

CHROM. 3748

Separation of some polynuclear aromatic hydrocarbons by gas-solid chromatography on graphitized carbon black

In recent years considerable attention has been given to the separation and identification of polynuclear aromatic hydrocarbons in such complex mixtures as coal-tar pitch¹, cigarette smoke², pyrolytic products³, and air-borne particulate matter⁴. The existing gas chromatographic methods for separating the polynuclear aromatic hydrocarbons are based on gas-liquid chromatography⁵⁻⁹, whereas gas-solid chromatography has seen limited application¹⁰⁻¹².

In the present paper we have studied the separations of 3- and 4-ring polynuclear aromatic hydrocarbons by gas-solid chromatography using graphitized carbon black. This adsorbent has been used recently in the separation of biphenyl and terphenyls¹³.

Experimental

A Varian Aerograph Model 1520-B gas chromatograph with an electron-capture detector (tritium foil) was used for studies ranging to 415°. For higher oven temperatures, a Barber-Colman Model Selectra-System 5000 was used with a flame ionization

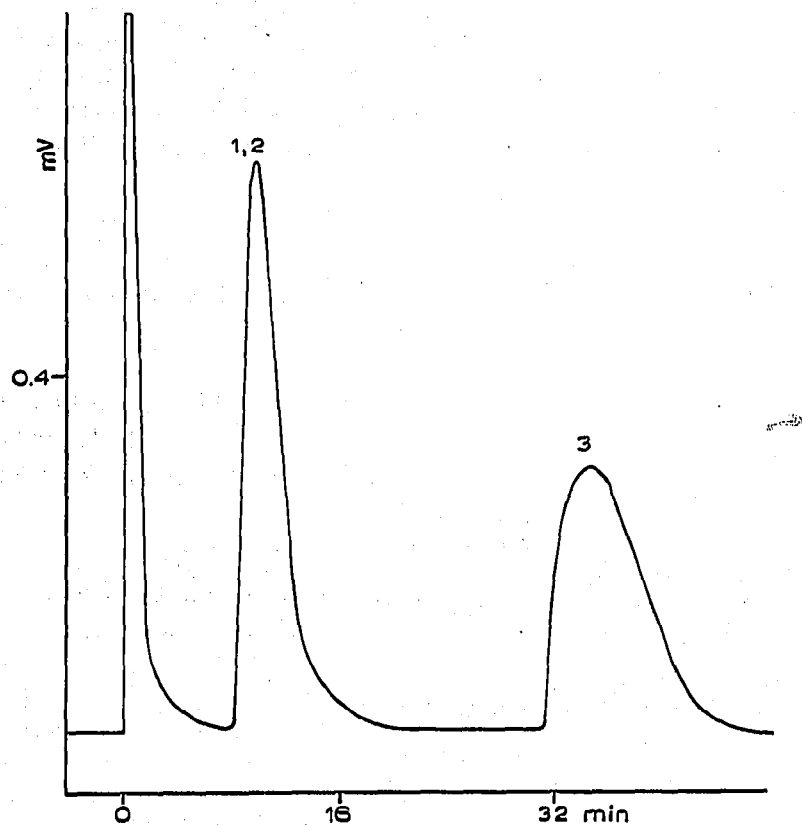


Fig. 1. Chromatogram of a mixture of anthracene (4.8 μg ; 1), phenanthrene (2.4 μg ; 2), and pyrene (10 μg ; 3) on graphitized carbon black at 470°. Attn. 5×10^{-11} . Flame ionization detector.

TABLE I

RETENTION TIMES AT 350° FOR POLYNUCLEAR AROMATIC HYDROCARBONS ON GRAPHITIZED CARBON BLACK

80/100 Mesh; carrier gas flow rate of 70 ml/min at 350°.

Hydrocarbon	Retention time (min)
Acenaphthene	1.8
Acenaphthylene	1.9
Fluorene	14.0
Phenanthrene	15.0
1-Methylphenanthrene	19.2
Anthracene	20.0
Pyrene	80.0
Fluoranthene	80.0

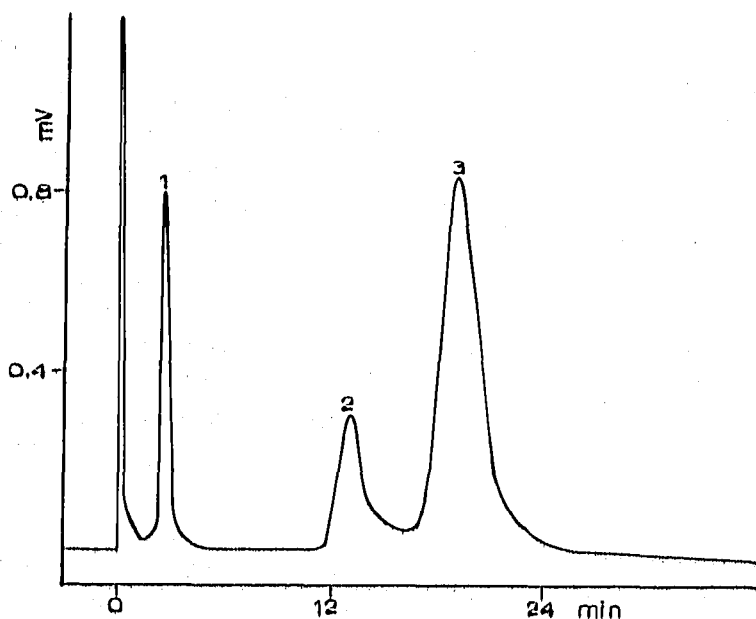


Fig. 2. Chromatogram of a mixture of acenaphthene (0.1 μ g; 1), phenanthrene (0.5 μ g; 2) and anthracene (0.1 μ g; 3) on graphitized carbon black at 415°. Attn. 8, Electron-capture detector.

detector. The chromatographic conditions were: Injector temperature, 320°; detector temperature, 210° (for electron capture) and 340° (for flame ionization); nitrogen carrier gas with an inlet pressure of 5.7 atmospheres; and carrier gas flow rate of 60 ml/min at 30°.

