

APPLICATION OF POROUS ETHYLVINYLBENZENE POLYMERS TO THIN LAYER CHROMATOGRAPHY. SEPARATION OF AROMATIC AND HETEROCYCLIC HYDROCARBONS AND HIGHER PHENOLS ON PORAPAK Q*

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SUMMARY

Organic porous hydrocarbons like Porapak Q and related types have been found to be very suitable as lipophilic solid phases for thin layer chromatography and/or column chromatography.

Many solvents in the polarity range from carbon tetrachloride up to methanol travel well along the layer in a reasonable time.

Separation of aromatic hydrocarbons is due to the dispersion forces (solute-sorbent) which act not only according to the number of nuclei but also according to the spatial configuration of the respective molecule (*e.g.* phenanthrene-anthracene). Very sharp separations can be obtained if the electron cloud of the hydrocarbon part of any molecule is disturbed and/or sterically shielded by a heteroatom and/or a non-hydrocarbon functional group (*e.g.* carbazole-diphenylene oxide-diphenylene sulphide-2-azafuorene; diphenylene sulphide-6,7-benzothionaphthene; biphenyl-hydroxybiphenyls etc.).

The material is very convenient for the production of standard thin layer plates *e.g.* by cold-pressing the powdered polymer on plates of suitable materials.

Some years ago¹ one of us pointed out how stationary phases which had been theoretically and extensively investigated in the field of gas chromatography could be usefully applied in other chromatographic techniques, such as column and/or thin layer chromatography. He referred to the novel results which can be obtained in thin layer chromatography by using substituted montmorillonites, molecular sieves and other materials which are well known as gas chromatographic packings. This idea was followed up successfully by RITTER, MEYER, AND GEISS² who used Bentones as stationary phases for the TLC separation of isomeric polyphenyls.

Recently JANÁK³ introduced porous organic polymers such as Porapak Q (Waters Associates Inc., Framingham, Mass., U.S.A.) into thin layer chromatography. This material, an ethylvinylbenzene polymer crosslinked with divinylbenzene, had been developed by HOLLIS⁴ as an interesting packing for gas analysis by gas chromatography. In thin layer chromatography, new separation possibilities for aromatic

* Dedicated to Prof. Dr. F. Čižka on the occasion of his 70th anniversary.

hydrocarbons have been described⁸ as a result of the perfect lipophilic nature of Porapak (an aromatic polyhydrocarbon) and its very convenient physical properties (white, hard powder or granular material, very good wetting ability).

In this paper we wish to refer to new separations of aromatic and heterocyclic hydrocarbons achieved on Porapak Q, N and P. Some correlations between the structure of substances to be separated and their chromatographic behaviour on given porous polymers are demonstrated and discussed.

EXPERIMENTAL AND RESULTS

For our experiments, we used Porapak Q of particle size 100/120 mesh (batch 455), 120/150 mesh (batch 399), 150/200 mesh (batch 132 and 413) and 200/325 mesh (batch not given), Porapak N of particle size 120/150 mesh (batch 500) and Porapak P 100/120 mesh (batch 381).

The development was carried out by the ascending technique in an S-chamber⁹. In order to reduce the amount of material necessary we used plates with longitudinal grooves of triangular cross section (0.7 mm deep, and 1.0 mm wide). The solvents used were: ethyl acetate, acetone, acetone-propanol (1:1, v/v), propanol, and ethanol (Lachema N.E., Brno, C.S.S.R.). The inclination of the plate was 10 degrees.

The model substances were several aromatic hydrocarbons and their derivatives, and heterocyclic compounds of like structure (Urx Works N.E., Ostrava, C.S.S.R.; Koch-Light Co. Ltd., London; Aldrich Chemical Laboratory, Inc., U.S.A.; Gesellschaft für Teerverwertung, Duisburg, West Germany). The samples were applied in benzene solutions. The spots were detected by observing their fluorescence under a U.V.-source; non-fluorescent or slightly fluorescent compounds were sprayed with saturated tetracyanoquinodimethane solution in anhydrous acetonitrile (0.12 g TCQM/100 ml) and subsequently with tetracyanoethylene in benzene (0.3 g TCE/100 ml).

The results obtained are summarized in the tables and figures.

Table I lists the flow rates of solvents used on Porapak of various particle size as well as on different types of Porapak of the same particle sizes as quoted above.

