

Note

Sorbents with cross-linked polysiloxane phases for gas-liquid chromatography with packed columns

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Immobilized or cross-linked stationary liquid phases (SLPs) are widely used in capillary chromatography and the chromatographic parameters of immobilized SLPs have been studied in detail¹⁻⁶. Capillary open-tubular columns with immobilized SLPs permit numerous important problems to be solved. These capillary columns are widely used in routine analysis, and their development and improvement are continuing⁷⁻¹⁰.

SLP immobilization improves the column operating conditions, increases the SLP film stability, enhances the thermal stability of the SLP used and produces SLP films that are non-extractable with organic solvents. The last condition allows the on-column injection of large liquid samples to be performed.

We considered it of interest to apply the SLP immobilization developed in capillary gas chromatography (GC) to GC with packed columns. The first attempt to produce packed columns with immobilized phases was made by Ghaoui *et al.*¹¹. They succeeded in cross-linking SE-54 on Chromosorb and the sorbent obtained showed higher thermal stability, lower bleeding and better base line stability.

Subsequently immobilization of SE-30 was described¹². Both peroxide and γ -radiation were used for phase immobilization. Ghysen *et al.*¹³ reported the immobilization of OV-101 and OV-3 on the macroporous silica Spherosil XOC 005. More recent work demonstrates the continuing interest in this problem. Sorbents with immobilized SLPs had been successfully used in high-performance gas chromatography with micropacked columns¹⁴. Immobilization by means of γ -radiation^{15,16} and ozonolysis^{17,18} has also been studied. Experimental comparison of both cross-linked and non-cross-linked phases has been carried out¹⁹, confirming the advantages of the former.

The purpose of this work was to study the influence of the cross-linking procedure used to immobilize an SLP coated on a diatomite support on the efficiency, polarity and thermal stability of the sorbent and to investigate the distribution of the SLP on the solid support, as diatomite supports are the most widely used in GC with packed columns.

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EXPERIMENTAL

The diatomite supports Inerton AW and Inerton AW-HMDS (Czechoslovakia) and Dinochrom N (U.S.S.R.) were used as solid supports. Siloxane gums, namely the non-polar polydimethylsiloxane SE-30 (Merck, F.R.G.) and the polar poly(dimethyl-fluoropropyl)siloxane SKTFT-50X (U.S.S.R.), were used as SLPs. The solid support was coated from the SLP solution as described elsewhere²⁰. Siloxane gums were immobilized by means of either benzoyl peroxide or γ -radiation (⁶⁰Co, 300 K). When the peroxide method was used the solid support was coated simultaneously with 3% of the cross-linking agent benzoyl peroxide (with respect to the SLP mass). After removal of the solvent, immobilization was carried out by slow heating to 200°C (2–4 h) in an inert gas flow, immobilization taking place in a chromatographic column.

To immobilize the sorbent by means of radiation, the sorbent was radiated with doses of 2–10 Mrad. After cross-linking, the residual non-immobilized phase was extracted directly in the column by passing an appropriate solvent (ethyl acetate, toluene or benzene) for 15–20 h.

An LKhM-8MD Model 5 gas chromatograph (U.S.S.R.) with a flame-ionization detector was used. The carrier gas was nitrogen or helium.

To evaluate the sorbent surface structure and distribution of SLP on the surface, scanning electron microscopy was used. A JSM-50A scanning electron microscope (Jeol, Japan) with an accelerating electron probe voltage of 25 kV under secondary electron emission was used. Sorbent surfaces were studied at magnifications of 1000 and 3000, corresponding to the surface areas of 10 000 and 300 μm^2 .

To estimate the immobilization yield, capacity factor (k') with respect to *n*-alkanes were determined before and after extraction. The thermal stability of the SLPs was characterized by the background value at 280°C. This value was determined as the baseline deviation with the carrier gas flow switched off.

Retention indices with respect to benzene, butanol, 2-pentanone, 1-nitropropane and pyridine were determined to evaluate the polarity of the SLPs.

The efficiency of analytical and micropacked columns was determined as the minimum height equivalent to a theoretical plate (H_{\min}). The H_{\min} value was determined experimentally from the Van Deemter equation (with respect to *n*-alkanes at several temperatures).

RESULTS AND DISCUSSION

The results of the comparative study of sorbents with cross-linked and non-cross-linked SLPs are given in Table I. The immobilization yield varied from 60 to 100% depending on the cross-linking conditions. The immobilization efficiency depends not only on the cross-linking conditions (temperature, amount of cross-linking agent), but also on the sorbent surface, in particular on the impurities present.

