Preparation and Evaluation of Capillary Columns with Phases with 5–33% Phenyl Substitution

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Key Words

Capillary GC
Film stability
Catalytic activity

Summary

A polysiloxane with 33% phenyl substitution, OV-61, and mixtures of this phase and SE-54 were coated on deactivated fused silica or borosilicate glass capillaries, using diphenyltetramethyldisilazane (DPTMDS) for high temperature silylation. Film stability was achieved also without crosslinking agents such as azo-tert-butane, thus avoiding the activity introduced by such treatment. Columns were stable up to 350°C.

Introduction

Capillary columns with phenyl silicone phases potentially have a wide applicability besides the well established non-polar silicone phases, for demanding separations where column inertness towards sensitive analytes and stability against elevated temperatures are essential. The polarizability of the phenyl group offers a significant change in selectivity compared to methyl silicone phases. Interactions between the phenyl group and solutes are unlikely to cause decomposition or irreversible adsorption of the solute. Phenyl phases have high resistance against oxidation [1] and hydrolysis that would cause depolymerization of the phase and create active groups which could react with the solutes. Such instability was observed for cyanopropyl phases [2] and for tolyl phases [3]. The thermal stability of phenyl phases allows for temperatures up to 375°C. A biphenyl substituted siloxane [4] and silarylene-siloxane copolymers [5, 6] have recently been introduced as extensions of the line of phenyl phases, making use of the temperature stability of such phases.

The problem encountered in making columns with phenyl phases is to successfully combine techniques for deactivation of the supporting wall with techniques to make the film stable up to the maximum temperature where the phase itself is chemically stable. The stationary phase must wet and form a uniform film on the deactivated surface during coating at low temperature and remain stable at elevated temperature. Immobilization after coating by treatment with radical generators may result in increased adsorptive and catalytic activity, although azo-compounds have been reported to be better than peroxides in this respect [7]. This work presents results from columns prepared by a selection of procedures and commercially available materials, with the aim to obtain columns with high inertness, high temperature stability and high coating efficiency.

Experimental

Fused silica columns were prepared from 25 or 50m lengths of 0.32mm i. d. capillaries (Quartz & Silice, Courbevoi, France). Capillaries were flushed with about 5 column volumes of 1% HCl, dried under nitrogen flow at 90°C, 200°C and finally 300°C overnight. The dried column was dynamically coated with diphenyltetramethyldisilazane (DPTMDS), (Fluka), sealed and heated slowly to a final temperature of 400°C and then kept there for 4 hours. No special precautions were taken to protect the outer polyimide coating on the fused silica tubing. The silylated capillary was washed with solvents, dried with nitrogen and filled with a 0.2% solution of the stationary phase in n-pentane. The stationary phase was SE-54, OV-61 or mixtures of these corresponding to 10, 15, 20 and 25% of phenyl content. Static coating was performed in a water bath held at 30°C with the capillary connected to a flask evacuated to 0.05 bar. The coated column was conditioned at 200°C before testing. Treatment with azo-tert-butane (Alfa Products) was carried out by bubbling nitrogen through the reagent at room temperature and heating the sealed column to 200°C (for 1 hour for SE-54, over night for OV-61).

Glass columns were prepared from pyrex glass tubing drawn to ca. 0.34mm i. d. capillaries. Etching was performed according to Traitler and Prevot [8] filling the capillary to 87% of its length with an 18% aqueous solution of NH_3, sealing under vacuum and heating at 10°/min up to 170°C. The column was kept at this temperature for 70 hours. Leaching with 18% HCl was performed according to Grob [9] at 170°C overnight. Deactivation with DPTMDS and coating was made as outlined above.

Presented at the 15th International Symposium on Chromatography, Nürnberg, October 1984

0009-5893/84 0151-04 $ 03.00/0

Columns were tested on a Perkin-Elmer model 3920 gas chromatograph modified for capillary work. Grob tests were performed by split injection of a commercial test mixture (Fluka, No. 86499 or 86501) using helium carrier gas at 0.30m/s and temperature programming from 50°C at 2°/min. Trennzahl was calculated from half-height widths of the E-10 and E-11 peaks. Tests on catalytic activity towards bis-TFA-metrolol (the trifluoroacetyl derivative of metoprolol) were performed according to Ahnoff and Johansson [10]. By injecting a solution of bis-TFA-metoprolol (110ng/µl), n-$C_{18}H_{38}$ (54ng/µl), n-$C_{20}H_{42}$ (74ng/µl) and n-$C_{18}H_{37}Br$ (191ng/µl) in isothermal runs at 200°C with two different carrier gas flow rates, the decomposition rate of bis-TFA-metoprolol was calculated.

