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GLASS CAPILLARY COLUMNS WITH MIXED STATIONARY PHASES

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SUMMARY

Deactivation of the glass capillary and coating of the stationary phase can be performed in one operation. Static coating with a solution of both 95% methyl 5% phenyl silicone and poly(ethylene glycol) gives capillaries of superior quality than by successive treatments.

INTRODUCTION

In order to change the selectivity of chromatographic systems, mixed stationary phases are often used. Capillary chromatography is a form of chromatography which has partition abilities so great that the selectivity, and even the polarity, of the stationary phase are of secondary importance. Increasing the selectivity as well as subtle modulation of polarity by mixing the solvents may therefore seem pointless. However, the main deficiency of glass capillary gas chromatography is the preparation of the column itself, and especially the formation of a stationary-phase homogenous film which always requires proper preparation of the capillary interior surface, *i.e.* its etching and deactivation.

Deactivation, which improves the wettability of the glass surface by the non-polar stationary phase, is carried out by means of binding silanes[1] or Carbowax 20M[2].

In the present work it was shown that using a mixed stationary phase, composed of poly(ethylene glycol) (Carbowax 20M) and non-polar 95% methyl 5% phenyl silicone oil (SE-52), the surface deactivation step may be omitted. Deactivation already occurs in the coating process itself owing to the preferential adsorption of Carbowax 20M. With regard to efficiency, the columns prepared are equivalent to those with pure SE-52 deposited on the previously silanized surface and are of higher efficiency than columns with pure SE-52 deposited on the previously silanized surface and are of higher efficiency than columns with pure Carbowax 20M.

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EXPERIMENTAL

Capillary tubes (0.3 mm I.D.) were drawn from tubes (1 m × 3 mm I.D.) made of Polish soda glass (Krosno Glass Works) using a drawing machine made in our laboratories. The internal capillary surface was increased by treatment with dilute hydrochloric acid[3].

All capillaries were coated by the static method with solutions of SE-52 and Carbowax 20M in the ratios 3:1 and 1:3 and with pure Carbowax 20M and pure SE-52 in dichloromethane. The concentration of the solution was adjusted to give a film thickness of 0.15, 0.3 and 0.5 μm for each kind of stationary phase (for Carbowax 20M also 0.25 μm). Two other columns were prepared: column 11 (Carbowax 20M coated) and column 1 (with pure SE-52 on the hexamethyldisilane (HMDS)-treated surface)[1].

A Pye Unicam GCD chromatograph was used for the work with capillary columns, in which the cage-located capillaries were removed, and the column endings were directly introduced into the injector and a flame-ionization detector (FID) burner. The samples were of 1 μl, with a splitting ratio of 1:30, and the concentration of the solutions corresponded to the concentration of the Grob test mixture[4].

The specific retention volumes (V_g) of various compounds were measured on pure Carbowax 20M, on pure SE-52 and on their mixtures in order to determine the stationary-phase film thickness. Gas-Chrom CLZ coated with 3% SE-52, Carbowax 20M, and their mixtures in ratios of 3:1, 1:1, and 1:3 were used as packing materials. The measurements were performed on a W. Giede GChF 18.3 (Leipzig, G.D.R.) gas chromatograph equipped with a katarometer. Nitrogen was used as the carrier gas. The temperature was 100°C. The stationary-phase film thickness was calculated from the retention data (V_g and k) of the methyl esters of C_{10} and C_{12} fatty acids.

RESULTS AND DISCUSSION

The properties of all capillary columns with the mixed stationary phases and individual solvents SE-52 and Carbowax 20M are given in Table I.

Columns 1 and 2 have an SE-52 film of the same thickness, but in the preparation of column 2 the silanization stage was omitted. The resolution of this column is almost five-fold smaller than that of column 1. In fact it is so small that the column can be regarded as completely useless. Column 2 was made only for underlining the contrast between its properties and the properties of the columns with mixed stationary phases, which were also prepared without predeactivation of the surface (columns 5–10 and 12–14).

Columns 11 and 12 with Carbowax 20M are characterized by their almost identical (within the limits of experimental error) properties despite the fact that column 11, before coating, underwent the deactivation stage. As can be seen in the case of the polar stationary phase, deactivation is not necessary since it does not improve the quality of the column.

