Journal of Chromatography, 319 (1985) 432–435
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

CHROM. 17,316

Note

Separation of polyaromatic hydrocarbons on caffeine-bonded silica gel

G. FELIX* and C. BERTRAND
Laboratoire de Chimie Organique du Silicium et de l'Etain (CNRS UA 35), Université de Bordeaux I, 351, Cours de la Libération, 33405 Talence Cédex (France)
(Received October 19th, 1984)

During the last 10 years, the use of charge-transfer interactions has continued to play an important role in high-performance liquid chromatographic (HPLC) separations[1,2]. Several publications have described the preparation and characterization of chemically bonded charge-transfer materials and their applicability as stationary phases.

The ability of caffeine to complex with a variety of polyaromatic hydrocarbons has been well demonstrated[3–6] but if impregnated layers with caffeine were used in thin-layer chromatography[4–6], none have chemically bonded caffeine on silica gel.

We report here the successful synthesis and use of a bonded caffeine stationary phase for donor–acceptor HPLC specifically designed to show high selectivity for polynuclear aromatic hydrocarbons.

EXPERIMENTAL

Apparatus

HPLC was performed with a Perkin-Elmer Series 4 liquid chromatograph equipped with a Perkin-Elmer LC 85 Autocontrol UV–visible detector and a Perkin-Elmer 3600 data station. Packing of the HPLC columns (250 × 4.6 mm I.D.) was achieved by the balanced-density slurry method[7].

Materials

Allyl bromide, dimethyl sulphoxide (DMSO) and benzyltriethylammonium chloride (TEBAC) were obtained from Aldrich and theobromine from Prolabo. The remaining chemicals and solvents were of analytical-reagent grade and were used as purchased.

The preparation of triethoxysilane from trichlorosilane (Rhône-Poulenc) has been described previously[8].

All of the bonded stationary phases were formed on a matrix of LiChrosorb Si 60 gel of 10 μm median particle size having a reported surface area of approximately 480 m^2/g (Merck-Clevenot). LiChrosorb-NH_2 (10 μm) (250 × 4.6 mm I.D.) and LiChrosorb Si 60 (10 μm) (250 × 4.6 mm I.D.) columns were obtained from Chrompack.

0021-9673/85/$03.30

Preparation of caffeine-bonded stationary phase

1-Allyltheobromine. Stirring a mixture of theobromine (20 g; 0.111 mole), allyl bromide (27 g; 0.220 mole), 50% aqueous sodium hydroxide (45 ml), DMSO (15 ml) and TEBAC (6 g) resulted in a moderate, exothermic reaction, which was carried out at 60°C for 1 h. The organic layer was extracted with methylene chloride, dried over anhydrous sodium sulphate and evaporated under reduced pressure, yielding 20 g of white powder (82%). The allyltheobromine was recrystallized from acetone; m.p. 146°C. NMR (C^2HCl_3): δ = 3.33 (3H, s), 3.78 (3H, s), 4.37 (2H, d, J = 5 Hz), 4.78–5.27 (2H, m), 5.38–6.09 (1H, m), 7.33 (1H, s).

1-(γ-Triethoxysilyl-n-propyl)theobromine. To 3.5 g (0.021 mole) of freshly distilled $HSi(OCH_2CH_3)_3$ was added a crystal of H_2PtCl_4 followed by adding dropwise a solution of allyltheobromine (4 g; 0.018 mole) in dry ethylene dichloride (50 ml). The mixture was stirred under reflux overnight and evaporated, yielding 6.9 g of a viscous brown product. NMR (C^2HCl_3): δ = 0.11–1.98 (13H, m) 0.96 (9H, t, J = 7 Hz), 3.23–4.04 (14H, m), 3.33 (3H, s), 3.79 (3H, s), 7.34 (1H, s).

Caffeine-bonded stationary phase. To LiChrosorb Si 60 (5 g) in dry ethylene dichloride (20 ml) a solution of 1-(γ-triethoxysilyl-*n*-propyl)theobromine (4 g) in dry ethylene dichloride (20 ml) was added and the mixture was stirred under reflux for 3 days. After filtration, the product was washed with methylene chloride (100 ml), methanol (100 ml), acetone (100 ml), methylene chloride (100 ml) and *n*-hexane (100 ml). The bonded silica was dried at 80°C for 12 h.

