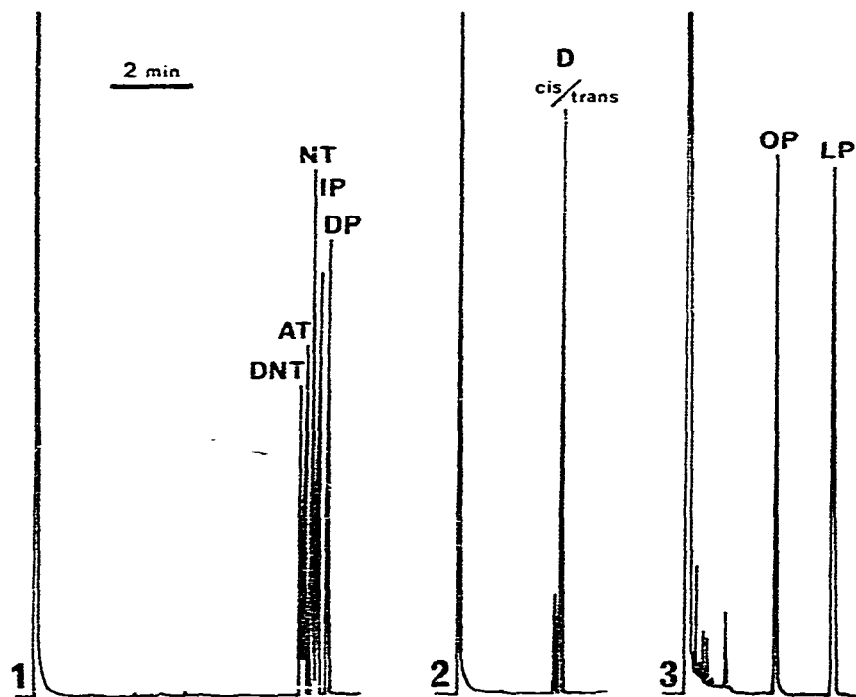
Fig. 6. Gas chromatograms (FID) of tricyclic antidepressant test mixtures on fused silica capillary columns coated with SE-54. (1) Initial temperature 180°C, programmed at 7°C/min. Peaks: DNT = desmethylnortriptyline; AT = amitriptyline; NT = nortriptyline; IP = imipramine; DP = desipramine. (2) Temperature: isothermal at 240°C. Separation of D = doxepine, *cis* and *trans*. (3) Temperature: isothermal at 320°C. Peaks: OP = opipramol; LP = lofepramine.

(HPLC), the grounds for this being that capillary columns have a much higher separation power. Moreover, sensitive detection can often be achieved without derivatization of the sample. Good separations of some aqueous test solutions on Carbowax-coated capillary GC columns have been demonstrated by Bastian *et al.*[36].

We consider that peroxide-cured silicone columns are suitable for such samples. The immobilized stationary phase cannot be displaced from the capillary surface by water, and non-volatile material deposited in the column upon injection can be rinsed out, provided, of course, that it is soluble. One must, however, be aware of the fact that injection of acids and bases together with water can lead to hydrolysis of the stationary phase; this problem also occurs in HPLC when silanized silica is used. The separation of a test mixture injected by an on-column technique is demonstrated in Fig. 7. Column activity as reflected by the elution of octanol was not influenced by 50 on-column injections at 110°C of 0.4 µl of aqueous solution.

Comparison of cross-linking techniques

Two types of cross-linked bonded silicones are now available. The cross-linking is based, in an earlier type, on Si–O–Si bonds and in a newer type on Si–C–C–Si bonds. The two types of columns do not have identical properties. We have shown in a previous paper[10] that silicone phases, where the cross-linking is based on Si–O–Si
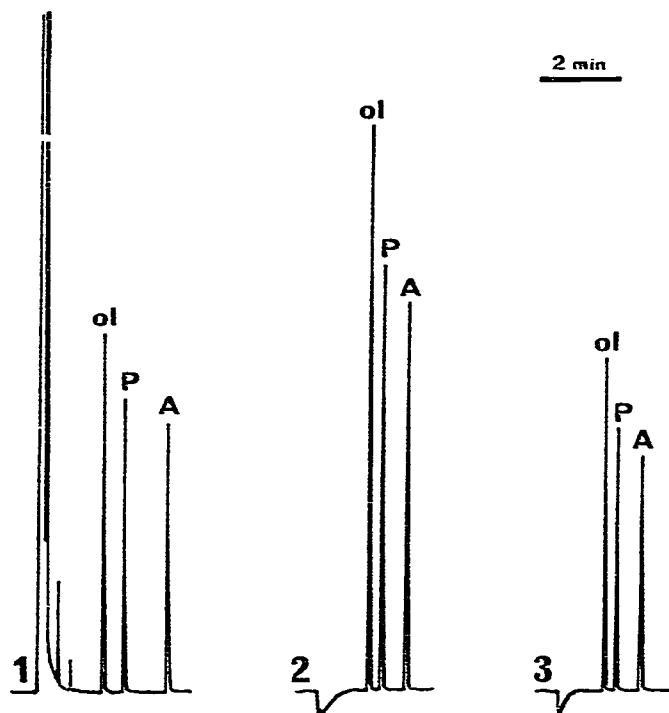
Fig. 7. Gas chromatograms (FID) of a polarity text mixture on an AR-glass capillary column coated with SE-54. On-column injection. 0.4 μl injected. (1) Temperature: isothermal at 100°C. Solvent: heptane. (2) Temperature: isothermal at 110°C. Solvent: water. (3) Conditions as in (2), but after 50 on-column injections of the aqueous test solution.

bonds, have much lower bleeding rates than corresponding conventional phases, especially at temperatures above 350°C. For peroxide-cured silicones, however, we obtain bleeding rates in the same range as for commercially available phases. A special merit of the earlier column types is their outstanding capability for the separation of polycyclic aromatic hydrocarbons[6–10]. We attribute this to a slight residue of silanol groups in the phase. Further, it is possible to prepare columns coated with cyanopropylsilicones when using the earlier curing method. The peroxide-cured columns are, on the other hand, easier to prepare, and show higher efficiencies and better deactivation. We consider that the two methods are complementary to each other.

ACKNOWLEDGEMENTS

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