Journal of Chromatography, 148 (1978) 37–41

CHROM. 10,466

GAS–LIQUID CHROMATOGRAPHY ON MICRO-PACKED COLUMNS WITH CHEMICALLY BONDED STATIONARY PHASES

J. GAWDZIK, Z. SUPRYNOWICZ and J. WÓJCIK

Department of Physical Chemistry, Institute of Chemistry, M. Curie-Skłodowska University, Nowotki 12, 20031 Lublin (Poland)

SUMMARY

Column packings with chemically bonded stationary phases of the "brush" type on controlled-porosity glass beads were prepared. The following organosilicon monomers with different functional groups were used: octadecyltrichlorosilane, phenyltrichlorosilane, 2-cyanoethylmethyldichlorosilane and 3-aminopropyltriethoxysilane. Micro-packed columns of length 5 m and I.D. 0.8 mm were prepared.

The efficiency and selectivity of micro-packed and packed columns of I.D. 4 mm were compared. The mean efficiency of micro-packed columns was 2500 theoretical plates per metre for a partition ratio $k' \geqslant 3$.

INTRODUCTION

The development of the synthesis of chemically bonded stationary phases enabled modern column packings to be obtained, which are employed mainly in liquid chromatography in view of their solvolytic stability. These sorbents have been increasing in importance, especially in reversed-phase chromatography. The high thermal stability of brush-type packings and their specific retention mechanism, with modified adsorption prevailing[1–4], indicate that they can also be applied successfully in gas chromatography. However, it is still difficult to predict the properties of a given liquid phase bonded to a given solid support, and it is necessary to investigate these problems more closely and to synthesize a larger number of packings with various properties. Selective adsorption, modified by the chemical bonding of various functional groups and organic radicals, has a stronger effect and is more widely applied in gas than in liquid chromatography. Further, if difficult separations must be performed in a short time, high efficiencies and selectivities of the columns are required.

These advantages are offered by capillary columns, but their capacities (sample sizes) are very low and often insufficient, and their lifetimes and thermal stability are generally poor. In trace analysis in particular it is difficult to maintain the necessary sensitivity of the detector (limit of detection) and the poor reproducibility of the separation results necessitates the frequent use of standard mixtures, which are often composed of extremely rare compounds. Some of these disadvantages can be partially eliminated by the use of PLOT (SCOT) columns, which have higher capacities and

are more stable; although they are difficult to prepare and have irreproducible properties, they may become a very good separation tool if the technical difficulties can be solved.

The reproducibility of the results (retention data) on micro-packed columns is satisfactory and much larger sample sizes do not lead to detection problems, while the separation efficiencies are relatively high[5,6]. The application of sorbents with chemically bonded stationary phases for the preparation of micro-packed columns may lead to new possibilities in selective and rapid separations, especially at elevated temperatures.

EXPERIMENTAL

Glass beads of controlled porosity prepared in this Laboratory[7–9] were used as the support for the chemical bonding of liquid phases. The surface of these beads is highly pure and the content of metal ions determined with an electron microprobe and by X-ray fluorescence spectrometry[10] was found to be very low. To remove excessive adsorption properties, due presumably to the presence of micro-pores, the porous beads were submitted to an additional thermal treatment[8,11]. Monomeric layers of the brush type (Si–O–Si) of various polarities were bound to the beads thus prepared[8,12,13]. Organosilicon monomers with various functional groups [octadecyltrichlorosilane (ODS), phenyltrichlorosilane (Ph), 2-cyanoethylmethyldichlorosilane (CN) and 3-aminopropyltriethoxysilane (NH_2)] were used in the synthesis. Part of the materials thus prepared was additionally silanized with a 5% solution of hexamethyldisilazane in toluene[13]. Derivatographic investigations[8] have shown a high thermal stability of the packings, even above 350°. Elemental analysis of the packings permitted the determination of the percentage of chemically bonded liquid phases before and after silanization, presented in Table I[6] as the percentage of carbon. The surface concentrations of radicals in the CN and NH_2 phases corresponded to the average values obtained for the packings investigated by Majors and Hopper[8,12]. Measurements of the energetic heterogeneity (distribution of adsorptive energy) indicated the predominance of the adsorption mechanism of retention on the packings with

TABLE I

RESULTS OF ELEMENTAL ANALYSIS

s = silanized, ns = not silanized.

