Journal of Chromatography, 328 (1985) 337–341
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

CHROM. 17 652

Note

Immobilization of polysiloxane films in capillary columns by radiation-induced cross-linking

V. TATAR* and M. POPL
Department of Analytical Chemistry, Prague Institute of Chemical Technology, Suchbátarova 5, CS-166 28 Prague 6 (Czechoslovakia)
and
M. MATUCHA and M. PEŠEK
Institute for Radioisotope Research, Production and Utilization, Radiová 1, CS-110 00 Prague 10 (Czechoslovakia)
(Received January 17th, 1985)

The present stage of evolution of capillary gas chromatography is associated with the development of capillary columns with immobilized stationary phases. Featuring not only high separation efficiency but also good thermal stability and resistance to organic solvents, these columns can be regenerated, which is convenient particularly in trace analysis using splitless and on-column techniques[1]. The columns are freed from impurities by flushing with suitable solvents.

The preparation of columns with immobilized stationary phases has been reported for polysiloxane phase types, which are cross-linked by an appropriate *in situ* reaction inside the column. Cross-linking of α,ω-hydroxypolymethylsiloxane polymers by Si–O–Si bonds can be achieved by allowing tetrachlorosilane vapour to act at room temperature on the phase coated on the column wall[2–5]. Siloxane polymers can also be cross-linked by a radical reaction resulting in polymerization via Si–C–C–Si bonds. Organic peroxides such as dibenzoyl peroxide, dicumyl peroxide and *tert.*-butyl peroxide are most frequently used as initiators[6–9]. Other peroxides such as 2,4-dichlorobenzoyl peroxide or di-*tert.*-butyl peroxide and some azo compounds such as azocumene, azo-*tert.*-butane, azo-*tert.*-octane, azocyclohexane, azo-*tert.*-dodecane or 1,1-diphenylazoethane have also been tried[10,11]. The use of azoisobutyronitrile[12] and ozone[13] has been reported.

The radical polymerization of polysiloxane stationary phases can also be initiated by gamma radiation[14–18]. Columns impregnated with the stationary phase are exposed for 2–3 h to gamma radiation to receive a dose of 2–5 Mrad. In comparison with the initiation by peroxides, this approach is advantageous in that the stationary phase does not become contaminated by polar groups formed on decomposition of the peroxides, and better symmetry of the peaks of polar substances results[15]. The cross-linking of polysiloxane phases is promoted by higher dose rates[17]. The effect of radiation on the mechanical properties of fused-silica capillaries has also been investigated and a slight decrease in the elasticity of this material has been observed[16].

The aim of this work was to examine the efficiency of immobilization of SE-54 and SE-30 stationary phases by means of gamma irradiation from a ^{60}Co source.

0021-9673/85/$03.30

TABLE I

RESULTS OF TESTING OF CAPILLARY COLUMNS

Column	*Parameter*	*After impregnation**			*After irradiation*								
		n-C_{15}	*n*-C_{16}	*n*-C_{17}	*First flushing***			*Second flushing****			*Third flushing*§		
					n-C_{15}	*n*-C_{16}	*n*-C_{17}	*n*-C_{15}	*n*-C_{16}	*n*-C_{17}	*n*-C_{15}	*n*-C_{16}	*n*-C_{17}
(A) Fused-silica (10 m × 0.2 mm I.D.), washed with HCl; SE-54	*k*	0.85	1.3	2.0	0.74	1.1	1.7	0.75	1.1	1.7	0.74	1.1	1.7
	plates/m	2270	2100	1860	2380	2200	2040	2360	2250	2080	2360	2220	2060
(B) Unihost (20 m × 0.25 mm I.D.), etched with fluoroether, washed with HCl, PSD; SE-54	*k*	0.64	1.0	1.5	0.55	0.87	1.3	0.54	0.85	1.3	0.55	0.86	1.3
	Plates/m	2920	2850	2540	3020	2890	2790	3100	3010	2800	3070	3000	2790
(C) Unihost (20 m × 0.25 mm I.D.), etched with fluoroether, silanized; SE-54	*k*	0.87	1.3	2.0	0.74	1.1	1.7	0.72	1.1	1.7	0.72	1.1	1.7
	Plates/m	2520	2460	2180	2840	2710	2540	2890	2720	2580	2890	2730	2600
(D) Unihost (26 m × 0.25 mm I.D.), etched with fluoroether, silanized; SE-30	*k*	0.72	1.0	1.5	0.62	0.88	1.3	0.61	0.87	1.3	0.61	0.88	1.3
	Plates/m	2560	2420	2300	2860	2710	2590	2860	2700	2600	2880	2710	2610

* The results are identical before and after irradiation.

