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EVALUATION OF THE SEPARATION OF PHENANTHRENE, ANTHRACENE AND CARBAZOLE IN PURE TAR PRODUCTS BY GAS–SOLID CHROMATOGRAPHY

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SUMMARY

The results of the gas–solid chromatographic separations of phenanthrene, anthracene and carbazole mixtures on graphitized carbon black, Bentone 34 and calcium chloride deposited on Chromosorb W are presented and compared.

The phenanthrene–anthracene separation decreases in the order graphitized carbon black > Bentone 34 > calcium chloride, and the retention of carbazole in relation to anthracene increases in the order graphitized carbon black < calcium chloride < Bentone 34.

Graphitized carbon black on Chromosorb W seems to be suitable for the fast analysis of technically pure anthracene and phenanthrene, and Bentone 34 on Chromosorb W for the fast determination of both hydrocarbons in technically pure carbazole on short columns.

INTRODUCTION

The separation of phenanthrene, anthracene and carbazole is a particular problem in the gas chromatography of polynuclear aromatics of practical interest especially in the coal-tar industry. It has been possible to separate carbazole (b.p. 353°) from phenanthrene and anthracene (b.p. 337 and 340°) by gas–liquid chromatography, especially with the use of polar phases[1], but the separation of phenanthrene from anthracene is not as easy[1–9] and has been achieved only by using open tubular columns[10–15]. The separation of phenanthrene from anthracene by gas–solid chromatography (GSC) has been more successful. This separation has been achieved on some inorganic salts fused on Chromosorb P, such as calcium chloride[16,17], lithium chloride[9], potassium carbonate[17,18] and potassium antimonate[18], and also on graphitized thermal carbon black[19,20] or on graphitized carbon black modified with phthalocyanine[21]. It is possible to deposit graphitized carbon black on an inert porous support[22–24]. GSC of carbazole has been studied only on some inorganic salts[9,16].

In this paper we present and compare results achieved in the GSC of phenanthrene, anthracene and carbazole mixtures on Chromosorb W coated with graphitized carbon black, Bentone 34 and calcium chloride, and on Chromosorb P coated with

calcium chloride. Such column packings and operating conditions are of practical value only if complete separation can be achieved for all components in mixtures that have a large excess of one component, *e.g.*, small amounts of phenanthrene and carbazole in anthracene.

EXPERIMENTAL

The experimental conditions were as follows.

A Fractovap Model GV gas chromatograph (Carlo Erba, Milan, Italy) connected with an EZ2 recorder (Laboratory Instruments N.E., Prague, Czechoslovakia) was used. The chromatograph had a flame-ionization detector. The column had a length of 1 m and I.D. 3 mm. The following column packings and temperatures were used:

(A) 20% of graphitized carbon black on Chromosorb W, 80–100 mesh, at 340°, 300°, 260°;
(B) 5% of graphitized carbon black on Chromosorb W, 80–100 mesh, at 300°;
(C) 1% of Bentone 34 on Chromosorb W, 80–100 mesh, at 180°;
(D) 1% of Bentone 34 + 1% of SE-30 on Chromosorb W, 80–100 mesh, at 180°;
(E) 0.5% of Bentone 34 + 5% of SE-30 on Chromosorb W, 80–100 mesh, at 180°;
(F) 0.5% of Bentone 34 + 5% of OV-17 on Chromosorb W, 80–100 mesh, at 180°;
(G) 20% of calcium chloride on Chromosorb W, 80–100 mesh, at 280°, 240°;
(H) 20% of calcium chloride on Chromosorb P, 80–100 mesh, at 280°.

The temperatures of both the injector and the detector were 300°. The carrier gas was argon at a flow-rate of *ca.* 40 ml/min.