Stationary phase	*Amount of carbon (%, w/w)*	*Surface concentration of radicals (radicals per 100 Å²)*	
		Main radical	*$-Si(CH_3)_3$*
ODS-ns	1.48	0.58	—
ODS-s	1.87	0.58	0.91
Ph-ns	1.81	2.11	—
Ph-s	1.95	2.11	0.32
CN-ns	1.51	2.65	—
CN-s	1.81	2.65	0.70
NH_2-ns	1.84	4.30	—
NH_2-s	1.96	4.30	0.28

chemically bonded liquid phases synthesized during the investigations[8,13]. The silanized and non-silanized sorbents were used to prepare chromatographic columns of both the classical and micro-packed type which were conditioned for 12 h at 200° before use in chromatographic experiments.

The packing of classical columns was assisted by electromechanical vibration with a simultaneous flow of nitrogen, using an apparatus for column packing constructed in this Laboratory[14]. The columns were 1 m long and 3 mm I.D. The experiments were carried out on a Model G.Ch.F.18.3.4. gas chromatograph manufactured by Giede (Berlin, G.D.R.), equipped with a thermal conductivity detector.

Micro-packed columns, (5 m × 0.8 mm I.D.) were made of glass (Sovirel, France) and filled by electromechanical vibration using an apparatus constructed in this Laboratory[15]. The experiments were carried out on a Polish Model 503 chromatograph equipped with a home-made splitter and a microcatharometer (3-μl cell volume).

RESULTS AND DISCUSSION

The average efficiency of a 5-m micro-packed column was 12,500 theoretical plates for solutes with $k' \geqslant 3$. In Fig. 1, HETP is plotted against flow-rate of the carrier gas for classical and micro-packed columns filled with chemically bonded liquid phases. For micro-packed columns the HETP values were less than half of those obtained for classical columns. Further, the range of average flow-rates of carrier gas corresponding to minor changes in HETP was much wider for the micro-

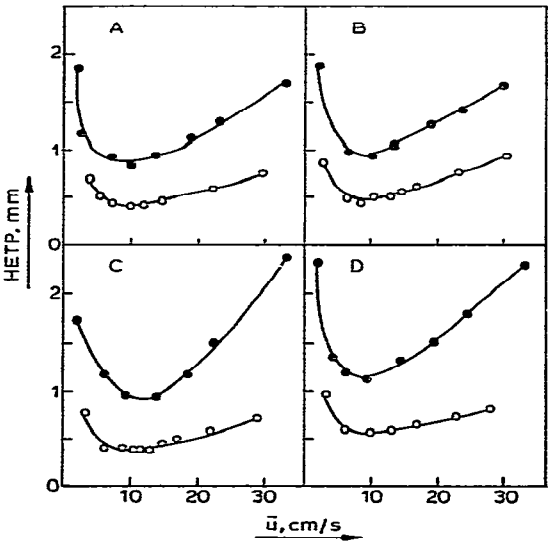

Fig. 1. Plot of HETP *versus* $\bar{u}$ for column packings with chemically bonded stationary phases: A, ODS-s (s = silanized) for *n*-heptane, $k_1' = 3.09$, $k_2' = 4.68$; B, Ph-s for *n*-nonane, $k_1' = 4.35$, $k_2' = 4.66$; C, CN-s for *n*-octane, $k_1' = 4.16$, $k_2' = 4.92$; D, NH_2-s for *n*-heptane, $k_1' = 5.49$, $k_2' = 5.62$. ●, k_1', classical packed column, 4 mm I.D.; ○, k_2', micro-packed column, 0.8 mm I.D. Column temperature, 100°; inlet temperature, 200°; carrier gas, hydrogen.

packed columns. All packings investigated had similar efficiencies, with the exception of the NH_2 type for which had poorer efficiences.

