

CHROM. 11,513

Note

Gas chromatographic separation of C_{10} – C_{12} naphthalene hydrocarbons and C_6 – C_8 monohydric phenols on cadmium chloride modified with Carbowax 20M

JOSEF FRYČKA

Research Institute for Coal Tar Chemistry, Úrxyovy závody n.p., 757 27 Valašské Meziříčí (Czechoslovakia)

(First received June 16th, 1978; revised manuscript received October 3rd, 1978)

The gas chromatographic separation of C_{10} – C_{12} naphthalene hydrocarbons has been discussed recently¹. The use of conventional liquid phases results in some difficulties in the separation (1- and 2-ethylnaphthalene, 2,6- and 2,7-, 1,3- and 1,6-, and 2,3-, 1,4- and 1,5-dimethylnaphthalene). It is possible to separate these critical pairs on special sorbents; liquid crystals and Bentone 34 proved to be suitable, but graphitized carbon black was only partly suitable.

The gas–liquid chromatography of C_6 – C_8 monohydric phenols, particularly the pairs 3- and 4-methylphenol, 3- and 4-ethylphenol, and 2,4- and 2,5-dimethylphenol, is critical^{2,3}. Only a few liquid phases, such as tri-2,4-xylenyl phosphate⁴, bis-3,3,5-trimethylcyclohexyl phthalate^{5,6} and dimethyl phthalate^{7,8}, particularly with capillary columns⁹, make the separation of these pairs possible. Liquid crystals proved to be unsuitable¹⁰. Unmodified adsorbents (gas–solid chromatography), such as Bentone 34¹¹, graphitized carbon black^{12,13} and rubidium benzenesulphonate¹⁴, show high selectivity but cause peak tailing. With a suitable liquid, modified Bentone 34^{15,16}, graphitized carbon black^{17,18} and rubidium benzenesulphonate¹⁹ (gas–liquid–solid chromatography) give selective separations with symmetrical peaks, but 2,4- and 2,5-dimethylphenol remain unresolved on the first two sorbents.

By modification of cadmium chloride with Carbowax 20M, a new stationary phase of exceptional selectivity for the separation of polyaromatics has been developed²⁰. The interesting order of elution obtained on this stationary phase could not be explained in terms of the usual concepts of retention. In a detailed study²¹, electron repulsion effects during penetration of sorbate molecules into the micropores of the sorbent were found to dominate in the separation mechanism. Sorbate molecules with lower repulsive forces penetrate deeper into the micropores of the sorbent, pass over a greater length of tortuous and constricted pathways, a greater effective surface area is available for them, and therefore they are more retarded. Of some naphthalene homologues studied, 1-methylnaphthalene and substituted 1-methylnaphthalenes were observed to be retarded more than the corresponding 2-substituted isomers.

It was of interest to us to complete the separation of naphthalene homologues and to examine the chromatographic behaviour of phenols, especially of the above-mentioned critical pairs, on this new stationary phase.

EXPERIMENTAL

A Fractovap GV instrument (Carlo Erba, Milan, Italy) with a flame-ionization detector was used.

A column packing consisting of cadmium chloride–Carbowax 20M–Chromosorb P AW (2:2:96) was prepared by dissolving appropriate amounts of cadmium chloride (analytical-reagent grade, Lachema, Brno, Czechoslovakia) and Carbowax 20M (Union Carbide, London, Great Britain) in aqueous methanol, adding Chromosorb P AW, 80–100 mesh, to the solution and evaporating the solvent. The glass column (2 m × 3.3 mm I.D.) was conditioned at 200° for 24 h.

The experimental conditions for gas chromatography are given in Table I.

TABLE I
EXPERIMENTAL CONDITIONS FOR GAS CHROMATOGRAPHY

<i>Condition</i>	<i>Naphthalenes</i>	<i>Phenols</i>
Column temperature (°C)	160	140
Injector temperature (°C)	230	250
Detector temperature (°C)	230	250
Carrier gas (argon) flow-rate (ml/min)	32	34
Carrier gas inlet pressure (kPa)	167	157
Sample solution	0.5% in cyclohexane	0.5% in acetone
Sample size (μl)	0.1–0.2	0.2

RESULTS AND DISCUSSION

Table II lists naphthalene and all methyl-, ethyl- and dimethylnaphthalenes in order of their boiling points, with their relative retention times (relative to naphthalene) measured on the column (a correction for the dead-time using the reten-

TABLE II
RELATIVE RETENTION TIMES OF C₁₀–C₁₂ NAPHTHALENE HYDROCARBONS ON CADMIUM CHLORIDE–CARBOWAX 20M–CHROMOSORB P AW (2:2:96) AT 160°

<i>Compound</i>	<i>Boiling point (°C)</i>	<i>Relative retention time</i>
Naphthalene	218	1.00
2-Methylnaphthalene	241	1.10
1-Methylnaphthalene	245	2.25
2-Ethylnaphthalene	258	1.43
1-Ethylnaphthalene	259	2.65
2,6-Dimethylnaphthalene	262	1.77
2,7-Dimethylnaphthalene	262	1.27
1,7-Dimethylnaphthalene	263	2.84
1,3-Dimethylnaphthalene	265	2.96
1,6-Dimethylnaphthalene	265	2.01
2,3-Dimethylnaphthalene	268	1.81
1,4-Dimethylnaphthalene	268	3.38
1,5-Dimethylnaphthalene	269	5.79
1,2-Dimethylnaphthalene	271	3.01
1,8-Dimethylnaphthalene	—	5.61

