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GAS CHROMATOGRAPHY OF THE SYSTEM PHENANTHRENE–ANTHRA-CENE–CARBAZOLE ON A COLUMN OF CADMIUM CHLORIDE MODI-FIED WITH CARBOWAX 20M

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SUMMARY

A complete separation of a phenanthrene–anthracene–carbazole mixture, with peak shapes and sample load capacity comparable to those in gas–liquid chromatography, has been achieved on a cadmium chloride column modified with Carbowax 20M. The effects of coating and of column temperature on the retention behaviour of phenanthrene and anthracene have been studied. A stationary phase composition of cadmium chloride–Carbowax 20M–Chromosorb P (20:1:50) has been found to be the most suitable. The interesting retention behaviour of several condensed aromatic compounds on this column suggests that other factors besides specific and non-specific interactions play a vital role in the retention mechanism. The column is suitable for the fast analysis of technically pure phenanthrene, anthracene and carbazole, especially for carbazole under isothermal conditions.

INTRODUCTION

In the gas chromatography of polynuclear hydrocarbons, especially in the coal-tar industry, the separation of the system phenanthrene–anthracene–carbazole presents an interesting problem. The separation of carbazole from the other two compounds is easily achieved by gas–liquid chromatography, especially with the use of polar phases. However, on the common isotropic liquid phases, the relative retentions of phenanthrene and anthracene are very similar; consequently, very little or no separation can be achieved on packed columns. The selectivity of liquid crystals towards the molecular shape of the sorbate has been recently used[1] in the separation of these compounds. In fact a major success in the separation of this crucial pair of compounds may be attributed to gas–solid chromatography. Thus, separation has been achieved on graphitized thermal carbon black[2–4] modified with phthalocyanine[5], on silica containing cross-linked polymer[6] and on some inorganic coated supports, such as calcium chloride[7], lithium chloride[8], cadmium chloride[9] and potassium carbonate and potassium antimonate[10]. Quantitative analysis on a column of cadmium chloride[9] was limited by peak tailing, and a limitation of graphitized thermal carbon black is its apparent irreversible adsorption of high-boiling condensed aromatic com-

pounds such as chrysene and benz[a]anthracene[2]. The relative advantages and disadvantages of columns of graphitized carbon black, Bentone 34 and calcium chloride were studied by Fryčka[11]. A limitation of Bentone 34 is its excessively high retention time for carbazole.

We have studied the selectivity of a column of cadmium chloride modified with Carbowax 20M, and the effect of coating and of the column temperature on the retention behaviour of phenanthrene and anthracene. Several polynuclear hydrocarbons exhibited interesting retention behaviour on this column.

EXPERIMENTAL

The experiments were carried out on a Perkin-Elmer 810 gas chromatograph equipped with a flame ionization detector and a 1-mV Honeywell strip-chart recorder. The columns were made of stainless steel (182 cm × 2 mm). They were packed by means of a conventional technique. The support used was Chromosorb P (mesh sizes, −60 and +80). The packing material was prepared by dissolving appropriate amounts of cadmium chloride and the stationary liquid phase in a suitable solvent (methanol and water). A few drops of very dilute hydrochloric acid were added to suppress hydrolysis of cadmium chloride. To this clear solution was added the support to be coated and the solvent was removed by evaporation. In each case, a dilute solution of the sample in benzene was injected using a 10-μl Hamilton microsyringe; the amount of sample injected varied from 0.2 to 1.0 μl.

The model compounds tested were either laboratory reagents or microanalytical reagents from BDH, Poole, Great Britain, except for pyrene (white puriss) which was obtained from Koch-Light, Colnbrook, Great Britain, and naphthalene and phenanthrene (extra pure) from E. Merck, Darmstadt, G.F.R.

The resolution (R_{ij}) was calculated from the equation

$$R_{ij} = (Rd_j - Rd_i)/2(\sigma_i + \sigma_j) \tag{1}$$

where Rd is the retention distance, and the standard deviation, σ, was determined from the peak width at the peak height of 0.607 from the base.