Cross-linking hardly influenced the sorbent efficiency, especially in the optimum range (Fig. 1). It can be noted that at carrier gas flow-rates higher than the optimum, sorbents cross-linked under radiation were less effective than those non-immobilized or cross-linked with peroxide (Table I). This phenomenon was probably due to the greater number of cross-linking sites between the SLP macromolecules. An increase in the radiation dose did not lead to a higher immobilization yield. The same effect has been noted with open-tubular columns²¹.

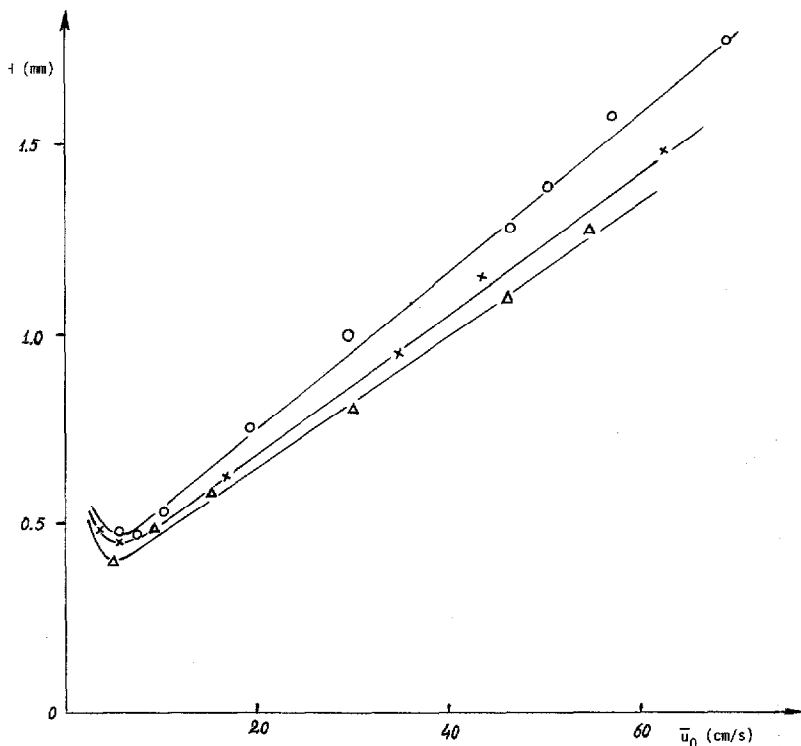


Fig. 1. Van Deemter dependences with respect to *n*-decane for the column packed with Inerton AW coated with immobilized and non-immobilized SE-30 at 80°C. \circ = Cross-linked with γ -radiation; Δ = cross-linked with benzoyl peroxide; \times = non-cross-linked. Fused-silica column, 57 cm \times 1 mm I.D. \bar{u}_0 is the carrier gas average linear rate corrected in accordance with the gas compressibility.

After immobilization the thermal stability of the sorbent was increased. Therefore, cross-linked phases can be used at high temperatures without any baseline deterioration. Polarity changes for both phases (SE-30 and SKTFT-50X) as a result of immobilization were also studied. Table II shows the retention indices for five compounds used to determine McReynolds constants. Immobilization caused virtually no change in the SLP polarity. An increase in the retention indices took place with SE-30 (irrespective of the cross-linking procedure). With SKTFT-50X γ -radiation caused a decrease in the retention indices and treatment with peroxide led to an increase.

The distribution of cross-linked SLPs over the surface after removal of non-immobilized residues was studied by scanning electron microscopy. Fig. 2 shows that immobilized SLPs provide a uniform cover on the sorbent surface. When γ -radiation was used (Fig. 2b) the SLP film was thinner than that obtained with peroxide (Fig. 2a). This is in agreement with chromatographic data on capacity factors. It should also be mentioned that there were no microcracks on the cross-linked SLP films, in contrast to non-immobilized SLPs²². The data obtained are in a good agreement with those for open-tubular capillary columns²¹.