TABLE III

RELATIVE RETENTION TIMES OF C₆-C₈ MONOHYDRIC PHENOLS ON CADMIUM CHLORIDE-CARBOWAX 20M-CHROMOSORB P AW (2:2:96) AT 140°

Compound	Boiling point (°C)	Relative retention time
Phenol	182	1.00
2-Methylphenol	191	1.11
4-Methylphenol	202	1.50
3-Methylphenol	202	1.78
2,6-Dimethylphenol	206*	1.00
2-Ethylphenol	207	1.54
2,4-Dimethylphenol	211	1.84
2,5-Dimethylphenol	211	1.62
2,3-Dimethylphenol	218	2.54
3-Ethylphenol	218	2.66
4-Ethylphenol	218	2.36
3,5-Dimethylphenol	220	3.53
3,4-Dimethylphenol	226	3.51

* Average value of varying (from 200.6 to 212.0°) literature data.

tion time of methane was made). Table III gives similar results for phenols (relative to phenol).

From a comparison of these results with those obtained on the other sorbents, it is clear that different orders of elution have been achieved for both the naphthalenes and the phenols. All of the critical pairs that were more difficult to separate using conventional stationary phases are separated on the new stationary phase. Figs. 1 and 2 show examples of such separations. As can be seen in Fig. 2, phenols are eluted with symmetrical peaks.

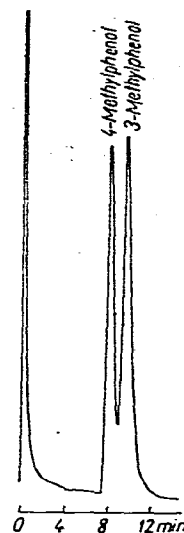
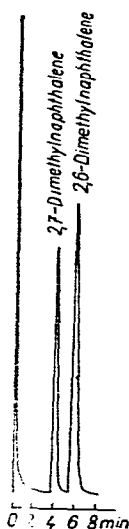


Fig. 1. Chromatogram of a mixture of 2,6- and 2,7-dimethylnaphthalene on a 2-m cadmium chloride-Carbowax 20M-Chromosorb P AW (2:2:96) column at 160°.

Fig. 2. Chromatogram of a mixture of 4- and 3-methylphenol on a 2-m cadmium chloride-Carbowax 20M-Chromosorb P AW (2:2:96) column at 140°.

The fact that the naphthalene homologues with occupied 1-positions are eluted after the isomers with occupied 2-positions (Table II) is the reverse of that observed on graphitized carbon black¹. The influence of the structure on the retention is so great that the order of elution methylnaphthalenes < ethylnaphthalenes < dimethylnaphthalenes, which is followed on all the other sorbents¹, is now altered (Table II): 1-methylnaphthalene is eluted after 2-ethylnaphthalene and after some dimethylnaphthalenes, 1-ethylnaphthalene is also eluted after some dimethylnaphthalenes, and 2-ethylnaphthalene after 2,7-dimethylnaphthalene.

ACKNOWLEDGEMENT

The author thanks Mrs. Eliška Zbránková for assistance with the experimental work.

REFERENCE

- 1 J. Fryčka, *Chromatographia*, 8 (1975) 413.
- 2 J. Janák, R. Komers and J. Šíma, *Collect. Czech. Chem. Commun.*, 24 (1959) 1492.
- 3 J. S. Fitzgerald, *Aust. J. Appl. Sci.*, 10 (1959) 306.
- 4 V. T. Brooks, *Chem. Ind. (London)*, 34 (1960) 1090.
- 5 W. Sassenberg and K. Wrabetz, *Z. Anal. Chem.*, 184 (1961) 423.
- 6 S. Husain, P. Kunzelmann and H. Schildknecht, *J. Chromatogr.*, 137 (1977) 53.
- 7 T. A. Rudolfi, R. I. Sharapova and V. I. Lushchik, *Zh. Anal. Khim.*, 19 (1964) 903.
- 8 N. A. Davtyan, in E. I. Kazakov (Editor) *Khimicheskaya Pererabotka Smol (Chemical Processing of Tars)*, Nauka, Moscow, 1965, p. 22.
- 9 J. Hrivňák and J. Macák, *Anal. Chem.*, 43 (1971) 1039.
- 10 L. E. Cook and R. C. Spangelo, *Anal. Chem.*, 46 (1974) 122.
- 11 M. A. Hughes, D. White and A. L. Roberts, *Nature (London)*, 184 (1959) 1796.
- 12 A. V. Kiselev and Ya. I. Yashin, *Zh. Fiz. Khim.*, 15 (1966) 603.
- 13 C. Vidal-Madjar, J. Ganansia and G. Guiochon, in R. Stock (Editor), *Gas Chromatography 1970*, Institute of Petroleum, London, 1971, p. 20.
- 14 A. Bhattacharjee and A. N. Basu, *J. Chromatogr.*, 71 (1972) 534.
- 15 J. Mortimer and P. Gent, *Anal. Chem.*, 36 (1964) 754.
- 16 D. W. Grant, R. B. Meiris and M. G. Hollis, *J. Chromatogr.*, 99 (1974) 721.
- 17 A. Di Corcia, *J. Chromatogr.*, 80 (1973) 69.
- 18 R. F. Brady, Jr., and B. C. Pettitt, *J. Chromatogr.*, 93 (1974) 375.
- 19 A. Bhattacharjee and A. Bhaumik, *J. Chromatogr.*, 115 (1975) 250.
- 20 O. K. Guha and A. Bhaumik, *J. Chromatogr.*, 119 (1976) 181.
- 21 O. K. Guha and T. K. Goswami, *J. Chromatogr.*, 135 (1977) 359.