Table II illustrates the repeatability of R_F values of several hydrocarbons on Porapak Q of four different particle sizes (100/120, 120/150, 150/200, 200/325 mesh). The separation power of the thin layers with the smallest and largest particle sizes, is expressed as the number of theoretical plates calculated in the usual manner, *i.e.*

TABLE I

FLOW RATE (SEC) OF SOLVENTS IN VARIOUS TYPES OF PORAPAK

Type of Porapak mesh size	S ₁	S ₂	S ₃	S ₄	S ₅
Porapak Q 100/120	90	60	230	330	155
Porapak Q 150/200	135	90	360	590	210
Porapak Q 200/325	210	190	580	930	410
Porapak P 100/120	60	40	195	290	96
Porapak N 100/120	80	70	200	300	150

S₁ = ethyl acetate; S₂ = acetone; S₃ = acetone-propanol (1:1, v/v); S₄ = ethanol; S₅ = propanol.

TABLE II

THE INFLUENCE OF PARTICLE SIZE OF PORAPAK Q ON REPEATABILITY OF R_F VALUES AND SEPARATION EFFICIENCY

Solvent: acetone.

Compound	Type of Porapak Q mesh	R_F	n (TP)
1,6-Dimethylnaphthalene	100/120	0.78	263
	120/150	0.75	—
	150/200	0.77	—
	200/325	0.78	780
Fluorene	100/120	0.73	178
	120/150	0.72	—
	150/200	0.70	—
	200/325	0.70	350
3,4-Benzopyrene	100/120	0.48	53
	120/150	0.48	—
	150/200	0.51	—
	200/325	0.47	230
1,12-Benzoperylene	100/120	0.48	43
	120/150	0.47	—
	150/200	0.46	—
	200/325	0.48	200

$n = 16(x/y)^2$ (where x is the distance from the spot centre to the start and y is the length of the spot).

Table III summarizes the R_F values of 46 compounds measured in 5 solvent systems. These values are the average values of 2–3 measurements, where differences in R_F did not exceed 0.03. The compounds are listed according to the number of aromatic nuclei and functional groups. The mode of detection and spot colours are listed, too.

DISCUSSION

Chromatographic parameters

The flow rates for the capillary flow through a thin layer are favourable, as can be seen from Table I. In fact, the flow rates decrease in the order Porapak P < N < Q, and for particle size 100/120 < 120/150 < 150/200 < 200/325 mesh. The reproducibility of R_F values on Porapak Q of the hydrocarbons used as model compounds, is good, even when using specimens of the above sorbent considerably differing in particle size (100/120 and 200/325 mesh). The particle size, however, exerts a considerable influence on the separating efficiency. The individual types of Porapak (Q, P, N) differ in the type of substituents on the benzene rings of the copolymer and in the degree of cross-linkage.

Fig. 1 shows the R_F values of a selected series of hydrocarbons having 1 to 6 nuclei in the system Porapak Q, N, and P—ethyl acetate, acetone, and propanol, respectively. Shifts in the retention sequence were observed only for durene and pyrene; the retention behaviour of other compounds had a monotonous course.

TABLE III

 R_F VALUES OF SOME AROMATIC COMPOUNDS IN DIFFERENT SOLVENT SYSTEMS

No.	Compound	Structure	Colour of spot	R_F in solvents (cf. Table I)				
				S ₁	S ₂	S ₃	S ₄	S ₅
1	Durene		Red ^a	0.88	0.78	0.74	0.43	0.55
2	Naphthalene		Light brown ^a	0.89	0.81	0.74	0.43	0.51
3	Biphenyl		Light red ^a	0.90	0.80	0.75	0.41	0.52
4	2,6-Dimethylnaphthalene		Grey ^a	0.87	0.79	0.74	0.27	0.42
5	1,5-Dimethylnaphthalene		Grey ^a	0.85	0.77	0.73	0.27	0.42
6	2,3,6-Trimethylnaphthalene		Violet ^a	0.88	0.80	0.68	0.34	0.47
7	4,4'-Dimethylbiphenyl		Blue-green ^a	0.86	0.77	—	0.27	0.40
8	Indole		Dark grey ^a	0.86	0.90	0.90	0.85	—
9	5-Hydroxyhydrindene		Dark green ^a	0.87	0.89	0.91	0.88	0.90
10	4-Hydroxyhydrindene		Red ^a	0.90	0.90	0.89	0.90	0.90
11	2-Hydroxybiphenyl		Light green ^a	0.92	0.90	0.92	0.89	0.86
12	4-Hydroxybiphenyl		Light green ^a	0.92	0.89	0.92	0.88	0.83
13	2,2'-Dihydroxybiphenyl		Brown ^a	0.94	0.89	0.92	0.88	0.83