RESULTS AND DISCUSSION

Separation of the system phenanthrene–anthracene–carbazole

A partial separation of phenanthrene and anthracene was achieved but with severe peak tailing (elution order, anthracene > phenanthrene) both on columns of Chromosorb P and of 40% cadmium chloride coated on Chromosorb P; the separation achieved with the latter column was better than that with the former. When Carbowax 20M was incorporated into the stationary phase a complete separation of the system phenanthrene–anthracene–carbazole (elution order, carbazole > phenanthrene > anthracene) was achieved with peak shapes and sample load capacity comparable to those of GLC (Fig. 1). The separation observed on the column containing only the support may be due to the specific interaction between the sorbate molecule and the calcium ion[7] present in the support as a minor component.
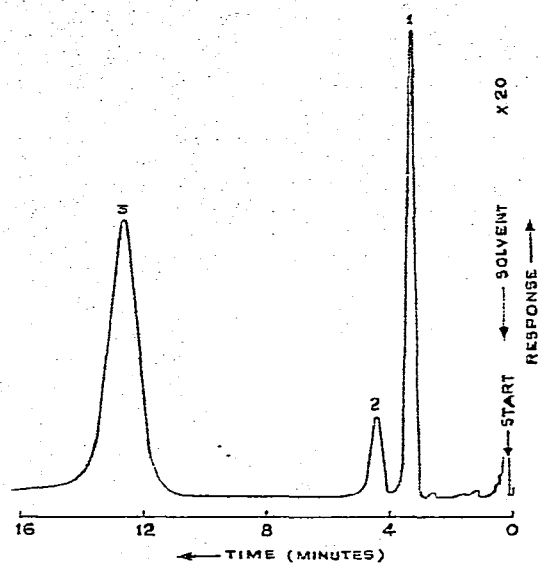
Fig. 1. Chromatogram of technical-grade carbazole on cadmium chloride–Carbowax 20M–Chromosorb P (20:1:50) at 210° and a flow-rate of 30 ml/min. Peaks: 1 = anthracene; 2 = phenanthrene; 3 = carbazole.
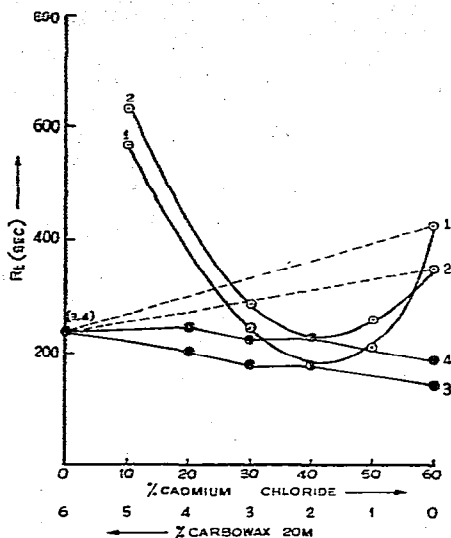
Fig. 2. Effect of coating on the retention time (R_t) of phenanthrene (2 and 4) and anthracene (1 and 3) determined at 210° and a flow-rate of 30 ml/min. (◉), Effect of coating by Carbowax 20M at 40% cadmium chloride; (●), effect of cadmium chloride at 2% Carbowax 20M.

Effect of coating

Figs. 2 and 3 show the interesting effects of coating on the absolute retention and resolution of phenanthrene and anthracene respectively. All of the data were collected at a column temperature of 210° and at a flow-rate of 30 ml/min.

With 2% of Carbowax 20M, the retention time of phenanthrene was always higher than that of anthracene when cadmium chloride was incorporated into the stationary liquid phase. Except for the retention time of phenanthrene at 20% cadmium chloride, both sets of graphs in Fig. 2 show a decreasing trend with increasing amount of salt, and there is a plateau between 30 and 40% salt. At 0% coating of Carbowax 20M, with 40% cadmium chloride, the retention time of anthracene was higher than that of phenanthrene. The data obtained on the column of 40% cadmium chloride are subject to error as severe peak tailing occurred. The correct retention values may be somewhat higher. Nevertheless, the data may be used to understand the observed trend. As the percentage coating of Carbowax increased, at 40% cadmium chloride, the retention time of both anthracene and phenanthrene first decreased up to 2% Carbowax 20M and then increased. Curiously, at *ca.* 0.3% Carbowax 20M, the retention time of both phenanthrene and anthracene was the same, while above this level the elution order was reversed. The data obtained with 2% Carbowax 20M and with 40% cadmium chloride are related by the broken lines in Fig. 2.