We tried to wash off the cross-linked SLPs by repeated sample injection into the

TABLE I
 CHROMATOGRAPHIC PARAMETERS OF SORBENTS WITH POLYSILOXANE SLPs BOTH CROSS-LINKED AND NON-CROSS-LINKED ON THE SURFACES OF DIATOMITE SOLID SUPPORTS

Column dimensions (length \times I.D.) and material	SLP (%); solid support	Cross-linking method	Yield (%)	Column temperature ($^{\circ}$ C)	Capacity factor, k'	H_{\min} (mm)	Column background ^a at 280 $^{\circ}$ C	Mass-transfer coefficient, C (s)
69 cm \times 0.3 mm, fused silica	3% SE-30,	—	—	100	30.2, n -C ₁₂	0.29	—	$3.8 \cdot 10^{-4}$
	Dinobrom N,	Peroxide	79	100	23.7, n -C ₁₂	0.34	—	$4.6 \cdot 10^{-4}$
	0.06-0.08 mm	γ -Radiation	90	100	27.0, n -C ₁₂	0.40	—	$18.0 \cdot 10^{-4}$
57 cm \times 1 mm, stainless steel	5% SE-30,	—	—	80	24.8, n -C ₁₀	0.45	—	$19.0 \cdot 10^{-4}$
	Inerton AW	Peroxide	86	80	21.3, n -C ₁₀	0.39	—	$16.0 \cdot 10^{-4}$
	0.06-0.1 mm	γ -Radiation	86	80	21.4, n -C ₁₀	0.47	—	$23.0 \cdot 10^{-4}$
100 cm \times 3 mm, stainless steel	5% SKTFT-50X,	—	—	120	10.4, n -C ₁₂	0.99	—	$33.0 \cdot 10^{-4}$
	Dinobrom N,	Peroxide	79	120	8.4, n -C ₁₂	1.10	—	$7.2 \cdot 10^{-4}$
	0.1-0.2 mm	—	—	—	—	—	—	—
200 cm \times 3 mm, stainless steel	2.5% SE-30,	—	—	120	9.1, n -C ₁₂	0.87	$1.24 \cdot 10^{-10}$	—
	Inerton	Peroxide	82	120	7.5, n -C ₁₂	0.86	$0.70 \cdot 10^{-10}$	—
	AW HMDS, 0.2-0.25 mm	γ -Radiation	82	120	7.5, n -C ₁₂	1.08	$0.40 \cdot 10^{-10}$	—

^a Column background is a deviation of the recorder pen with the carrier gas switched off.

TABLE II

RETENTION INDICES OF POLAR COMPOUNDS FOR SORBENTS WITH SILICONE SLPs CROSS-LINKED AND NON-CROSS-LINKED ON THE SURFACE OF INERTON AW AT 120°C

<i>SLP type^a</i>	<i>Retention index</i>					
	<i>Benzene</i>	<i>1-Butanol</i>	<i>2-Pentanone</i>	<i>1-Nitropropane</i>	<i>Pyridine</i>	<i>Total</i>
SE-30, non-cross-linked	672	650	681	722	877	3602
SE-30, cross-linked with γ -radiation, washed	668	647	672	719	865	3571
SE-30, cross-linked with peroxide, washed	671	646	674	720	861	3572
SKTFT-50X, non-cross-linked	731	740	848	937	1026	4282
SKTFT-50X, cross-linked, with peroxide, washed	740	735	851	938	1049	4313
SKTFT-50X, cross-linked with γ -radiation, washed	727	729	841	938	1026	4261

^a When Inerton AW was used, 10% (mass) SLP was coated. With of SE-30 and SKTFT-50X the cross-linking yield with benzoyl peroxide was 98 and 90%, respectively, and with γ -radiation 84 and 79%, respectively.

column. Samples of 100–1000 μ l were injected into the column (2 m \times 3 mm I.D.) at temperatures near the solvent boiling point. There was no phase removal, the capacity factors and column efficiency remaining unchanged. When five samples (200 μ l each) were injected into a column packed with non-immobilized SLP, the column parameters deteriorated irreversibly. It seems expedient to use cross-linked SLPs for preparative chromatography because it is well known that the SLP is often washed off the initial part of a preparative column.

Hence, sorbents with cross-linked phases can be used for trace analysis by injecting large samples, microimpurities being concentrated directly in the column. This is the most promising application of the sorbents discussed.

CONCLUSION

Sorbents based on SLPs cross-linked by means of peroxide or γ -radiation on a diatomite support and non-cross-linked SLPs are characterized by similar efficiency, polarity and distribution over the solid support, possessing all the advantages of cross-linked phases.