Owing to tailing of the peaks of the more polar substances in the McReynolds' mixture butanol–pyridine–2-methylpentanol, a simpler mixture was used to test the columns. The retention data are given in Table II. Comparison of the chromatograms showed that the ODS and CN packings have the best properties; the peak of nitropropane was asymmetrical for the Ph packing and on the NH_2 packing the solute was completely retained in the column.

TABLE II

PARTITION NUMBERS (k'), RELATIVE RETENTIONS ($r_{1,2}$) (RELATIVE TO *n*-HEPTANE) AND ELUTION OF SQUALANE ON MICRO-PACKED COLUMNS WITH CHEMICALLY BONDED STATIONARY PHASES

Solute	*ODS*			*Ph*			*CN*			*NH_2*		
	Peak No.	k'	$r_{1,2}$	*Peak No.*	k'	$r_{1,2}$	*Peak No.*	k'	$r_{1,2}$	*Peak No.*	k'	$r_{1,2}$
n-Pentane	1	0.82	0.30	1	0.41	0.38	1	0.58	0.34	1	1.15	0.29
n-Hexane	3	1.52	0.55	2	0.66	0.61	2	0.98	0.58	2	2.23	0.57
n-Heptane	5	2.74	1.00	4	1.08	1.00	4	1.69	1.00	4	3.92	1.00
n-Octane	8	4.92	1.80	7	1.74	1.61	5	2.88	1.70	5	8.00	2.04
n-Nonane	9	8.73	3.19	9	2.77	2.56	8	4.85	2.87	7	15.23	3.89
Nitropropane	4	1.92	0.70	8	1.88	1.74	9	7.71	4.56	—	—	—
Benzene	2	1.30	0.47	3	0.74	0.69	3	1.40	0.83	3	3.46	0.88
1-Iodobutane	6	3.64	1.33	5	1.53	1.42	7	3.65	2.16	8	17.77	4.53
1-Octene	7	4.43	1.62	6	1.70	1.57	6	2.96	1.75	6	8.46	2.16

The retentions (relative to *n*-heptane) of benzene, nitropropane and 1-iodobutane increased on the packings in the following order: ODS < Ph < CN < NH_2, whereas for 1-octene the sequence was Ph < ODS < CN < NH_2. In general, ODS is the less polar and NH_2 the most polar of the packings investigated. Benzene was

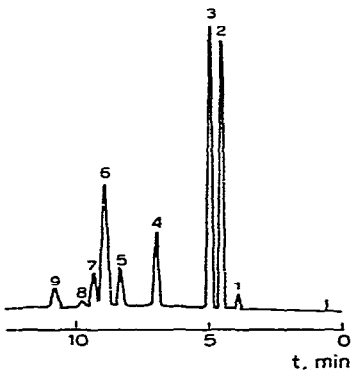

Fig. 2. Separation of light petroleum (b.p. 40–60°) on an ODS-s micro-packed column. Peaks: 1 = 2-methylbutane; 2 = *n*-pentane; 3 = cyclopentane; 4 = 2,2-dimethylbutane; 5 = 2,3-dimethylbutane; 6 = 2-methyl-pentane; 7 = 3-methylpentane; 8 = methylcyclopentane; 9 = *n*-hexane. Column temperature, 35°; inlet temperature, 200°; detector temperature, 100°; carrier gas (hydrogen) flow-rate, 4.6 ml/min; sample volume, 0.04 μl; splitting ratio, 1:5.

eluted ahead of *n*-hexane on the ODS packing after *n*-hexane and on the other packings. The CN packing is more selective towards more polar compounds, especially in the separation of esters. On the other hand, the ODS column is selective towards isomers of light hydrocarbons (Fig. 2), their elution being different from that obtained for a typical partition capillary column with an adhesionally held layer of a non-polar liquid phase (squalane).