Peak integration was performed with a model 3390A integrator (Hewlett-Packard) or a model 4416 chromatography data system (Nelson Analytical).

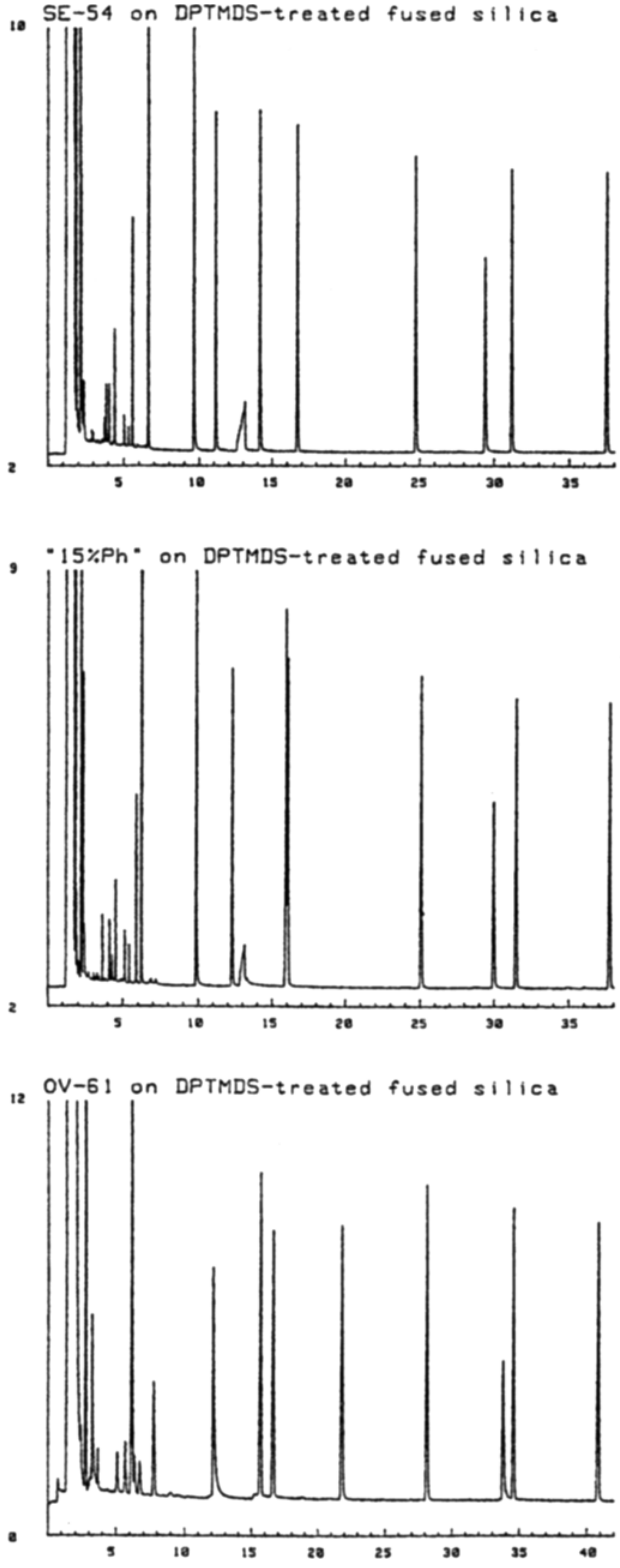

Fig. 1

Grob test chromatograms for columns made from DPTMDS-deactivated fused silica (25m X 0.32mm i.d.) statically coated with 0.2% solutions of stationary phase. (a) SE-54, (b) mixture of SE-54 and OV-61 corresponding to 15% phenyl (c) OV-61. (See Experimental for details.)

Results and Discussion

Figs. 1–4 show chromatograms from Grob tests and tests with bis-TFA-metoprolol for different columns. Column efficiencies measured as Trennzahl are given in Table I. Measured catalytic activities are listed in Table II.