RESULTS AND DISCUSSION

The prepared packing material was sent for analysis to the Service d'Analyses du CNRS, Vernaison, France. Microanalysis showed a carbon content of 11.57%. The calculations of surface coverage were based on a unit $R\text{–}\overset{|}{\underset{|}{Si}}OCH_2CH_3$ and gave a surface concentration[9] of α_{exp} = 2.30 μmole/m².

With a flow-rate of 3 ml/min using *n*-hexane–methylene chloride (75:25) as the solvent system, the number of theoretical plates was 3840 (measured on acenaphthene, k': 0.35).

Table I shows the elution of a number of polynucleararomatic hydrocarbons (PAHs) on the caffeine-bonded column, on a commercial amino column and on a silica column. The mobile phase was *n*-hexane–methylene chloride (95:5) saturated with water at a flow-rate of 1.5 ml/min.

The retention times of the aromatic hydrocarbons were longer on the caffeine-bonded than on the other phases. The relative binding parameter, θ, defined by Karger *et al.*[10] and which reflects the increase in retention due to the presence of caffeine groups in the stationary phase, was calculated (Table I).

The values are in agreement with a charge-transfer retention mechanism and increase with increase in the number of aromatic rings.

Fig. 1 shows the separation of eleven PAHs. The separation is too long (45 min), so in donor–acceptor chromatography in general and with our caffeine-bonded phase, a gradient of solvents is recommended. Fig. 2 shows the reduction of the chromatogram at 20 min with no change in the resolution.

Some useful separations have been achieved using the caffeine-bonded column.

TABLE I

ELUTION OF AROMATIC HYDROCARBONS USING DIFFERENT COLUMNS

No.	*Hydrocarbon*	*Column*			$\Theta_1 = \frac{k' - k'_1}{k'_1}$	$\Theta_2 = \frac{k' - k'_2}{k'_2}$
		Silica (k'_1)	NH_2 (k'_2)	*Caffeine* (k')		
–	Benzene	0.00	0.00	0.00	–	–
1	Indan	0.00	0.00	0.00	–	–
2	Indene	0.11	0.09	0.24	1.18	1.67
3	Biphenyl	0.15	0.13	0.46	2.07	2.47
4	Naphthalene	0.11	0.13	0.61	4.55	3.69
5	Acenaphthene	0.11	0.12	0.76	5.91	5.33
6	Fluorene	0.19	0.19	1.42	6.47	6.47
7	Acenapththylene	0.19	0.20	1.50	6.84	6.50
8	Anthracene	0.25	0.28	3.02	11.08	9.78
9	Phenanthrene	0.25	0.26	3.24	11.96	11.46
10	Pyrene	0.33	0.44	7.02	20.27	14.95
11	Chrysene	0.49	0.65	12.00	23.49	17.46