The packings with chemically bonded phases gave also interesting results in classical columns; for instance, the CN packing is suitable for the rapid analysis of the less volatile aromatic hydrocarbons (separation of six hydrocarbons in 2 min, Fig. 3A) and the Ph packing for the separation at the relatively low temperature of 120° of a mixture of C_5–C_{16} *n*-alkanes within 6 min (without temperature programming, Fig. 3B).

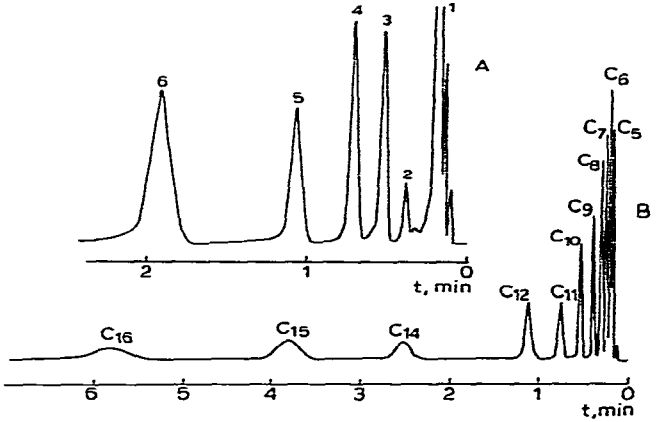

Fig. 3. Chromatograms of rapid separation on packings with chemically bonded stationary phases. A, aromatic hydrocarbons on CN-s: 1 = toluene; 2 = naphthalene; 3 = 2-methylnaphthalene; 4 = 1,3-dimethylnaphthalene; 5 = fluorene; 6 = phenanthrene. Column temperature, 185°; sample volume, 0.5 μl. B. C_5–C_{16} *n*-alkanes on Ph-s. Column temperature, 120°. Packed columns, 1 m × 3 mm I.D.; carrier gas (hydrogen) flow-rate, 50 ml/min; catharometer, 200 mA; sample volume, 0.5 μl.

REFERENCES

1 M. Uihlein and I. Halász, *J. Chromatogr.*, 80 (1973) 15.
2 E. Grushka and J. Kikta, *Anal. Chem.*, 46 (1974) 1370.
3 M. Uihlein and I. Halász, *J. Chromatogr.* 80 (1973) 1.
4 J. J. Pesek and J. E. Daniels, *J. Chromatogr. Sci.*, 14 (1976) 288.
5 C. A. Cramers, J. Rijks and P. Boček, *J. Chromatogr.*, 65 (1972) 29.
6 V. G. Berezkin, L. A. Shkolina and A. T. Svyatoshenko, *J. Chromatogr.*, 99 (1974) 111.
7 A. Waksmundzki, Z. Suprynowicz, J. Gawdzik and A. Dawidowicz, *Chem. Anal. (Warsaw)*, 19 (1974) 1033.
8 J. Gawdzik, *Ph.D. Thesis*, M. C. S. University, Lublin, Poland, 1976.
9 J. Gawdzik, Z. Suprynowicz and M. Jaroniec, *J. Chromatogr.*, 121 (1976) 185.
10 Z. Suprynowicz, E. Tracz and J. Gawdzik, to be published.
11 J. Gawdzik, Z. Suprynowicz and M. Jaroniec, *Chromatographia*, 10 (1977) 191.
12 R. E. Majors and M. J. Hopper, *J. Chromatogr. Sci.*, 12 (1974) 767.
13 J. Gawdzik, Z. Suprynowicz and M. Jaroniec, *J. Chromatogr.*, 131 (1977) 7.
14 Z. Suprynowicz, A. Waksmundzki, A. Gorgol and J. Wójcik, M.C.S. University, Lublin, Poland, unpublished results.
15 Z. Suprynowicz and J. Wójcik, unpublished results.