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Note

Preparation of capillary columns coated with phenylsilicone gum

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Phenylsilicones have been used extensively as stationary phases in packed column gas chromatography. As such phases have a wide field of application, there is considerable interest in the development of capillary columns with the same type of stationary phase. At present, the performance of phenylsilicone columns is by far surpassed by that of equivalent non-polar columns. Therefore, the use of phenyl columns instead of non-polar columns will mostly lead only to marginal improvements in separation. The advantages of phenylsilicones will be evident, however, when the efficiency and thermostability of such columns are of the same magnitude as those of a corresponding non-polar column. To obtain this, a glass surface is required that is readily wetted by phenylsilicones, and a phenylsilicone stationary phase that forms a stable film. Further, the support must be well deactivated. One possibility of achieving wettability and deactivation is to silanize the support surface with reagents having phenyl groups. Grob and Grob presented a method for silanization with some phenyldisilazanes¹, but this modification method facilitates wetting only with silicones that have a low phenyl content. Further, Schomburg *et al.*² attempted to obtain capillary deactivation and wettability by treatment with OV-17 at high temperatures.

High-temperature silanization with cyclic siloxanes is a powerful method for the modification of glass surfaces. Silanization with octamethylcyclotetrasiloxane was described by Stark *et al.*³, and this method gives excellently deactivated non-polar columns. We have developed methods for silanization with cyclic siloxanes having special side-groups, 3,3,3-trifluoropropyl^{4,5} and cyanopropyl⁵. By applying these methods, we obtained deactivation and also wettability for silicone stationary phases having corresponding functional groups.

Modification of glass capillaries by silanization with hexaphenylcyclotrisiloxane is described in this paper. Capillaries treated in this manner are well deactivated and they are readily wetted by phenylsilicone stationary phases.

A stationary phase film of silicone gum is generally much more stable than a film of silicone fluid⁶. Phenylsilicone gums were not commercially available, however, when this work was started: we therefore synthesized such a gum to be used as a stationary phase.

Stable columns are also obtained when the stationary phase is bonded to the glass surface and/or cross-linked^{7,8}. The highest column efficiencies could not be attained, however, when using these methods. More promising results in this respect

TABLE I

PROPERTIES OF TYPICAL 20-m AR-GLASS CAPILLARY COLUMNS, DEACTIVATED WITH HEXAPHENYLCYCLOTRISILOXANE AND COATED WITH METHYLPHENYLSILICONES

Efficiency measured for naphthalene at 100°C.

Stationary phase	Column diameter (mm)	Film thickness (μm)	Capacity ratio, <i>k</i> (naphthalene)	HETP (mm)	UTE* (%)	Kováts retention index	
						Octanol	Naphthalene
Phenyl gum	0.22	0.28	15.5	0.24	84	1181	1390
OV-25	0.23	0.29	12.3	0.33	66	1197	1468
OV-17	0.24	0.30	13.7	0.46	47	1155	1373
OV-1701	0.23	0.29	9.9	0.21	98	1180	1288

* UTE = Utilization of the theoretical best efficiency.

were achieved by peroxide-initiated stationary phase vulcanization^{9,10}. This method, however, cannot be directly applied to phenylsilicones, as such vulcanization is sterically hindered by the phenyl groups⁹.

EXPERIMENTAL

An OV-17 type siloxane was synthesized from methylphenyldichlorosilane¹¹ (Silar Labs., Scotia, NY, U.S.A.). This siloxane was further polymerized to a gum using sodium trimethylsilanolate (Ventron, Beverly, MA, U.S.A.) as a catalyst according to Johannson¹². In order to remove the catalyst after reaction, the gum was carefully rinsed with dilute hydrochloric acid ($\text{pH} = 1$) and then with distilled water to neutrality. Methylene chloride was added and, after separation, the gum was dried over calcium sulphate. Finally, capping with trimethylchlorosilane (Merck, Darmstadt, G.F.R.) was performed under refluxing toluene. The product was a thick, clear gum.

AR-glass capillaries were leached according to Grob *et al.*¹³, then the capillaries were coated dynamically with a saturated solution of hexaphenylcyclotrisiloxane (Petrarch Systems, Levittown, PA, U.S.A.) in ethyl acetate, at a speed of 4 cm/sec. After solvent evaporation, the capillaries were filled with dry ammonia gas (Matheson Gas Products, East Rutherford, NJ, U.S.A.), sealed with caution in a microflame and heated at a rate of 5°C/min to 400°C, then isothermal at 400°C for 15 h and finally slowly cooled. Excess of reagent was rinsed out with 5 ml of methylene chloride.

The silanized capillaries were statically coated with a 0.5% (w/v) solution of the methylphenylsilicone gum, OV-25, OV-17 or OV-1701 in methylene chloride.

RESULTS

Silanization with diphenylsilanes leads mostly to low coverages (*e.g.*, see ref. 14). Reaction at high temperatures in the presence of a catalyst (ammonia), however gave a surface modification suitable for our purposes.