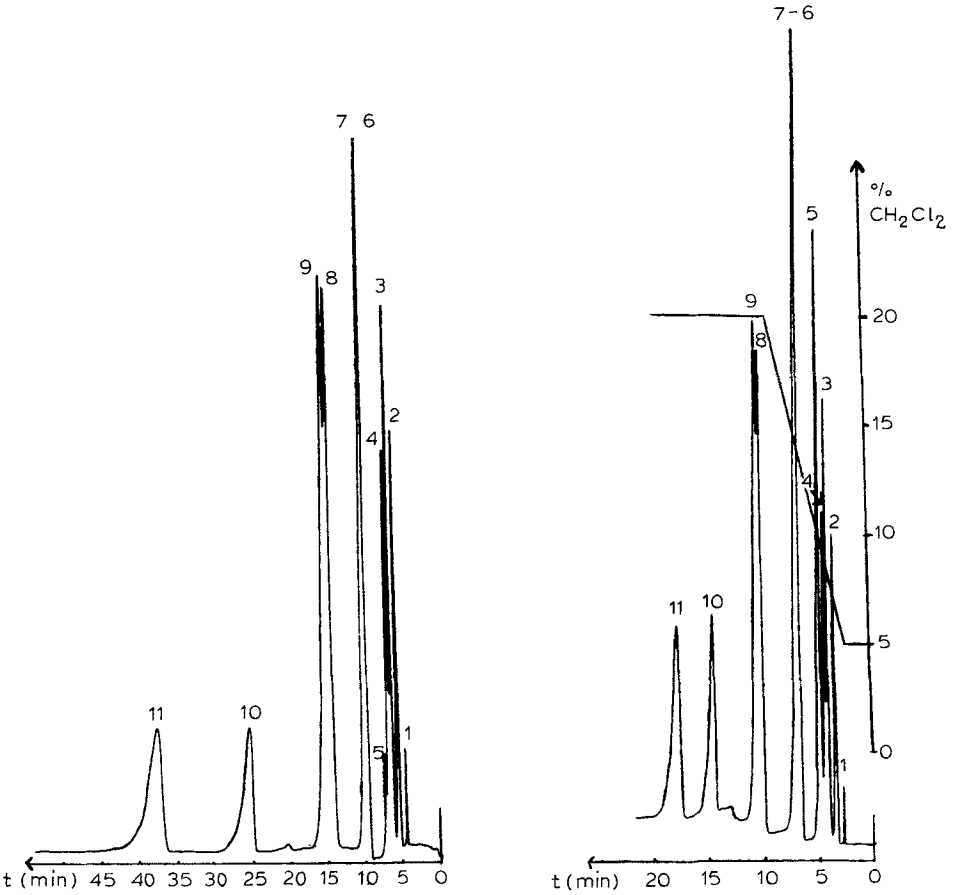

Fig. 1. Separation of PAH standards on the caffeine-bonded column. Conditions: mobile phase, *n*-hexane–methylene chloride (95:5) saturated with water at a flow-rate of 1.5 ml/min; detection, UV (253.7 mn). Compounds as in Table I.

Fig. 2. Separation of PAH standards on the caffeine-bonded column. Conditions: mobile phase, *n*-hexane–methylene chloride saturated with water at a flow-rate of 1.5 ml/min; detection, UV (253.7 nm). Compounds as in Table I.

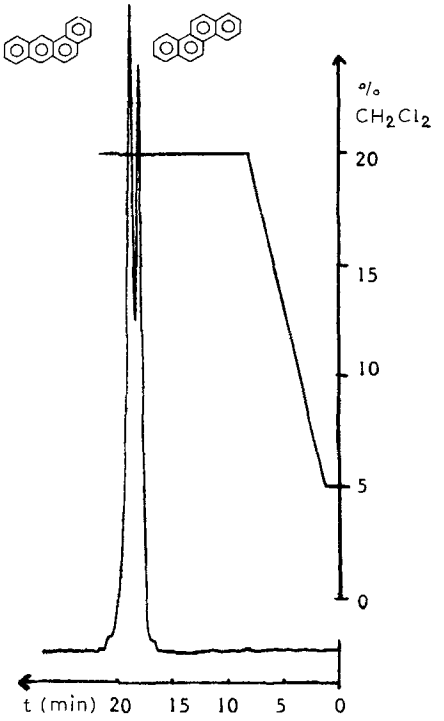

Fig. 3. Separation of chrysene and benzanthracene on the caffeine-bonded column. Conditions as in Fig. 2.

Of particular note are two PAHs chrysene and benzanthracene (Fig. 3). Although not separated by reversed-phase chromatography or by an amino column, they are readily separated by the caffeine-bonded column.

The stationary phase described appears to be very promising for applications in charge-transfer chromatography, especially in the petroleum industry, *e.g.*, for the separation of asphaltenes[11].

ACKNOWLEDGEMENT

We thank A. M. L. Chromato Company for financial support.

REFERENCES

1 W. Holstein and H. Hemetsberger, *Chromatographia*, 15 (1982) 186.
2 W. Holstein and H. Hemetsberger, *Chromatographia*, 15 (1982) 251.
3 E. Sondheimer and I. E. Pollak, *J. Chromatogr.*, 8 (1962) 413.
4 J. Lam and A. Berg, *J. Chromatogr.*, 20 (1965) 168.
5 V. Libíčková, M. Stuchlík and Ľ. Krasnec, *J. Chromatogr.*, 45 (1969) 278.
6 J. Lam, *Planta Med.*, 24 (1973) 107.
7 J. J. Kirkland, *J. Chromatogr. Sci.*, 9 (1971) 208.
8 L. M. Shorr, *J. Amer. Chem. Soc.*, 76 (1953) 1390.
9 K. K. Unger, N. Becker and P. Roumeliotis, *J. Chromatogr.*, 125 (1976) 115.
10 B. L. Karger, M. Martin, J. Loheac and G. Guiochon, *Anal. Chem.*, 45 (1973) 496.
11 G. Félix and C. Bertrand, *Characterization of Heavy Crude Oils and Petroleum Residues, International Symposium, Lyon, France, June 25–27, 1984*, Technip, Paris, 1984, p. 368.