With increasing percentage of coating of Carbowax 20M at 40% cadmium chloride, the resolution of phenanthrene and anthracene (Fig. 3) increased sharply up to 2% Carbowax 20M and then decreased rapidly. Although the effect of salt on
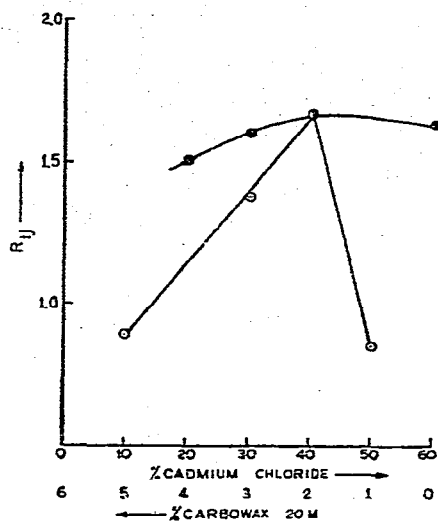
Fig. 3. Effect of coating on the resolution (R_{ij}) of phenanthrene and anthracene determined at 210° and a flow-rate of 30 ml/min. (⊙), Effect of coating of Carbowax 20M at 40% cadmium chloride; (●), effect of cadmium chloride at 2% Carbowax 20M.
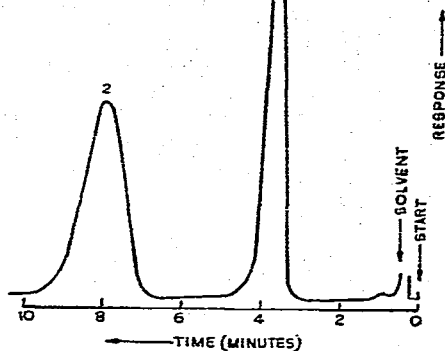
Fig. 4. Chromatogram of 1-methylnaphthalene (2) and 2-methylnaphthalene (1) on cadmium chloride–Carbowax 20M–Chromosorb P (8:1:20) at 160° and a flow-rate of 30 ml/min.

the resolution at a 2% Carbowax 20M was not as dramatic, the resolution increased up to 40% cadmium chloride and then decreased with further amounts of salt. The results suggest an optimum composition of cadmium chloride–Carbowax 20M–Chromosorb P of 20:1:50. On such a column, the maximum resolution of phenanthrene and anthracene would be obtained with the minimum total elution time.

Retention behaviour of the modified column of cadmium chloride

The relative retention and retardation factors of some polynuclear hydrocarbons as measured on the modified column of cadmium chloride are shown in Table I. For the purposes of comparison, results obtained on 30% cadmium chloride coated on superinsulation brick[9] are also included in the table. The retardation factor was calculated as the ratio of the adjusted retention time of a given solute on a modified cadmium chloride column to that on a column containing the corresponding amount of Carbowax 20M only. On a modified column, containing a solution of a metal salt, the experimental retention of a compound is a result of the contributions of the stationary liquid and of the salt. At a high level of coating, the contribution of the support may be ignored. Results similar to those obtained on column B in Table I were observed on a column of cadmium chloride–Carbowax 20M–Chromosorb P (8:1:20). However, the retention time of each compound was increased due to an increased contribution of the stationary liquid phase. Unlike the phenanthrene–anthracene system, a better resolution of 1- and 2-methylnaphthalenes was found on this column than on column B at 160° (Fig. 4).

The retention characteristics of the cadmium chloride column indicate the presence of non-specific and specific interactions as suggested by Sawyer and his

TABLE I

RELATIVE RETENTION (α) AND RETARDATION FACTORS (R_f) OF SOME POLY-NUCLEAR HYDROCARBONS OBTAINED ON COLUMNS OF CADMIUM CHLORIDE MODIFIED WITH CARBOWAX 20M

Columns: A, 30% cadmium chloride on superinsulation brick[9]; B, cadmium chloride–Carbowax 20M–Chromosorb P (20:1:50); C, 2% Carbowax 20M on Chromosorb P. Flow-rates: (A), 50 ml/min; (B and C), 30 ml/min. Column temperatures: A, 180° (220° for phenanthrene, anthracene, carbazole and pyrene); B and C, 160° (210° for phenanthrene, anthracene and carbazole).