** Pentane–methylene chloride (1:1), about two column volumes.

*** Pentane–methylene chloride (1:1), about ten column volumes.

§ Column A, 2 ml of toluene; B, 2 ml of acetone; C, 5 ml of toluene; D, 5 ml of chloroform.

EXPERIMENTAL

Apparatus

Soft glass (Unihost) capillary columns (20–26 m × 0.25 mm I.D.) and a fused-silica capillary column (10 m × 0.2 mm I.D.) were impregnated with SE-54 and SE-30 polysiloxane stationary phases (Becker, Delft, The Netherlands) after surface treatment as described later.

The column performances were tested on a mixture of C_8, C_{10} and C_{15}–C_{17} *n*-alkanes. The efficiency of immobilization was examined by flushing the columns with pentane–methylene chloride (1:1), chloroform, toluene and acetone.

The source of gamma radiation was a Gammacell 220 (AECL, Canada) emitting at a dose rate of 2.48 kGy/h (19.1 mA/kg).

The fused-silica column was tested on a Packard Model 428 gas chromatograph and the glass columns on a Chrom 5 instrument (Laboratorní přístroje, Prague, Czechoslovakia). The inlet splitter technique and flame-ionization detection were used.

Procedure

Treatment of the internal surface of the capillary column. The fused-silica column (A) was washed with dilute (1:1) hydrochloric acid according to Blomberg *et al.*[9]. The glass columns (B, C and D) were etched with hydrogen fluoride gas obtained by *in situ* thermal decomposition of 2-chloro-1,1,2-trifluoroethyl methyl ether, making use of the experience gained by Tesařík *et al.*[19] with etching of Unihost glass capillaries. Similarly to column A, column B was then washed with dilute hydrochloric acid and its surface was silanized by polysiloxane degradation (PSD) according to Schomburg *et al.*[20], whereas the etched columns C and D were subjected to silanization for 2 h with trimethylchlorosilane vapour in the sealed columns at 150°C.

Column impregnation and testing. Columns A, B and C were impregnated by the dynamic procedure by means of a mercury plug[21]. A 7% solution of SE-54 in toluene was used for these columns, whereas a 5% solution of SE-30 in toluene was used for column D. The columns were then conditioned using a stream of nitrogen at a flow-rate of approximately 0.2 ml/min; the temperature programme was 50°C for 2 min at 2°C/min to 180°C, held for 30 min, increased at 1°C/min to 280°C, held for 120 min.

The columns were tested on an *n*-alkane mixture and the capacity factors and the numbers of theoretical plates were determined for the C_{15}–C_{17} *n*-alkanes.

Column irradiation. After testing, the columns were exposed to gamma radiation at a dose rate of 2.48 kGy/h for 20 h; the total dose was about 5 Mrad.

Column flushing and testing. After the irradiation, the column were flushed with two column volumes of pentane–methylene chloride (1:1) and nitrogen purged, and the test described under *Column impregnation and testing* was repeated. Then the columns were flushed with ten column volumes of this mixed solvent and the test was repeated again. Finally, other solvents, *viz.*, toluene, chloroform, and acetone, were used and a subsequent test was carried out.

RESULTS AND DISCUSSION

The results of the tests are given in Table I. The capacity factors of the test substances, calculated in the various stages of the experiment, indicate that the immobilization was successful for all four columns. No changes in the properties, *i.e.*, in the capacity factors or the numbers of theoretical plates, occurred on irradiation. The non-cross-linked molecules of the stationary phase were removed during the first washing with two column volumes of pentane–methylene chloride (1:1) and the column capacity was decreased by 12–15%, as indicated by the decrease in the capacity factors of the test substances. Prolonged washing of the column with this mixed solvent did not lead to additional removal of the stationary phase, the capacity remaining unchanged. This was unaffected by the flushing rate; identical results were obtained on flushing the columns at rates of 5 cm/sec or less than 1 cm/sec or on allowing the filled columns to stand overnight. Additional flushing of the columns with the solvents employed for the preparation of the stationary phase solutions, *viz.*, toluene and chloroform, or with acetone also did not bring about any changes in the column capacity.