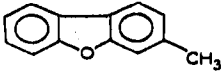
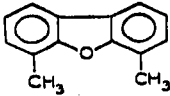
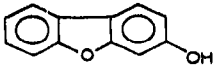
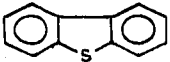
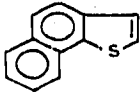

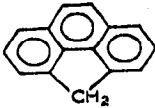
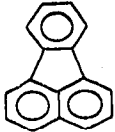

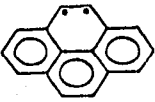
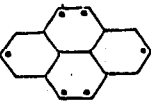
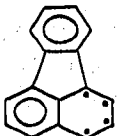
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TABLE III (continued)

No.	Compound	Structure	Colour of spot	R_F in solvents (cf. Table I)				
				S_1	S_2	S_3	S_4	S_5
14	2-Phenyl-naphthalene		Blue-green ^a	0.80	0.74	0.67	0.14	0.25
15	Anthracene		Violet ^b	0.85	0.73	0.48	0.16	0.22
16	Phenanthrene		Violet ^a	0.82	0.74	0.70	0.26	0.33
17	Fluorene		Violet ^a	0.80	0.70	0.66	0.27	0.36
18	Acenaphthene		Green ^a	0.82	0.77	0.68	0.32	0.35
19	1,2,3,4-Tetrahydroanthracene		Violet ^b	0.88	0.74	0.50	0.20	0.26
20	1-Methyl-anthracene		Violet ^b	0.85	0.73	0.47	0.15	0.23
21	2-Methyl-anthracene		Violet ^b	0.85	0.73	0.51	0.15	0.22
22	Acridine		Brown ^a	0.73	0.76	0.80	0.80	0.64
23	Carbazole		Blue ^a	0.90	0.83	0.85	0.62	0.65
24	4-Azafluorene		Orange ^a	0.87	0.75	0.85	0.85	0.71
25	2-Methyl-acridine		Violet ^a	0.81	0.76	0.69	0.31	0.40
26	2-Hydroxy-fluorene		Green ^a	0.87	0.89	0.86	0.66	0.80

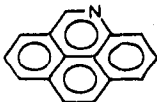
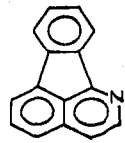
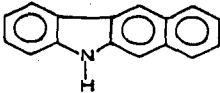
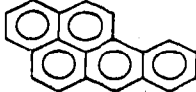
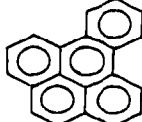
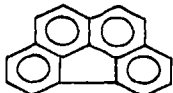
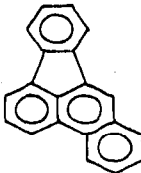
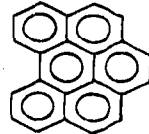
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TABLE III (continued)

No.	Compound	Structure	Colour of spot	R_F in solvents (cf. Table I)				
				S_1	S_2	S_3	S_4	S_5
27	2-Methyldiphenylene oxide		Violet ^a	0.82	0.71	0.68	0.31	0.47
28	1,8-Dimethyldiphenylene oxide		Violet ^a	0.80	0.70	0.66	0.32	0.41
29	2-Hydroxydiphenylene oxide		Green ^a	0.96	0.86	0.91	0.75	0.97
30	Diphenylene sulphide		Yellow ^a	0.82	0.70	0.66	0.60	0.60
31	6,7-Benzothionaphthene		Violet ^a	0.82	0.74	0.61	0.28	0.38
32	Pyrene		Green ^b	0.75	0.70	0.61	0.16	0.28
33	4,5-Methylenephenanthrene		Violet ^a	0.74	0.65	0.61	0.15	0.26
34	Fluoranthene		Green ^b	0.75	0.64	0.47	0.05	0.10
35	2,3-Benzofluorene		Violet ^b	0.75	0.61	0.48	0.05	0.12
36	Dihydropyrene		Green ^b	0.74	0.68	0.61	0.14	0.27
37	Hexahydropyrene		Green ^a	0.74	0.65	0.56	0.13	0.26
38	1,2,3,4-Tetrahydrofluoranthene		Yellow ^b	0.79	0.62	0.42	0.09	0.10