Compound	B.p. (°C)	α			R_f
		A	B	C	
Indane	177.8		0.29		
Naphthalene	218.0	0.80	1.00	1.00	1.33
2-Methylnaphthalene	241.1	1.17	1.15	1.47	1.04
1-Methylnaphthalene	244.4	1.00	2.03	1.63	1.66
Biphenyl	255.2	—	0.95	2.13	0.59
2,6-Dimethylnaphthalene	261.0	3.08	1.79	1.93	1.23
1,6-Dimethylnaphthalene	264.0	2.00	1.93	2.20	1.17
2,3-Dimethylnaphthalene	268.0	3.17	1.90	2.40	1.06
Acenaphthene	277.2	2.92	4.90	3.09	2.11
Dibenzofuran	287.0	1.25	3.00	4.40	0.91
Fluorene	297.9	4.00	5.95	5.48	1.45
Phenanthrene	338.4	1.00	1.00	1.00	0.98
Anthracene	339.9	1.25	0.79	1.00	0.78
Carbazole	354.8	3.50	3.21	3.90	0.81
Pyrene	393.0	2.80			

co-workers[12–13] in their studies with solid supports modified with salts. The specific interaction between the metal ion of the salt and the electronegative part of the sorbate molecule, *i.e.*, the π-electrons of the aromatic ring or an unshared pair of electrons on an oxygen or nitrogen atom, depends on the polarity, position and size of the substituted group and the planarity, etc., of the sorbate molecule. The greater dipole moment of the 2-methylnaphthalene possibly caused it to be retained for a longer time than the 1-methyl isomer. A longer retention time for 2-methylnaphthalene was also observed by Sauerland and Zander[8] on calcium chloride. The interaction between Cd^{2+} and the lone pair of electrons on the nitrogen atom of carbazole causes the carbazole to be retained for a longer time than pyrene. The retention and resolution of phenanthrene and anthracene can be explained in terms of their benzenoid character. Anthracene has only one sextet of electrons, which is shared between three rings, while phenanthrene has two sextets. The mobility of the π-electrons results in a dilution of the benzenoid character of anthracene, which makes it less stable and more reactive. The aromatic energy of phenanthrene is 7–12 kcal greater than that of anthracene. We cannot explain the earlier elution of dibenzofuran which has a lone pair of electrons.

When Carbowax 20M is incorporated into the stationary phase, the retention characteristics do not follow any regular pattern and are different from those of columns of cadmium chloride and Carbowax 20M. The elution order of the 1- and 2-methylnaphthalenes on column B is the reverse of that on the cadmium chloride column, but similar to that on the Carbowax 20M column. However, very good

separation of the naphthalenes was obtained on column B, while columns A and C gave only a partial separation. The earlier elution of biphenyl can be explained in terms of its non-planar configuration in the gaseous state. With the exception of acenaphthene and fluorene, all of the compounds with a fused three-ring homocyclic or heterocyclic structure showed negative retardation ($R_f < 1.0$). A most interesting result is the reverse elution order of phenanthrene and anthracene. To our knowledge, such an elution order (phenanthrene > anthracene) has not been observed previously. This peculiar elution order was independent of the column temperature within the range 170–210°. All these facts, together with the extrema in Figs. 2 and 3, suggest that other factors besides specific and non-specific interactions play a vital role in the retention mechanism of Carbowax-modified columns of cadmium chloride.

Formation of a new phase through an interaction between the glycol and cadmium chloride is ruled out as the infrared spectrum of the phase did not show any band shift for the glycol; the spectrum of the phase was merely a superimposition of those of cadmium chloride and Carbowax 20M. Moreover, Carbowax 20M incorporated into the stationary phase could be extracted with chloroform. The salting-out effect of aromatic compounds which has been observed[14] when an electrolyte is dissolved in polyethylene glycol 400 is quite unlikely here as cadmium chloride is insoluble in Carbowax 20M. It is also quite unlikely that a solubilization process can play role in the selectivity of this phase. A further study with different stationary liquid phases and metal salts may provide insight into the separation mechanism of this column. The present liquid phase seems to be suitable for the fast analysis of technically pure phenanthrene, anthracene and carbazole, especially for carbazole under isothermal conditions.

ACKNOWLEDGEMENT

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