Columns with mixed stationary phases are characterized by relatively high resolution values ($R_s = \frac{1}{2} R_s$ obtained for these esters). The highest resolution can be observed at the predominance of SE-52 (columns 5–7) and its value of EPN (effective peak number) is close to the EPN of the columns with pure SE-52. When Carbowax

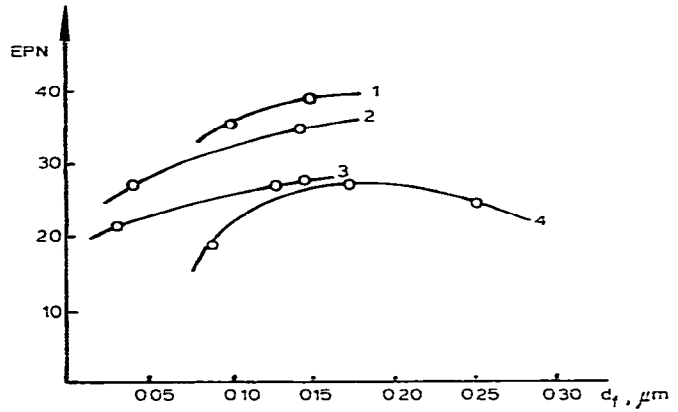

Fig. 1. Effective peak numbers (EPN) as a function of film thickness (d_f). Stationary phases: 1 = SE-52; 2 = SE-52 + Carbowax 20M (3:1); 3 = SE-52 + Carbowax 20M (1:3); 4 = Carbowax 20M.

20M predominates, EPN is comparable to the one obtained on Carbowax 20M itself, whereas the values of the capacity ratio (k) for all columns with the mixed stationary phase remain at the same k as in the columns with pure SE-52. This means that in the columns with mixed stationary phases we observe a non-linear dependence of the retention data as a function of the stationary phase composition. A lengthening of the retention time can be observed which occurs without simultaneous broadening of chromatographic bands; thus the high resolution (and also efficiency) of these columns is preserved.

The resolution of the peaks and their retention remain a function of the

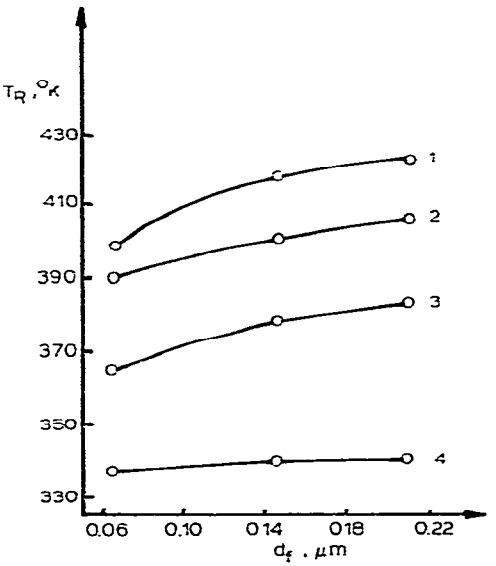

Fig. 2. Variation of retention temperatures with stationary phase film thickness for Carbowax 20M columns. Initial temperature, 333°K; programming rate, 4°/min. Curves: 1 = 2,3-dimethylnaphthalene; 2 = 2,6-dimethylaniline; 3 = methyl decanoate; 4 = *n*-decane.

TABLE I

CHARACTERISTICS OF GLASS CAPILLARY COLUMNS WITH SILICONE SE-52, CARBOWAX 20M AND THEIR MIXTURES

Characteristic	*Stationary phase and column no.*													
	SE-52				*SE-52 + Carbowax 20M (3:1)*			*SE-52 + Carbowax 20M (1:3)*			*Carbowax 20M*			
	1	*2*	*3*	*4*	*5*	*6*	*7*	*8*	*9*	*10*	*11*	*12*	*13*	*14*
Column length (m)	24.0	24.5	22.3	24.5	24.5	24.5	23.5	24.5	24.5	24.5	24.5	24.5	28.9	24.5
Film thickness (μm)														
provided	0.15	0.15	0.30	0.50	0.15	0.30	0.50	0.15	0.30	0.50	0.15	0.15	0.25	0.30
obtained	0.14	0.14	0.11	0.18	0.04	0.14	0.14	0.03	0.12	0.13	0.08	0.07	0.16	0.23
Capacity ratio, k', for methyl dodecanoate at 100°C	58.0	49.6	40.0	63.0	16.7	61.0	61.3	12.6	46.7	51.6	10.8	8.8	21.1	28.3
EPN for methyl esters	39.0	8.0	20.2	25.1	26.0	35.8	27.0	21.6	29.0	26.0	18.8	17.3	27.8	23.0