The graphitized carbon black used was a Sterling M.T. FF (D-6) 100g specimen (Cabot Corp., Boston, Mass., U.S.A.). A stainless-steel tubing (70 cm \times 2.3 mm ID) was packed with graphitized carbon black (100/120 mesh) by tapping the sides of the tubing. A second column was loosely packed with the same adsorbent (80/100 mesh). The columns were conditioned in the instrument for two hours at 415° before use.

The sample mixtures in benzene were injected with a Hamilton 10 μ l micro-syringe. The results of the separations are shown in Figs. 1 and 2 and in Table I.

Discussion

The chromatographic separations of some 3- and 4-ring polynuclear aromatic hydrocarbons on 100/120 mesh graphitized carbon black are shown in Figs. 1 and 2. The retention times obtained when the loosely packed 80/100 mesh material was used are shown in Table I. The larger mesh size permitted operation at oven temperature of 350° instead of 415°, without affecting the chromatographic separations.

Although anthracene and phenanthrene were found to have the same retention times at 470°, these hydrocarbons were separated well at 415° and 350° on 100/120 and 80/100 mesh columns respectively. The separation was superior to those previously reported on potassium antimonate and potassium carbonate-potassium hydroxide columns¹². Good resolution of anthracene and phenanthrene on gas-liquid packed columns has not been graphically demonstrated⁷⁻⁹.

In Fig. 2, the poorer electron absorptivity of phenanthrene as compared to that of anthracene accounts for the formation of a smaller peak for phenanthrene on the chromatogram. Electron-capture response *versus* sample size for anthracene and phenanthrene has been demonstrated in an earlier study¹⁴.

We were unable to separate fluoranthene from pyrene, nor acenaphthene from acenaphthylene on these short columns.

At column temperature of 470° injected samples of chrysene and benz(a)-anthracene produced no peaks on the chromatogram after two hours, even when sample sizes of 20 µg were used. It appears that these polynuclear aromatic hydrocarbons were irreversibly adsorbed on the graphitized carbon black.

Conclusions

Gas-solid chromatography using graphitized carbon black was tried on several 3- and 4-ring polynuclear aromatic hydrocarbons. This adsorbent was found to have a unique ability of being able to separate a mixture of anthracene and phenanthrene on a short column.

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Gaschromatographische Trennung aller neun struktur- und stereoisomeren Cyclohexantricarbonsäuren

Im Verlauf unserer Arbeiten über Cyclohexanpolycarbonsäuren* konnten wir die drei strukturisomeren Cyclohexantricarbonsäuren gaschromatographisch in die neun möglichen stereoisomeren Formen auftrennen und bestimmen.

In Fig. 1 sind die Strukturformeln aufgezeichnet. Man erkennt, dass es für die Cyclohexantricarbonsäure-1,3,5 zwei, für die Cyclohexantricarbonsäure-1,2,3 drei

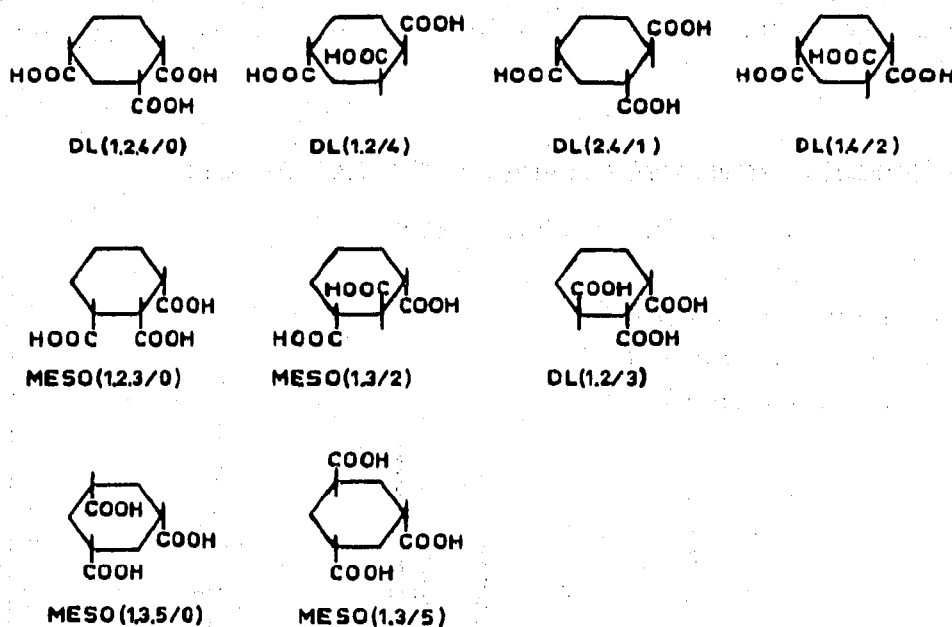


Fig. 1. Strukturformeln der neun isomeren Cyclohexantricarbonsäuren.

und für die Cyclohexantricarbonsäure-1,2,4 vier *cis-trans* isomere Formen gibt. Die Nomenklatur entspricht einem Vorschlag von McCASLAND¹, nach der die Substituenten in *cis*-Stellung vor und die Substituenten in *trans*-Stellung hinter dem Schrägstrich angegeben werden.

* Veröffentlichung in Vorbereitung.