OV-61 is a methyl phenyl silicone with 33% phenyl substitution. It has a high viscosity, 50000 cSt at 25°C, and high molecular weight, 40000, compared to OV-17 (1300–1500cSt, MW 4000, Ref. [1]), making it better suited as a stationary phase for capillary columns. This and the somewhat lower phenyl content, compared to OV-17, makes it possible to obtain stable films with no need for immobilization with crosslinking agents after coating.

OV-61 was successfully coated on nondeactivated fused silica and the column conditioned at 375°C with no loss in column efficiency (Table I). When coated on DPTMDS-treated fused silica, the efficiency was often somewhat lower. Nevertheless, the columns retained their efficiency after conditioning overnight at 350°C. The column activity towards bis-TFA-metoprolol was in no case increased by this treatment.

Table I. Column efficiency measured as Trennzahl (TZ) for methyldecanoate/methylundecanoate in the Grob test (for chromatographic conditions, see Experimental)

Column	TZ Conditioning temperature 200°C	 350°C
I. DPTMDS-treated fused silica, i.d. 0.32mm		
SE-54	36.0	36.5
"10% Ph"	33.6	–
"15% Ph"	33.5	35.1
"20% Ph"	31.3	–
"25% Ph"	29.6	–
OV-61	29.9	29.3
II. Untreated fused silica, i.d. 0.32mm		
OV-61	35.4	36.3
III. NH_3-etched, HCl-leached, DPTMDS-treated Pyrex, i.d. = 0.34mm		
OV-61	30.1	29.6

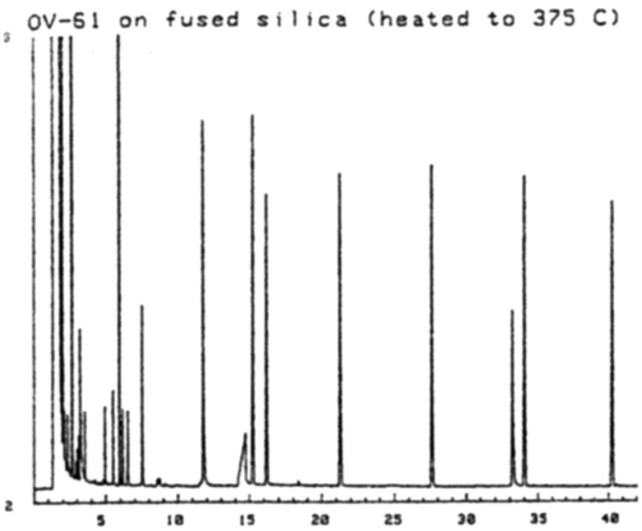

Fig. 2
Grob test chromatogram for a column made from untreated fused silica (25m X 0.32mm i.d.) coated with OV-61 (0.2%) and conditioned at 375°C (16h).

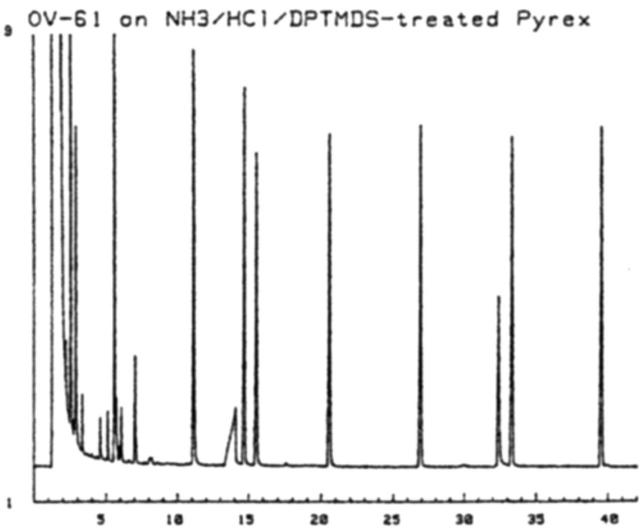

Fig. 3
Grob test chromatogram for a column made from NH_3 etched, HCl leached and DPTMDS-deactivated Pyrex glass (25m X 0.34mm i.d.). (See Experimental for details.)