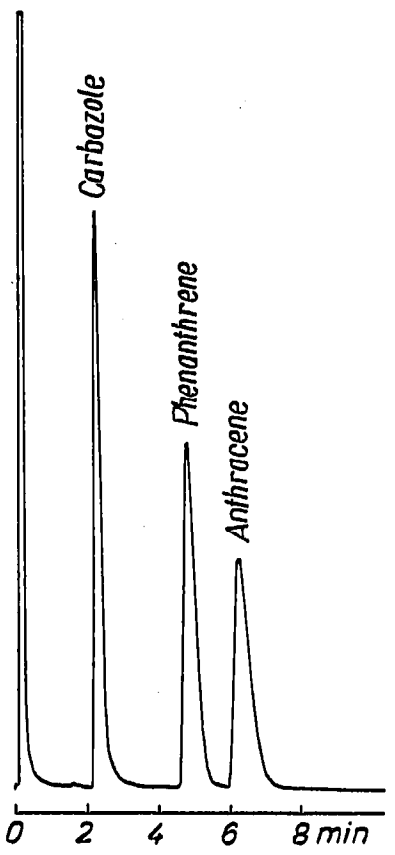
Graphitized carbon black (thermal carbon black TeG-10 produced in the U.S.S.R., graphitized at 2200° for 8 h, specific surface area 7.9 m^2/g) was deposited on Chromosorb W (80–100 mesh, Carlo Erba) from a suspension in benzene (Chromo-

TABLE I

RELATIVE RETENTION VOLUMES, V_R, OF THE COMPONENTS

Column packing (see EXPERIMENTAL*)*	*Column temperature (°C)*	V_R		
		Phenanthrene	*Anthracene*	*Carbazole*
A	340	0.80	1.00	0.42
	300	0.77	1.00[a]	0.36
	260	0.76	1.00	0.32
B	300	0.79	1.00	0.70
C	180	0.81	1.00[b]	>30
D	180	0.83	1.00	>30
E	180	0.87	1.00	25
F	180	0.92	1.00	9.7
G	280	0.89	1.00[c]	3.9
	240	0.87	1.00	5.6
H	280	0.85	1.00[d]	6.1

Retention times: [a] 6.5 min; [b] 10.0 min; [c] 1.0 min; [d] 4.2 min.



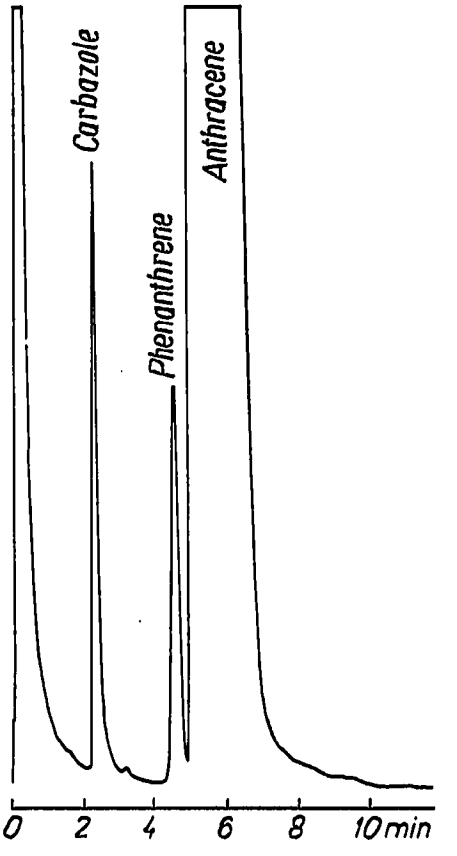


Fig. 1. Separation of an equimolar mixture of phenanthrene, anthracene and carbazole on the column containing 20% of graphitized carbon black on Chromosorb W (packing A). Column temperature, 300°; column length, 1 m.

Fig. 2. Separation of impurities in technically pure anthracene. Conditions as in Fig. 1.

sorb W was poured into this suspension and benzene was evaporated on a water bath with continuous mixing). Bentone 34 (F. W. Berk and Co. Ltd., London) was deposited in the same way. The phases containing SE-30 (methylsilicone) or OV-17 (methylphenylsilicone) were applied from toluene solutions. Impregnation with calcium chloride (pure $CaCl_2 \cdot 2H_2O$, Lachema N.E., Brno, Czechoslovakia) was performed from a methanolic solution and the dry packing was muffled at 640° for 2 h. These materials were packed by vibration into U-shaped glass columns with the ends connected to a vacuum. Samples (0.2–1.0 μl) of 0.5–1.0% benzene solutions of phenanthrene, anthracene and carbazole (refined by zone melting by Lachema N.E.) and their mixtures were injected with a 10-μl Hamilton microsyringe.

The results of the separations are presented in Table I and the best separations in Figs. 1 and 2.

RESULTS AND DISCUSSION

Fig. 1 shows the separation on the column containing graphitized carbon black on Chromosorb W. The elution of the components is much easier than that previously reported on graphitized carbon black alone[19]. Phenanthrene and anthracene are well separated and carbazole is eluted before them owing to non-specific dispersion interactions. Fig. 2 shows a practical example of the analysis of impurities.