TABLE II

RETENTION INDICES AND RELATIVE COLUMN POLARITY

Characteristic	*Stationary phase and column no.*							
	SE-52		*SE-52 + Carbowax 20M (3:1)*		*SE-52 + Carbowax 20M (1:3)*		*Carbowax 20M*	
	1	*packed*	*5*	*7*	*8*	*10*	*14*	*packed*
Film thickness, μm	0.14		0.04	0.14	0.03	0.13	0.23	
1-Octanol (retention indices)	1079	1065	1165	1168	1347	1397	1550	1474
1-Octanol (relative polarity %)	0.0	–	18.3	19.7	56.9	67.5	100.0	–

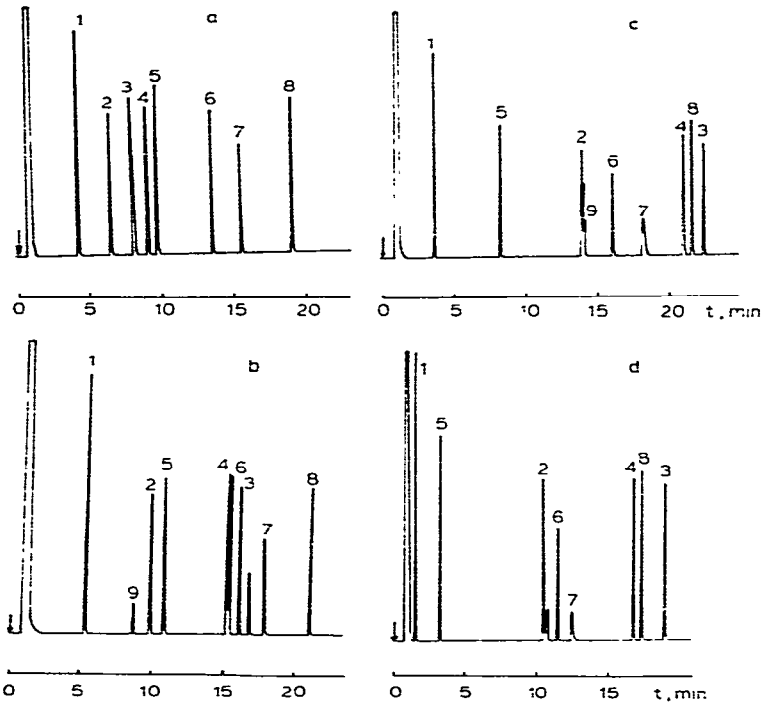

Fig. 3. Grob's tests for columns coated with SE-52, Carbowax 20M and their mixtures. Initial temperature, 333°K; programming rate, 4°/min. Sample, 1 μl; carrier gas, H_2. Columns: a = column 2 with SE-52; b, = column 6 with SE-52 + Carbowax 20M (3:1); c, = column 10 with SE-52 + Carbowax 20M (1:3); d, = column 13 with Carbowax 20M. Peaks: 1 = *n*-decane; 2 = 1-octanol; 3 = 2,6-dimethylphenol; 4 = 2,6-dimethylaniline; 5 = *n*-dodecane; 6 = methyl decanoate; 7 = dicyclohexylamine; 8 = methyl dodecanoate; 9 = 2,3-butanediol.

stationary phase film thickness (Figs. 1 and 2). The peak resolution reaches its maximum value at $d_f = 0.13$–0.17 μm (Fig. 1). The dependence of the retention temperature (T_R) in the analysis with the programmed temperature on the film thickness is different for different types of compounds (Fig. 2). The aliphatic hydrocarbon (C_{10}) is least sensitive to the changes in the film thickness; the aromatic hydrocarbon (2,3-dimethylnaphthalene) is the most sensitive to these changes.

Chromatograms of the Grob text mixture[4], shown in Fig. 3, show that the columns with the mixed stationary phase do not exhibit adsorptive properties, despite the fact that they were not predeactivated. The peaks of the polar compounds, 1-octanol, 2,6-dimethylphenol, and 2,6-dimethylaniline, retain *ca.* 100% of their height[4].