When azo-tert-butane was used for immobilization, the non-extractable fraction was 95% for SE-54 and 65% for OV-61. However, column activity towards bis-TFA-metoprolol was increased (Fig. 6 and Table II). Mixtures of SE-54 and OV-61 corresponding to 10, 15, 20 and 25% phenyl were immobilized to 95, 82, 59 and 47%, respectively. They were less suited for rinsing with solvent since this affected the phenyl content of the remaining phase.

Efficient and highly inert OV-61 columns were prepared from pyrex glass by a combination of aqueous ammonia etching, Grob leaching and silylation with DPTMDS (Fig. 3, Table I and II). The measured Trennzahl was slightly better than for the fused silica columns coated with OV-61, if corrected for the somewhat larger inner diameter of the glass column (0.34mm instead of 0.32mm). Elimination of the etching step or use of a mixture of HMDS and DPTMDS, instead of DPTMDS only, resulted in droplet formation during coating or after a few days' use at 200°C. Evidently, the leached and DPTMDS-treated glass surface had a lower surface energy than the acid-rinsed and DPTMDS-treated fused silica surface, which was wettable with OV-61 (see above).

Table II. Catalytic activity measured at 200°C with bis(trifluoroacetyl)metoprolol as test substance. (k = decomposition rate constant, t1/2 = half life). Columns were conditioned overnight prior to testing.

Column	Conditioning temp	$k(10^{-3}s^{-1})$	t1/2(min)
I. DPTMDS-treated fused silica			
SE-54	350°C	< 0.1	> 110
SE-54/ATB/rinsed	200°C	1.9	6.0
	350°C	0.58	20
"15% Ph"	350°C	0.25	46
"15% Ph"/ATB/rinsed	200°C	3.5	3.0
OV-61	350°C	0.37	31
OV-61/ATB/rinsed	200°C	3.9	3.0
II. Untreated fused silica			
OV-61	200°C	9.3	1.2
	375°C	1.0	11.4
III. NH_3-etched, HCl-leached and DPTMDS-treated Pyrex			
OV-61	350°C	< 0.1	> 110

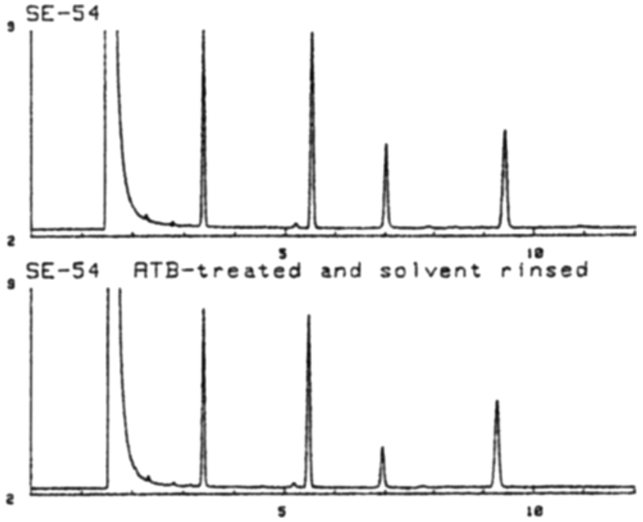

Fig. 4
Chromatogram from tests with bis(trifluoroacetyl)metoprolol (7.0min) and reference substances $n\text{-}C_{18}H_{38}$, $n\text{-}C_{20}H_{42}$ and $n\text{-}C_{18}H_{37}Br$, on two SE-54 columns with different catalytic activity: (a) same column as in Fig. 1a, (b) azo-tert-butane treated and CH_2Cl_2-rinsed column. Both columns originated from a single 50m column.

Etching of glass capillaries with ammonia, followed by leaching, silylation with HMDS + DPTMDS (1:1) and coating with OV-17 has been reported [8] but never succeeded in our hands. Attempts to achieve efficient deactivation and increased wettability of leached glass or fused silica by treatment with hexaphenylcyclotrisiloxane, a reagent with higher density of phenyl groups than DPTMDS, were not successful. Addition of gaseous ammonia to promote reaction resulted in adsorption of hydrocarbons, an observation also made by Welsch [11].

Deactivation by the stationary phase itself, introduced as a technique by Schomburg et al. [12] might explain why the columns in Table I when conditioned at 350°C often showed a decrease in activity against bis-TFA-metoprolol. The effect was most pronounced for an untreated fused silica capillary coated with OV-61 (Table II).

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Received: Oct. 1, 1984
Accepted: Nov. 8, 1984