Journal of Chromatography, 455 (1988) 323–326
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

CHROM. 20 872

Note

Isothiocyanate as a liquid crystalline stationary phase in capillary gas chromatography for the separation of polyaromatic hydrocarbons

J. MAZUR, Z. WITKIEWICZ* and R. DĄBROWSKI
Institute of Chemistry, Military Technical Academy, 01-489 Warsaw 49 (Poland)
(First received April 27th, 1988; revised manuscript received August 2nd, 1988)

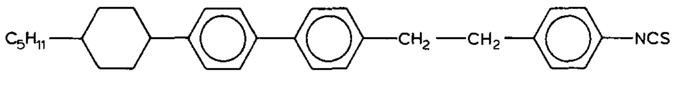
Polycyclic aromatic hydrocarbons (PAHs) occur in diverse materials such as atmospheric particulate matter, tobacco smoke, processed food, high-boiling petroleum distillates and other environmental situations. Some of the strongest carcinogens are members of, or directly derived products of, this class of compound. Methods for their separation and determination have been widely studied[1–5]. PAHs can be separated by various methods, *e.g.*, high-performance liquid chromatography, supercritical fluid chromatography and capillary gas chromatography (GC). GC has been used with a considerable number of stationary phases, such as organopolysiloxanes, liquid crystals and mixtures of both. Liquid crystalline stationary phases provide a unique selectivity for the separation of isomers whose molecules have different length-to-breadth ratios. The combination of the high selctivity of liquid crystals and the high efficiency of capillary columns seems to be one of the best methods for PAH separations. The use of polymeric mesomorphic stationary phases is the most efficient method[1,6–8], but low-molecular-weight liquid crystalline phases are still in the use because of the simplier method for the preparation of capillaries[2,3].

This paper deals with a new liquid crystalline stationary phase in GC capillary columns and the possibility of using it for PAH separations.

EXPERIMENTAL

Materials

A new group of rod-like liquid crystalline stationary phases were applied in glass capillary columns. The method for their synthesis and some of their chromatographic applications have been reported[9–11]. The formula of the liquid crystal is



1-[4′-(4-*trans*-Pentylcyclohexyl)biphenylyl]-2-(4-isothiocyanatophenyl)ethane

and the temperatures of the phase transitions are $K \overset{135°C}{\rightleftharpoons} S \overset{163°C}{\rightleftharpoons} N \overset{280°C}{\rightleftharpoons} I$, the phases being the solid crystal (K), smectic mesophase (S), nematic mesophase (N) and

0021-9673/88/$03.50 © 1988 Elsevier Science Publishers B.V.

isotropic liquid (I). The temperatures of phase transitions were measured using a polarizing microscope with a heated stage, type PHMK (Analytik, Dresden, G.D.R.).

The purity of the compound was checked by high-performance liquid and thin-layer chromatography.

Column preparation

The columns (12.5 m × 0.3 mm I.D.) were drawn from soft sodium glass (Glass Factory, Krosno, Poland), prepared according to the carbonate procedure of the Grobs[12,13] and deactivated with Carbowax 1000. The columns were coated with the stationary phase using the static procedure. The film thickness was 0.3 μm. Capillary columns were installed in the chromatograph oven and conditioned by heating from room temperature to the clearing temperature at 1°C/min and maintaining the maximal temperature for 4 h. A Pye Unicam GCV gas chromatograph equipped with a split-stream injector and a flame ionization detector was used. The carrier gas was helium and the make-up gas was nitrogen.

RESULTS AND DISCUSSION

The capillary columns attained about 700 m^{-1} real plates according to Kaiser[14]. The separation of a 3–5-ring PAH mixture was performed (Fig. 1). No special attempts

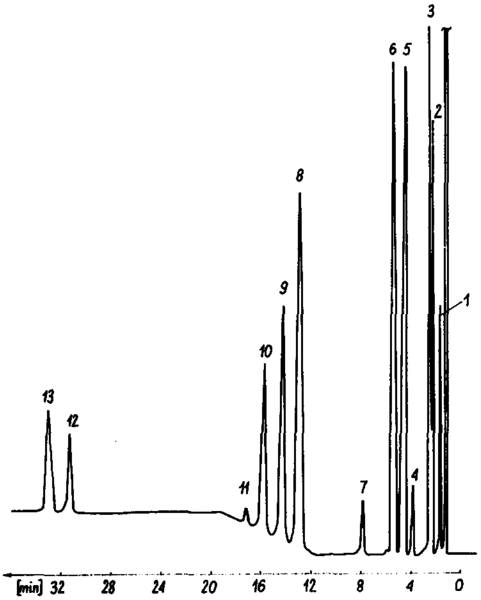


Fig. 1. Separation of selected 3–5-ring PAH isomers. Temperature programme: 9 min at 246°C, heated to 279°C at 3°/min. Injector and detector temperature, 360°C; carrier gas, helium with a linear velocity of 20 cm/s; splitting ratio, 1:100. Peaks: 1 = fluorene; 2 = phenanthrene; 3 = anthracene; 4 = unidentified impurity to fluoranthene; 5 = fluoranthene; 6 = pyrene; 7 = 2,3-benzofluorene; 8 = triphenylene; 9 = benz[*a*]anthracene; 10 = chrysene; 11 = naphthacene; 12 = perylene; 13 = benzo[*a*]pyrene.