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TABLE III (continued)

No.	Compound	Structure	Colour of spot	R_F in solvents (cf. Table I)				
				S_1	S_2	S_3	S_4	S_5
39	1-Azapyrene		Green ^b	0.80	0.74	0.62	0.30	0.30
40	2-Azafluoranthene		Green ^b	0.79	0.76	0.70	0.27	0.31
41	2,3-Benzocarbazole		Violet ^b	0.80	0.73	0.76	0.27	0.25
42	3,4-Benzopyrene		Violet ^b	0.65	0.47	0.34	0.05	0.06
43	1,2-Benzopyrene		Light green ^b	0.69	0.59	0.42	0.06	0.10
44	2,3-Benzofluoranthene		White ^b	0.68	0.55	0.43	0.06	0.08
45	3,4-Benzofluoranthene		Green ^b	0.67	0.56	0.33	0.05	0.07
46	1,12-Benzoperylene		Violet ^b	0.60	0.46	0.35	0.06	0.08

^a Coloured spots: TCQM + TCE complexes.

^b Fluorescence.

Correlation of R_F values of model substances (on Porapak Q) with their structure

The material used for TLC is chemically an aromatic polyhydrocarbon, a lipophilic solid stationary phase. The most important intramolecular forces controlling

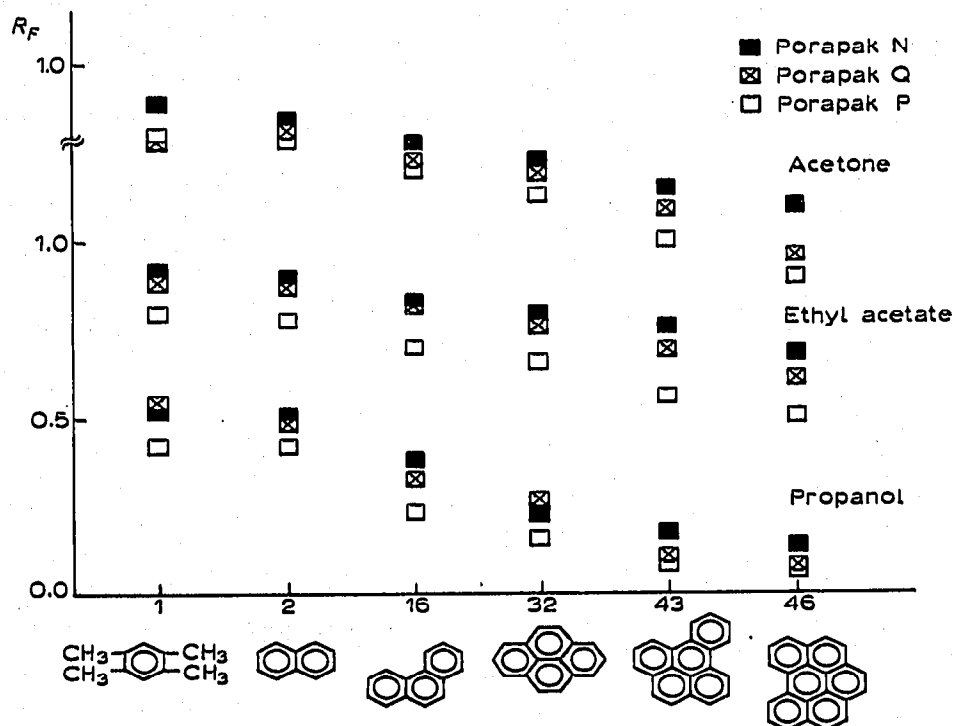


Fig. 1. R_F values of a selected series of hydrocarbons for systems of Porapak Q, N, or P-ethyl acetate, acetone, or propanol.

the degree of sorption are dispersion forces; *i.e.* solute sorption, and consequently the R_F value will be the lower the more the solvent is akin to a hydrocarbon. The hydrocarbons, therefore, will be preferentially sorbed while structural characteristics, *e.g.* number of aromatic rings and the presence of heteroatoms or substituents, will suppress the sorption in the stationary phase and the increase in molecular size will enhance the sorption. In Fig. 2 we can see that the R_F values decrease with increasing number of nuclei in the molecule of the model compound.