Three types of methylphenylsilicone stationary phases were applied to phenyl-modified capillaries (Table I). Capillaries coated with the methylphenylsilicone gum, prepared in this Laboratory, show high efficiencies. The gum has 50% phenyl substitution and it was of interest to test a phase having 75% phenyl substitution. For this

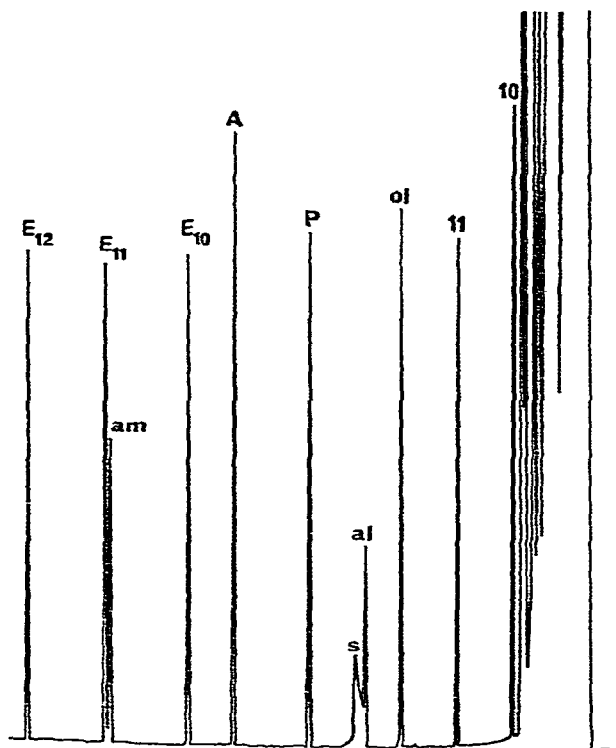


Fig. 1. Gas chromatogram (flame-ionization detector) of a Grob test mixture on a 20-m AR-glass capillary column, modified with hexaphenylcyclotrisiloxane and coated with methylphenylsilicone gum. Initial temperature 60°C, programmed to 150°C at 5°C/min. Peaks: 10 = decane; 11 = undecane; ol = octanol; al = nonanal; s = 2-ethylhexanoic acid; P = 2,6-dimethylphenol; A = 2,6-dimethylaniline; am = dicyclohexylamine; E₁₀, E₁₁, E₁₂ = C₁₀, C₁₁, C₁₂-acid methyl ester, respectively. Each peak corresponds to ca. 1 ng of substance.

purpose OV-25, which is a silicone oil but still relatively viscous, was chosen¹⁵. As might be expected, an increased phenyl content led to decreased column efficiencies. Finally, the methylphenylsilicone oil OV-17 (50% phenyl) was tested and was found to give poor results.

All three phases gave columns of low adsorptive activity. A typical test chromatogram is shown in Fig. 1.

The gum showed the best temperature stability of the three phases tested. Columns coated with this phase can be used isothermally at 320°C without difficulty. OV-25 can be used up to 300°C but bleeding is much higher than with the gum phase. OV-17 could only be used up to 240°C.

An example of the possibilities of efficient, deactivated and temperature-stable phenylsilicone columns is demonstrated in Fig. 2, where the separation of a mixture of underivatized tricyclic antidepressants is shown.

A viscous substitute for OV-17, OV-1701, will soon be commercially available (Alltech Europe, Eke, Belgium), and a sample was obtained and tested. The phase was slightly opaque. Preliminary results indicated that highly efficient columns can be prepared and that the polarity is lower than that for our home-made phenylsilicone gum (Table I). The bleeding properties seems to be in the same range as for OV-25.

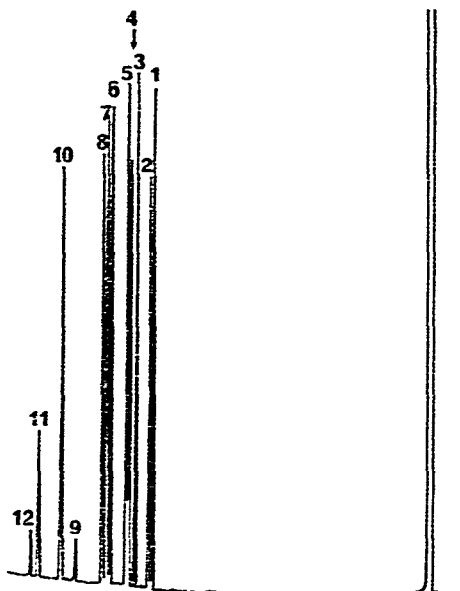


Fig. 2. Gas chromatogram (flame-ionization detector) of a test mixture of underivatized tricyclic antidepressants. Column as in Fig. 1. Initial temperature 185°C, programmed at 5°C/min. Peaks: 1 = amitriptyline; 2 = trimipramine; 3 = imipramine; 4 = nortriptyline; 5 = desmethylnortriptyline; 6 = desipramine; 7 = protriptyline; 8 = desmethyldoxepine; 9 = desmethylmaprotiline; 10 = chlomidipramine; 11 = maprotiline; 12 = desmethylchlomidipramine. Each peak corresponds to ca. 1 ng of substance.

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