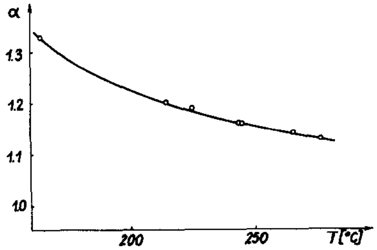


Fig. 2. Relationship between the separation factor (α) for anthracene–phenanthrene and column temperature.

were made to improve this separation. Noteworthy is the resolution of the 4-ring isomers triphenylene, benz[*a*]anthracene, chrysene and naphthacene. The separation factors measured isothermally at 276°C are as follows: benz[*a*]anthracene–triphenylene = 1.14, chrysene–benz[*a*]anthracene = 1.16 and naphthacene–chrysene = 1.34. Under the same conditions the separation factor of benzo[*a*]pyrene and perylene was 1.09.

Anthracene and phenanthrene were not separated to the baseline, but an excellent resolution was obtained by decreasing the column temperature to 200–210°C. Fig. 2 shows the relationship between the separation factor of anthracene–phenanthrene and column temperature.

Many PAHs were identified in the extract of carbon black from a gas stove. The chromatogram is shown in Fig. 3. The peaks were identified by comparison with the retention times of known standards.

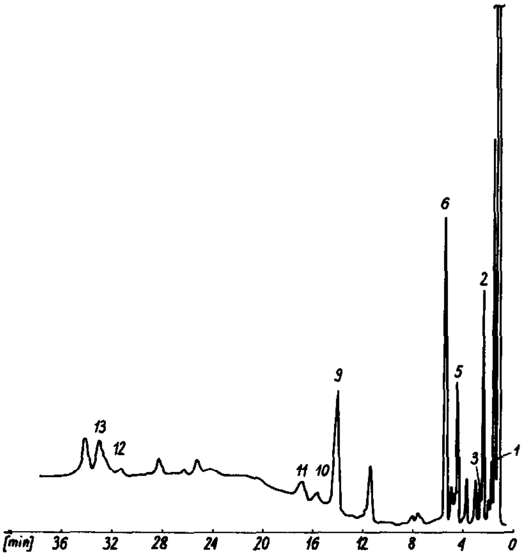


Fig. 3. Chromatogram of PAHs in an extract of carbon black. Conditions and peak identification as in Fig. 1.

Chromatographic separations might be possible only in the nematic region of the mesophase because of the very low column efficiency below the temperature of the smectic–nematic transition (in the smectic region). However, the nematic region from 163 to 280°C is fairly wide and sufficient for using temperature programming. The columns containing the liquid crystalline phase have useful lifetimes of the order of several months without any special operating care.

It has been shown that with short capillary columns coated with the new liquid crystalline stationary phase it is possible to separate mixtures of 3–5-ring PAHs including real samples in a short time.

ACKNOWLEDGEMENT

This work was carried out as a part of the research program RP 1.08.

REFERENCES

1 K. E. Markides, H.-C. Chang, C. N. Schregenberger, B. J. Tarbet, J. S. Bradshaw and M. L. Lee, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 8 (1985) 516

2 S. Rokushika, K. P. Naikwadi, A. L. Jadhav and H. Hatano, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 8 (1985) 480.

3 H. Moser and H. Arm, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 7 (1984) 637.

4 K. P. Naikwadi, A. M. McGovern and F. W. Karasek, *Can. J. Chem.*, 65 (1987) 970.

5 A. Ziółek, Z. Witkiewicz and R. Dąbrowski, *J. Chromatogr.*, 299 (1984) 159.

6 K. E. Markides, M. Nishioka, B. J. Tarbet, J. S. Bradshaw and M. L. Lee, *Anal. Chem.*, 57 (1985) 1296.

7 M. A. Apfel, H. Finkelmann, G. M. Janini, R. J. Laub, B.-H. Luhmann, A. Price, W. L. Roberts, T. J. Shaw and C. A. Smith, *Anal. Chem.*, 57 (1985) 651.

8 A. L. Jadhav, K. P. Naikwadi, S. Rokushika, H. Hatano and M. Ohshima, *J. High. Resolut. Chromatogr. Chromatogr. Commun.*, 10 (1987) 77.

9 R. Dąbrowski, J. Dziaduszek, T. Szczucinski, W. Drzewinski and E. Gołas, *Polish Patent Application*, (1986) P-260393.

10 J. Mazur, Z. Witkiewicz, R. Dąbrowski, *Polish Patent Application*, (1987) P-268841.

11 J. Mazur, Z. Witkiewicz and R. Dąbrowski, *Biul. Wojsk. Akad. Tech.*, 9 (1988) 33–47.

12 K. Grob and G. Grob, *J. Chromatogr.*, 125 (1976) 471.

13 K. Grob, Jr., G. Grob and K. Grob, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 1 (1978) 149.

14 R. E. Kaiser, *Chromatographia*, 10 (1977) 323.