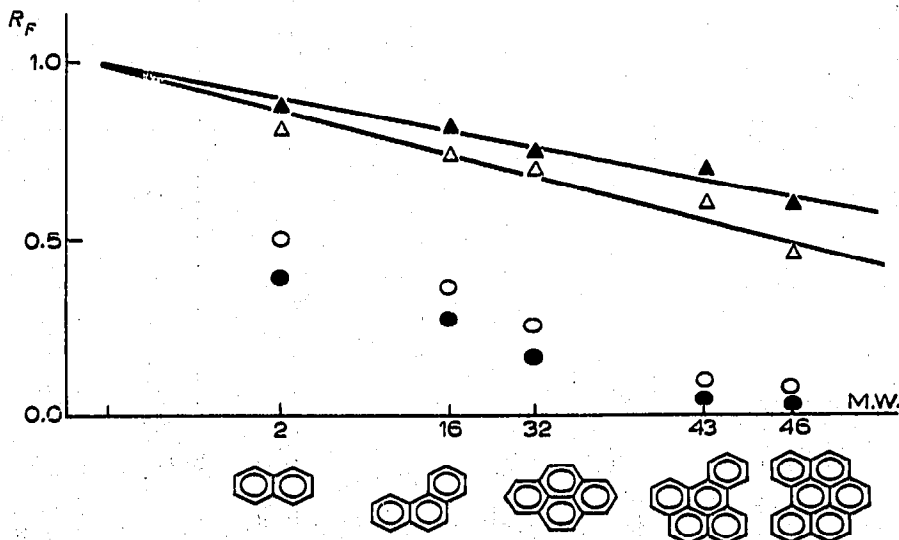


Fig. 2. Plot of R_F values of selected hydrocarbons against the molecular weight, respectively the number of aromatic rings. ▲ = Ethyl acetate; △ = acetone; ○ = propanol; ● = ethanol.

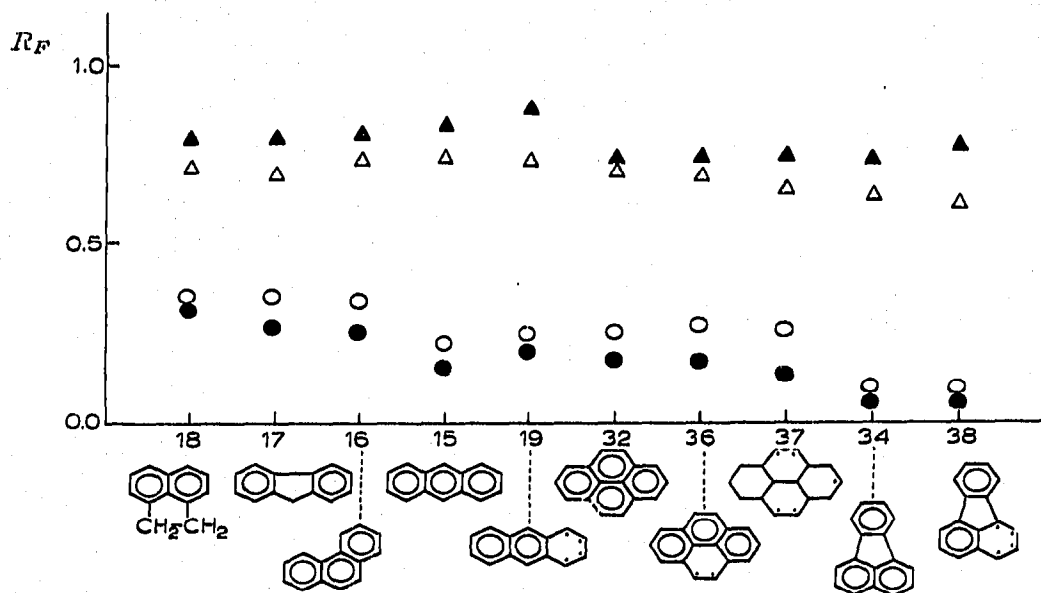


Fig. 3. Relation between the size, and structural features of some compounds and R_F values on Porapak Q (for designations see Table III and Fig. 2).