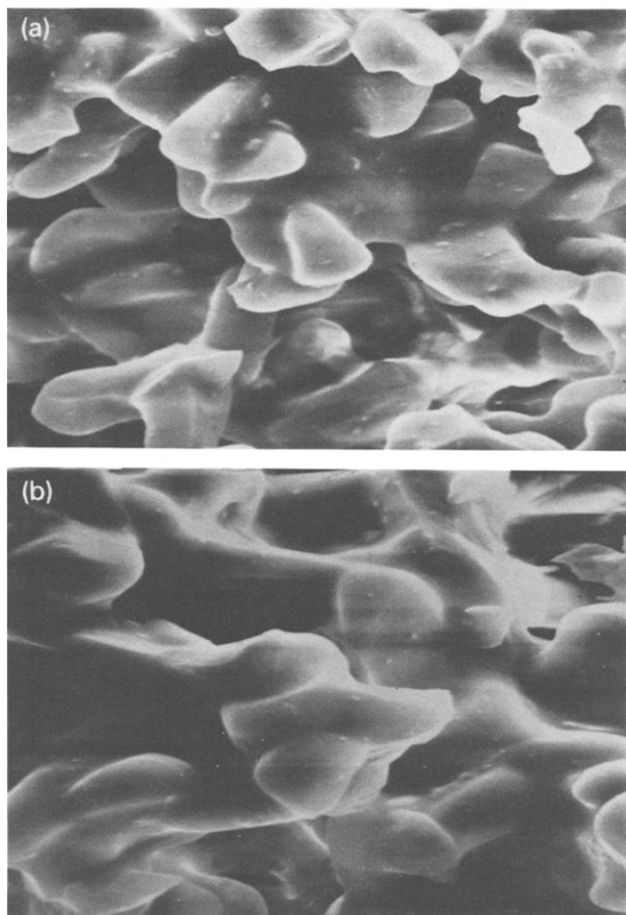


Fig. 2. Microsection of Interton AW surface coated with dimethylsilicone gum SE-30 cross-linked with (a) γ -radiation and (b) benzoyl peroxide. Magnification $\times 1000$.

REFERENCES

- 1 K. Grob and G. Grob, *J. Chromatogr.*, 213 (1981) 211.
- 2 B. W. Wright, P. A. Peaden, M. L. Lee and T. J. Stark, *J. Chromatogr.*, 248 (1982) 17.
- 3 G. Schomburg, H. Husmann, S. Ruthe and M. Herraiz, *Chromatographia*, 15 (1982) 599.
- 4 J. K. Haken, *J. Chromatogr.*, 300 (1984) p. 38.
- 5 L. G. Blomberg and K. E. Markides, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 8 (1985) 632.
- 6 V. Borek, J. Hůbaček and V. Rehakova, *Chem. Listy*, 79 (1985) 364.
- 7 C.-Y. Wu, Z.-R. Zeng and W.-L. Zhao, *Sepu*, 6 (1988) 340.
- 8 Z.-R. Zeng, C.-Y. Wu and X. M. Zhou, *Sepu*, 6 (1988) 200.
- 9 R. F. Arandal and R. M. Martin, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 11 (1988) 157.
- 10 F. David, P. Sandra and G. Dricks, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 11 (1988) 256.
- 11 L. Ghaoui, H. Shanfield and A. Zlatkis, *Chromatographia*, 18 (1984) 11.
- 12 K. N. Shukurova, V. R. Alishoev and V. G. Berezkin, *Tezisy Dokladov Vsesoyuznogo Soveschaniya po Sorbentam dlya Khromatografii*, Scientific Council for Chromatography of the Academy of Sciences of the U.S.S.R., Moscow, 1986, p. 71.

- 13 R. T. Ghijsen, F. Nooitgedacht and H. Poppe, *Chromatographia*, 26 (1988) 201.
- 14 F. Ve, V.-B. Guo, B.-C. Lin and P.-C. Lu, *Sepu*, 6 (1988) 136.
- 15 M. A. Basso, M. J. T. F. Dos Santos, K. E. Collis and C. H. Collins, *J. High Resolut. Chromatogr.*, 12 (1989) 500.
- 16 C. H. Chuang, *Dissertation*, University of Houston, Houston, TX, 1987; *C.A.*, 108 (1988) 31016n.
- 17 E. A. Lyons, *Dissertation*, University of Lowell, Lowell, MA, 1987; *C.A.*, 108 (1988) 160642n.
- 18 C. H. Chuang, H. Shanfield and A. Zlatkis, *Chromatographia*, 23 (1987) 169.
- 19 V. G. Berezkin, K. N. Shukurova and V. R. Alishoev, *Zavod. Lab.*, 55, No. 8 (1988) 22.
- 20 W. Supina, *Packed Columns in Gas Chromatography*, Supelco, Bellefonte, PA, 1974.
- 21 J. A. Hubball, P. Di Mauro, E. E. Barry and G. Chabot, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 6 (1983) 241.
- 22 V. G. Berezkin, E. Yu. Sorokina, G. F. Shaligin, I. A. Litvinov and M. N. Budantseva, *J. Chromatogr.*, 193 (1980) 132.