It can be seen from Table I that the obtained film thickness is considerably different from the planned one. As the static-coating method was used this result is very surprising, and was probably caused by "creeping" of the stationary phase out of the capillary in the course of prolonged (24–48 h) vacuum evaporation of the solvent. This "creeping out" certainly changes the composition of the mixed stationary phase. A new absolute determination of the components is very difficult, and therefore an indirect method was used.

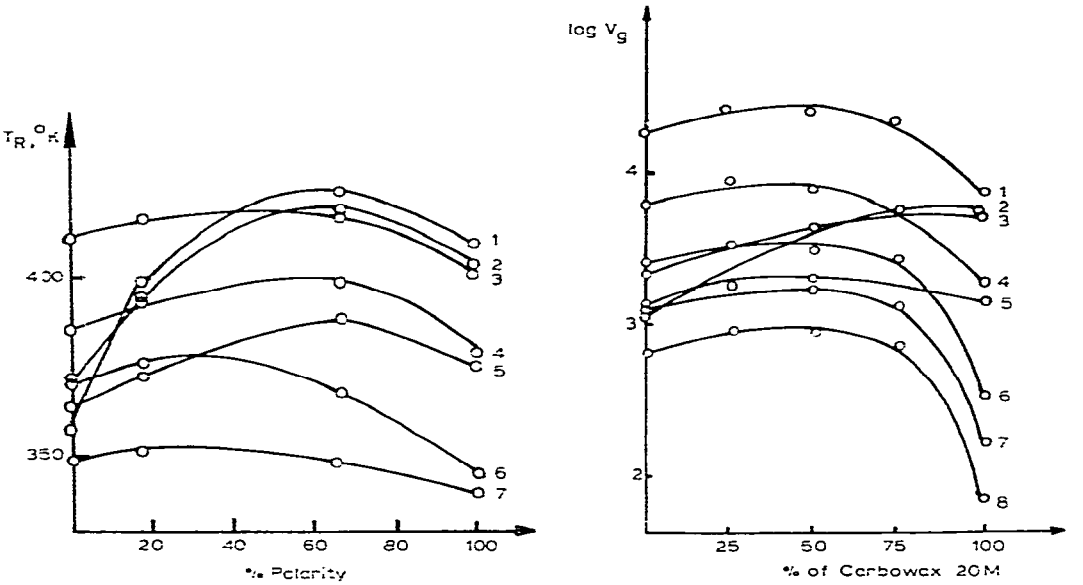

Fig. 4. Retention temperatures of various solutes as a function of polarity of capillary columns. Columns and conditions as in Fig. 3. Solutes: 1 = 2,6-dimethylphenol; 2 = 2,6-dimethylaniline; 3 = methyl dodecanoate; 4 = methyl decanoate; 5 = 1-octanol; 6 = *n*-dodecane; 7 = *n*-decane.

Fig. 5. log V_g of various solutes *versus* stationary phase composition on packed columns with SE-52, Carbowax 20M and their mixtures. Solutes: 1 = methyl dodecanoate; 2 = 2,6-dimethylphenol; 3 = 2,6-dimethylaniline; 4 = methyl decanoate; 5 = 1-octanol; 6 = *n*-dodecane; 7 = *n*-undecane; 8 = *n*-decane.

The polarity of the column with the mixed stationary phase, relative to the column with pure components, was determined. The differences of retention indices of 1-octanol (calculated from the retention temperature[5]) (ΔI) were used as the basis of the determination.

The polarity of a given column was determined by relating the difference in the retention indices on this column and on the column with pure SE-52 to the difference of the indices on the columns containing Carbowax 20M and SE-52 (Table II).

The relative polarity of the columns is slightly smaller than one would predict from the composition of the coating solution. The retention indices obtained from capillaries are higher than the values measured in the packed columns, which is probably due to the influence of the glass surface on the retention data and also to higher adsorption occurring at the surface of the coating than in packed columns.

Fig. 4 shows the retention temperatures of compounds of different polarity as a function of the relative polarity of the stationary phase, for the column with d_f = 0.15 μm, and Fig. 5 shows log V_g as a function of the stationary phase composition for the same compounds chromatographed on the packed columns. Owing to the different form of the retention expression it is difficult to speak about a quantitative comparison between these relations. One can see, however, that for polar compounds, there is a greater deviation from linearity in the capillary columns than in the packed ones.