For donor acting solvents (*e.g.* ethyl acetate or acetone) we can, as a first approximation, draw a straight line on which the decreasing R_F values will lie, and also extrapolate for compounds having a larger number of rings. With solvents which are acceptors (*e.g.* propanol, ethanol) where dispersion forces play a smaller role, the major forces are the inductive ones. A solute substance is polarised by the mobile phase and, accordingly, more or less firmly retained in the stationary phase or extracted into the liquid mobile phase.

In Fig. 3, we can see the above-mentioned differences. The degree of hydrogenation of the aromatic molecule is barely reflected by the R_F values in any system

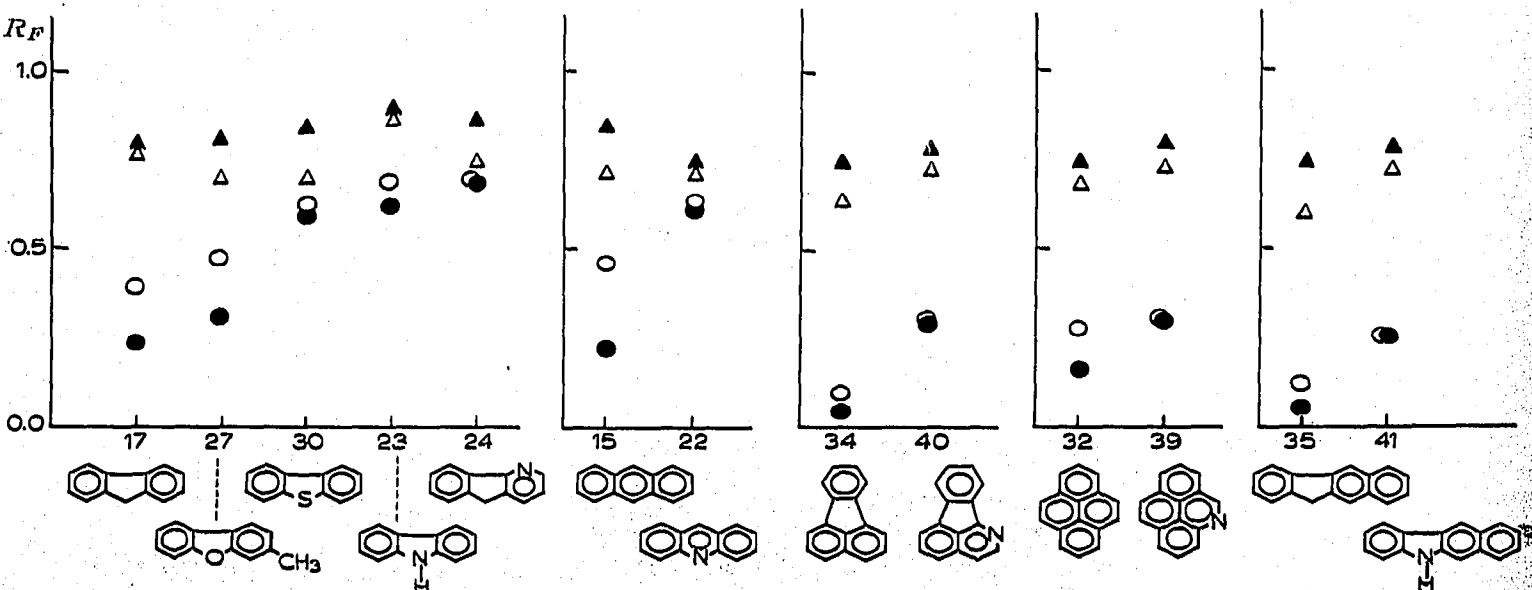


Fig. 4. Comparison of R_F values of aromatic hydrocarbons and their heterocyclic analogues on Porapak Q (for designations see Table III and Fig. 2).

(*cf.* anthracene–tetrahydroanthracene; pyrene–dihdropyrene–hexahdropyrene; fluoranthene–tetrahydrofluoranthene). In the system Porapak Q–ethanol, however, we can find a dependence of the R_F values on the size and structural features of the compound in question (*cf.* acenaphthene (0.32)–fluorene (0.26)–phenanthrene (0.25)–anthracene (0.17)–methylantracene (0.15)).