Since Bentone 34 requires a relatively low working temperature, a low concentration on the support must be used to achieve reasonable retention times. The separation of phenanthrene from anthracene is good, with symmetrical peaks, but carbazole is not eluted even after 5 h owing to specific interactions. This packing is of practical value for the determination of very small amounts of both hydrocarbons in technically pure carbazole.

The separation of the same mixture on the column containing calcium chloride on Chromosorb W or Chromosorb P under isothermal conditions is relatively poor. Separation of phenanthrene from anthracene is not easy and, although carbazole is held back sufficiently relative to anthracene, tailing occurs.

The ease of the phenanthrene–anthracene separation decreases in the order graphitized carbon black > Bentone 34 > calcium chloride, and the retention of carbazole in relation to anthracene increases in the order graphitized carbon black < calcium chloride < Bentone 34.

The best and fastest GSC separations of phenanthrene from anthracene can thus be achieved on short columns packed with graphitized carbon black on Chromosorb W and with Bentone 34 on Chromosorb W under isothermal conditions. Graphitized carbon black may be preferred for the analysis of technically pure anthracene or phenanthrene and Bentone 34 has certain advantages in the analysis of technically pure carbazole.

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REFERENCES

1 H. D. SAUERLAND, *Brennst. Chem.*, 44 (1963) 37.
2 F. DUPIRE AND G. BOTQUIN, *Anal. Chim. Acta*, 18 (1958) 282.
3 A. J. SOLO AND S. W. PELLETIER, *Chem. Ind. (London)*, (1961) 1755.
4 F. ECKHARDT AND H. O. HEINZE, *Brennst. Chem.*, 42 (1961) 136.
5 A. F. BOYER AND P. PAYEN, *Chim. Anal. (Paris)*, 44 (1962) 107.
6 W. I. LIJINSKY, G. DOMSKY, G. MASON, H. I. RAMAHI AND T. SAFAVI, *Anal. Chem.*, 35 (1963) 952.
7 M. H. ABRAHAM AND R. E. MARKS, *J. Chromatogr.*, 13 (1964) 344.
8 J. R. WILMHURST, *J. Chromatogr.*, 17 (1965) 50.
9 H. D. SAUERLAND AND M. ZANDER, *Erdoel Kohle*, 19 (1966) 502.
10 D. W. GRANT, *Ind. Chem.*, 40 (1964) 240.
11 V. CANTUTI, G. P. CARTONI, A. LIBERTI AND A. G. TORRI, *J. Chromatogr.*, 17 (1965) 60.
12 E. PROKSCH, *Oesterreich. Chem. Ztg.*, 67 (1966) 105.
13 D. W. GRANT, *J. Chromatogr. Sci.*, 6 (1968) 18.
14 K. GROB AND J. A. VOELLMIN, *J. Chromatogr. Sci.*, 8 (1970) 218.
15 T. H. GOUW, I. M. WHITTEMORE AND R. E. JENTOFT, *Anal. Chem.*, 42 (1970) 1394.
16 H. D. SAUERLAND, *Brennst. Chem.*, 45 (1964) 55.
17 R. A. KONJASHINA, T. S. NIKIFOROVA AND V. P. PAKHOMOV, *Khim. Tverd. Topl.*, No. 3 (1967) 60.
18 A. ZANE, *Tobacco Sci.*, 12 (1968) 77.
19 A. ZANE, *J. Chromatogr.*, 38 (1968) 130.
20 C. VIDAL-MADJAR, J. GANANSIA AND G. GUIOCHON, in H. STOCK AND S. G. PERRY (Editors), *Gas Chromatography 1970*, Institute of Petroleum, London, 1971, p. 20.
21 C. VIDAL-MADJAR AND G. GUIOCHON, *Nature*, 215 (1967) 1372.
22 V. S. VASILJEVA, A. V. KISELEV, YU. S. NIKITIN, R. S. PETROVA AND K. D. SHCHERBAKOVA, *Zh. Fiz. Khim.*, 35 (1961) 1889.
23 A. V. KISELEV, in M. VAN SWAAY (Editor), *Gas Chromatography 1962*, Butterworths, London, 1963, p. 34.
24 B. VERSINO AND F. GEISS, *Chromatographia*, 2 (1969) 354.