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Note

Long-term use of liquid-crystalline stationary phase for separation and determination of polynuclear aromatic hydrocarbons in carbochemical products

Comparison of results obtained by different methods

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Modern technology for the isolation of pure anthracene and carbazole from anthracene oil[1] requires appropriate analytical techniques. Gas chromatography (GC) has been used for the determinaton of the components of such samples[2], particularly with the use of a liquid-crystalline phase[3,4]. The method[5] has been improved by modification of the support. In this work, the precision and accuracy of this method were evaluated by comparing the results with those obtained with polarography and UV spectrophotometry[6–8].

EXPERIMENTAL

Instrumentation

A MERA-ELWRO differential gas chromatograph, Type 504, with a flame ionization detector and Hitachi Model 356 and Pye Unicam PU 880 recording spectrophotometers were used.

Reagents

Chromosorb G AW (60–80 mesh) was obtained from Johns-Manville and N,N′-di(*p*-butoxybenzylidene)-α,α'-di-*p*-toluidine (BBBT) and silicone GE SE-30 from Applied Science Labs. Potassium carbonate was of analytical reagent grade.

The carrier and auxiliary gases were argon containing less than 0.01% oxygen impurity, air and hydrogen.

RESULTS AND DISCUSSION

The stationary phase consisted of a homogeneous mixture of liquid crystalline BBBT and a non-mesogenic phase, silicone elastomer GE SE-30. The support was modified by the addition of 2% of potasium carbonate.

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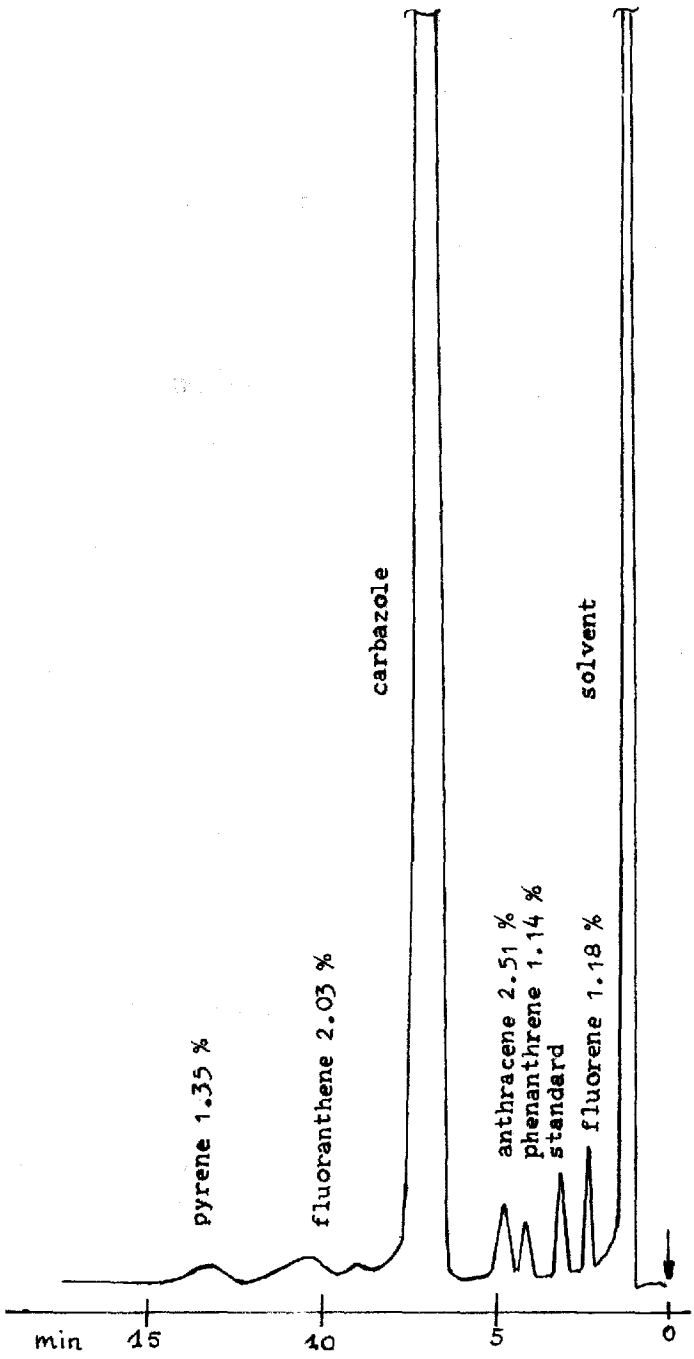

Fig. 1. Chromatogram of isolated carbazole. The separation was carried out on a glass column (190 × 4 mm I.D.) containing 3% BBBT + 2% GE SE-30 on Chromosorb G AW + 2% K_2CO_3 modifier. Column temperature, 230°C; carrier gas, argon at a flow-rate of 45 cm^3/min. Standard, triphenylmethane.