A mixture of polycyclic aromatic hydrocarbons was chromatographed in order

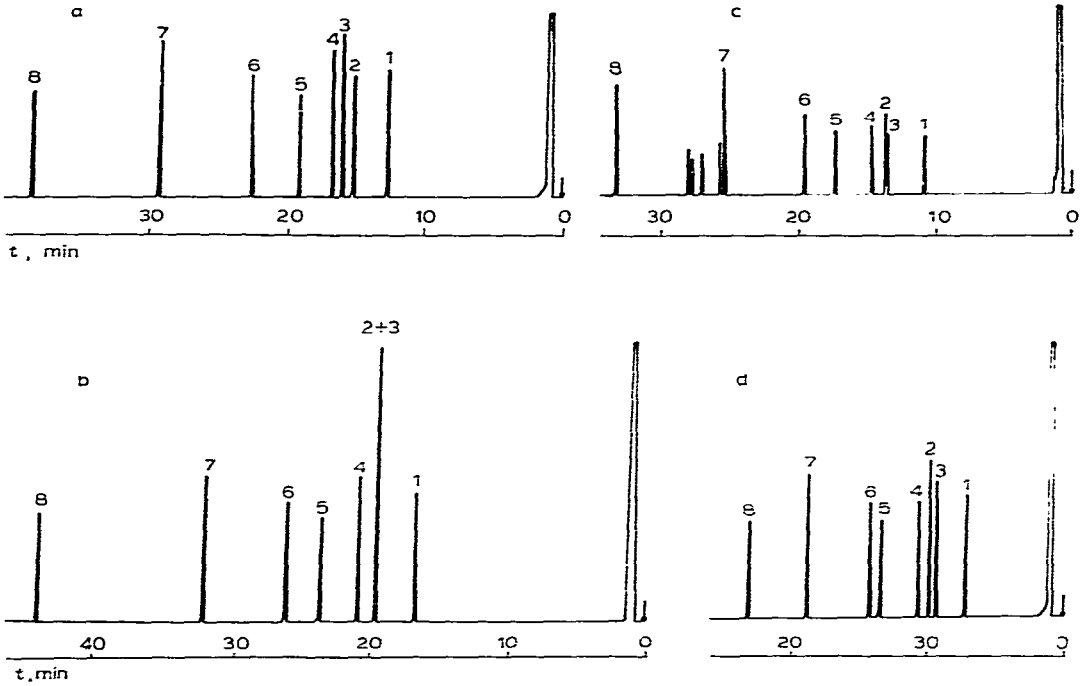

Fig. 6. Chromatograms of mixtures of polynuclear aromatic hydrocarbons on (a) column 13 (Carbowax 20M, d_f = 0.16 μm), (b) column 6 [SE-52 + Carbowax 20M (3:1), d_f = 0.14 μm], (c) column 5 [SE-52 + Carbowax 20M (3:1), d_f = 0.04 μm], (d) column 1 (SE-52, d_f = 0.14 μm). Initial temperature, 333°K; programming rate, 4°/min; carrier gas, H_2; sample, 1 μl. Peaks: 1 = 2-methylnaphthalene; 2 = 2,6-dimethylnaphthalene; 3 = biphenyl; 4 = 2,3-dimethylnaphthalene; 5 = 2,3,6-trimethylnaphthalene; 6 = fluorene; 7 = phenanthrene; 8 = pyrene.

to test the analytical abilities of columns with mixed stationary phases. Best results were obtained when the initial composition of the stationary phase was SE-52: Carbowax 20M in the ratio of 3:1, *i.e.* at 19% relative polarity.

Columns with thin films were very useful for the analysis of polycyclic aromatic hydrocarbons. Fig. 6c shows a chromatogram run on a column having the same composition of the stationary phase as in Fig. 6b, but with d_f = 0.04 μm. As can be seen, the resolution of the column does not decrease while, at the same time, considerable shortening of the analysis time is achieved.

CONCLUSION

The preparation of capillary columns with a mixed stationary phase composed of non-polar silicone oil and poly(ethylene glycol) (Carbowax 20M) allows one to omit the deactivation stage in the laborious and time-consuming preparation of columns.

Although the process of solvent evaporation in the static-coating procedure is accompanied by loss of a certain amount of the stationary phase, the polarity of these columns can be estimated using the retention indices, or even on the basis of the

position of the peaks of the polar components of the Grob test mixture on the chromatogram.

The columns obtained are characterized by good analytical properties, *viz.*, high resolution ability (to 40 units of EPN for 24 m of the column length).

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