The 12–15% decrease in the capacity factors on the first column washing and all the above results agree well with the results obtained by Schomburg *et al.*[15].

The immobilization efficiency was unaffected by the different column surfaces and their previous treatment. This supports the concept of the formation of the unextractable stationary phase being caused primarily by its *in situ* cross-linking rather than its chemical bonding to the active centres in the capillary surface.

From the point of view of the separation efficiency, it is of importance that the column flushing resulted in an increase in the number of theoretical plates, which is consistent with the associated decrease in the column capacity.

The immobilization of SE-30, which differs from SE-54 by the absence of vinyl groups, was equally successful as that of SE-54, which indicates that the presence of vinyl groups is not a prerequisite for the immobilization of polysiloxane stationary phases.

CONCLUSION

It was the aim of these experiments to examine the possibility of immobilization of SE-54 and SE-30 polysiloxane stationary phases by the use of gamma radiation from a Gammacell 220 source at a dose rate that was about ten times lower than that used previously. The results indicated that this immobilization procedure is practicable, and the results obtained were identical with those found in the literature.

The problem of the immobilization was the sole objective of this treatment, and no other factors determining the quality of capillary columns were considered.

REFERENCES

1 K. Grob, Jr. and M. Bossard, *J. Chromatogr.*, 294 (1984) 65.
2 L. Blomberg, J. Buijten, K. Markides and T. Wännman, *J. Chromatogr.*, 208 (1981) 231.
3 L. Blomberg, J. Buijten, J. Gawdzik and T. Wännman, *Chromatographia*, 11 (1978) 521.
4 L. Blomberg and T. Wännman, *J. Chromatogr.*, 168 (1979) 81 and 186 (1979) 159.

5 L. Blomberg, K. Markides and T. Wännman, *J. Chromatogr.*, 203 (1981) 207.
6 K. Grob, G. Grob and K. Grob, Jr., *J. Chromatogr.*, 211 (1981) 243.
7 P. Sandra, G. Redant, E. Schlucht and M. Verzele, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 4 (1981) 411.
8 L. Blomberg, J. Buijten, K. Markides and T. Wännman, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 4 (1981) 578.
9 L. Blomberg, J. Buijten, K. Markides and T. Wännman, *J. Chromatogr.*, 239 (1982) 51.
10 B. W. Wright, P. A. Peaden, M. L. Lee and T. J. Stark, *J. Chromatogr.*, 248 (1982) 17.
11 B. E. Richter, J. C. Kuel, H. J. Park, S. J. Crowley, J. S. Brandshow and M. L. Lee, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 6 (1983) 371.
12 S. R. Springston, K. Melda and M. V. Novotný, *J. Chromatogr.*, 267 (1983) 395.
13 J. Buijten, L. Blomberg, K. Markides and T. Wännman, *J. Chromatogr.*, 283 (1984) 341.
14 W. Bertsch, V. Pretorius, M. Pearce, J. C. Thomson and N. G. Schnautz, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 5 (1982) 432.
15 G. Schomburg, H. Husman, S. Ruthe and M. Herraiz, *Chromatographia*, 15 (1982) 599.
16 E. F. Barry, G. E. Chabot and P. Ferioli, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 6 (1983) 300.
17 J. A. Hubball, P. R. Di Mauro, E. F. Barry, E. A. Lyons and W. A. George, *J. Chromatogr. Sci.*, 22 (1984) 185.
18 J. A. Hubball, P. R. Di Mauro, E. F. Barry and G. E. Chabot, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 6 (1983) 241.
19 K. Tesařík, K. Komárek, H. Hlavičková and J. Churáček, *Chem. Listy*, 75 (1981) 1091.
20 G. Schomburg, H. Husmann and H. Borowitzky, *Chromatographia*, 12 (1982) 651.
21 G. Schomburg and H. Husmann, *Chromatographia*, 8 (1975) 517.