TABLE I

CHARACTERISTICS OF THE CHROMATOGRAPHIC COLUMN

Column parameters	*Characteristic*
Material	Glass
Stationary phase	BBBT + GE SE-30 (3% + 2%, w/w)
Support	Chromosorb G AW, 0.250–0.200 mm, + 2% K_2CO_3 modifier
Dimensions	1.9 m × 4 mm I.D.
Number of theoretical plates/m	1689
Lifetime	6 years (*ca.* 500 h/year of effective work)

The concentrations of particular compounds were calculated by using triphenylmethane as the internal standard. The amount of internal standard added was close to the percentage of the determined component. The calculations were made by using the following equation:

$$x_i = \overline{k}_{i/s} \frac{A_i \,/\, m_p}{A_s \,/\, m_s} \cdot 100$$

where x_i is the percentage of component i, $\overline{k}_{i/s}$ is the correction coefficient for component i, relative to the internal standard (s), A_i,A_s are the peak areas (mm^2) of component i and the standard (s), respectively, calculated as the products of the peak height and the width at half-height, and m_p, m_s are the masses (g) of the sample and the standard, respectively.

A good separation of fluorene, phenanthrene, anthracene, carbazole, fluoranthene and pyrene was obtained (Fig. 1). The carbazole peak, even at low concen-

TABLE II

RESULTS OF GC ANALYSES OF TECHNICAL SAMPLES

Sample	*Analyte*			
	Fluorene	*Phenanthrene*	*Anthracene*	*Carbazole*
Carbazole crude ($\bar{X}$ + S.D.)	11.5 ± 0.9	5.5 ± 0.25	10.2 ± 0.3	72.9 ± 2.0
Phenanthrene fraction ($\bar{X}$ ± S.D.)	17.4 ± 0.2	46.4 ± 0.3	6.2 ± 0.2	30.1 ± 0.3
Carbazole fraction	12.8	17.6	10.8	55.0
	17.4	28.1	9.9	40.6
	18.2	24.8	12.3	47.1
	16.7	33.7	7.9	25.8
Anthracene	5.8	11.2	75.9	6.9
	0.86	1.62	95.12 (as difference)	2.16

TABLE III

CHARACTERISTICS OF THE UV METHODS USED

Component	*Concentration range (%, w/w)*	*Analytical wavelength (nm)*
Anthracene	0.5–85	377: 374; 380
	85–99	377; differential method[7]
Carbazole	60–95	293; 290; 296; if phenanthrene content is below 3%
	0.5–5	293; 290; 296; sum of phenanthrene and carbazole
Phenanthrene	15–95	250; 247; 253; correction for anthracene (not more than 10%)
	0.5–5	293; 290; 296; sum of carbazole and phenanthrene

tration, is sharp. The column lifetime is more than 6 years (Table I). The time of analysis is short (*ca.* 15 min).

The precision was calculated on the basis of five independent determinations on the same sample. The results are given in Table II. Characteristics of the UV method are given in Table III.

The results of analyses of pure anthracene and standard mixtures obtained by GC and UV spectrophotometry are given in Table IV. The anthracene content obtained by the UV method is always lower, which may be indicative of the presence of impurities; the lower GC results for impurities may be due to adsorption on the column.

The GC results for the determination of anthracene and carbazole in various samples are given in Table V and compared with the results obtained by other methods. For the determination of anthracene in crude anthracene, GC, UV and polarographic techniques are suitable. The polarographic technique fails for aromatic

TABLE IV

COMPARISON OF RESULTS OF ANTHRACENE PURITY ANALYSIS IN STANDARD MIXTURES

Sample	*Component (%, w/w)*					
	Antracene		*Phenanthrene (GC)*	*Carbazole (GC)*	*Others (GC)*	*Phenanthrene + carbazole (UV)*
	GC[a]	*UV*[b]				
Anthracene, pure	99.7	98.1	traces	0.14	0.12	
Anthracene, pure + 2% carbazole	98.25	96.3	0.06	1.59	0.10	1.84
Anthracene, pure + 2% phenanthrene	98.06	96.3	1.72	0.05	0.17	1.80
Anthracene, pure + 1.5% carbazole + 1.5% phenathrene	96.8	95.2	1.33	1.79	0.09	3.11

[a] Anthracene determined as the difference (100 − sum of impurities) %.
[b] Anthracene determined as the main component by differential method.

TABLE V

COMPARISON OF RESULTS OF ANTHRACENE AND CARBAZOLE DETERMINATONS BY DIFFERENT METHODS

Sample No.	*Anthracene (%, w/w)*			*Carbazole (%, w/w)*	
	GC	*UV*	*Polarography*	*GC*	*Polarography*
1	42.8	42.6	42.3	13.5	15.7
2	44.0	44.5	43.7	13.1	15.2
3	42.1	41.2	42.3	13.9	14.5
4	41.4	42.5	43.3	14.7	16.6
5	11.2	11.3	—[a]	40.9	40.4
6	11.7	12.1	—[a]	43.8	44.0
7	12.6	11.8	—[a]	50.9	51.3
8	11.5	10.9	—[a]	45.1	47.5

[a] Results too high.

hydrocarbons in carbazole fractions. For carbazole determinations the GC and polarographic techniques are acceptable, although some systematic errors occur.

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