The presence of any heteroatom in the ring exerts a considerable influence on the R_F value as it brings about a change in the magnitude of the dispersion forces displayed by the molecule as well as a pronounced change in the electron density of the molecule with a consequent alteration of sensitivity towards donor–acceptor properties of the mobile phase.

Fig. 4 serves as an illustration of some of the above postulates (*cf.* fluorene–2-methyldiphenylene oxide–carbazole–diphenylene sulphide–4-azafluorene–[indole]; anthracene–acridine; fluoranthene–2-azafluoranthene; pyrene–1-azapyrene; 2,3-benzofluorene–2,3-benzocarbazole). In some particular cases (see Fig. 5) the differences

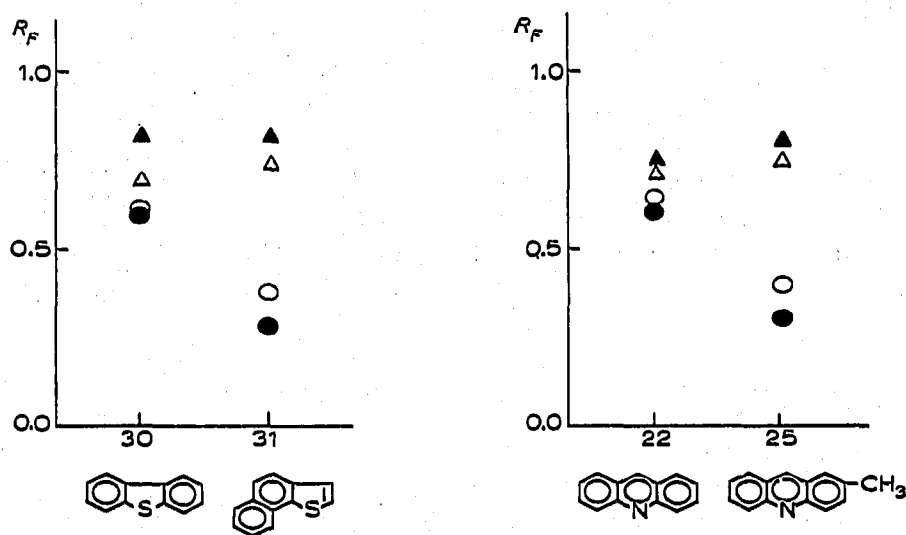


Fig. 5. Differences in R_F values of very similar heterocyclic structures on Porapak Q (for designations see Table III and Fig. 2).

are especially pronounced (*cf.* diphenylene sulphide–6,7-benzothionaphthene; acridine–2-methylacridine).

A non-hydrocarbon substituent has the greatest influence on the R_F values. On the one hand, it reduces by steric hindrance the possibility of adsorption of the hydrocarbon part of the molecule on the “hydrocarbon” surface of the stationary phase, thus considerably reducing that part of solute–sorber molecular interactions based on dispersion forces, while on the other hand, it is prone to interaction with the mobile phase by displaying donor and/or acceptor properties. This is illustrated in Fig. 6 (*cf.* biphenyl–4-hydroxybiphenyl; 2-methyldiphenylene oxide–2-hydroxyfluorene–2-hydroxydiphenylene oxide).

Analytical applications

Thin layer chromatography on Porapak Q permits easy separation of:

- (i) Small quantities of polar substances and several heterocyclic compounds in

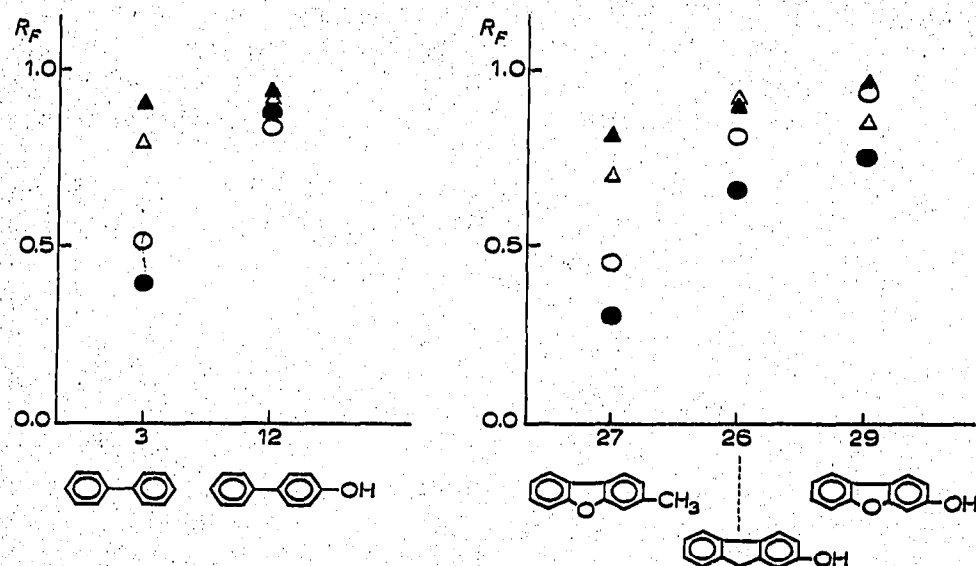


Fig. 6. Influence of a non-hydrocarbon substituent on R_F values on Porapak Q (for designations see Table III and Fig. 2).

hydrocarbons, *e.g.* extremely weak phenols, oxygen, nitrogen, and sulphur-containing compounds in tar and petroleum products.

(ii) Hydrocarbons differing in molecular shape and polarisability, *e.g.* anthracene

TABLE IV

R_F VALUES OF SEVERAL COMPOUNDS PRESENT IN TECHNICAL ANTHRACENE AND PHENANTHRENE

Compound	b.p. (°C)	R_F		
		Ethanol	Acetone	Acetone- propanol (1:1, v/v)
Phenanthrene	337	0.26	0.74	0.70
Anthracene	341	0.16	0.73	0.48
Acridine	344	0.80	0.76	0.80
Carbazole	353	0.62	0.83	0.85
4-Hydroxybiphenyl	319	0.88	0.89	0.92
2,2'-Dihydroxybiphenyl	325	0.88	0.89	0.92
2-Hydroxyfluorene	352	0.66	0.89	0.86
1,8-Dimethyl-diphenylene oxide	316	0.32	0.70	0.66
6,7-Benzothionaphthene	330	0.28	0.74	0.61
Diphenylene sulphide	331	0.60	0.70	0.66

and phenanthrene. Table IV summarises the R_F values of several compounds present in technical anthracene or phenanthrene.

(iii) It is relatively easy to prepare the pressed thin layer plates which are well suited for standard use.

ACKNOWLEDGEMENTS

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DISCUSSION

GRUBHOFFER: How were the small Porapak beads applied to form a usable layer?

KUBECOVÁ: The beads were applied in the form of loose layers to a metal plate with lines engraved parallel with the direction of flow. A transverse groove in the plate accommodates the solvent which is supplemented by means of a syringe during chromatography but it is possible to prepare normal plates by pouring an inert solvent suspension of Porapak on a glass plate and drying at room temperature. A homologous layer has been obtained frequently.

BRENNER: Are molecular sieve effects involved in the separation on Porapak®?

JÄNCHEN: What led you to suppose that the separation is based on dispersion forces?

KUBECOVÁ: Porapak (a copolymer of styrene, vinylbenzene and ethylvinylbenzene) is usually not considered as acting as a molecular sieve. It acts as an adsorbent with a large specific surface area ($10^2 \text{ m}^2/\text{g}$) due to the high microporosity. Because Porapak is a pure polyhydrocarbon without any polar group, the adsorbent-sorbate interactions have been represented by dispersion forces only. The role of dispersion forces in the interaction between solute substances (hydrocarbons) and Porapak (a polyhydrocarbon) is illustrated by Fig. 2, which shows the sequence of R_F values of naphthalene, phenanthrene and benzopyrene; R_F values decrease with the increasing number of condensed rings.

JÄNCHEN: Molecules with the lowest molecular weight migrate fastest; this indicates that the separation cannot be due to a molecular sieve effect, if we understand that molecular sieve is a wrong expression—it should be called a molecular trap, yet molecular sieve is the standard terminology.

HAI: If I understand it correctly, Porapak is the polystyrene matrix of an ion-exchange resin, but without any ion-exchange groups attached. It would thus make it possible to isolate in pure form the non-polar molecular interactions often encountered in the chromatography of, say, purine derivatives on ion-exchange resins. I wonder whether with very high molecular weights and with loads exceeding the capacity of the external surface of the beads, molecular sieve (exclusion) effects would not become operative? Naturally, if only the external surface of the beads is available for adsorption, this suggestion is not justified.