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SELECTIVE CHROMATOGRAPHIC SEPARATION OF AROMATIC HYDROCARBONS AND THEIR HYDROGENATED DERIVATIVES ON PORAPAK T

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SUMMARY

Porapak T is a new separation material suitable for the selective separation of aromatic hydrocarbons and their partially hydrogenated derivatives by chromatography in both a flat bed (thin-layer chromatography) and a columnar (liquid chromatography) arrangement. The differences in retention in the system Porapak T–non-polar solvent are analytically significant and enable substances that differ in structure by only one double bond to be separated. The regularities ascertained are obviously of general applicability and may be utilized also for substituted analogues.

INTRODUCTION

Organic porous polymers based on ethylvinylbenzene, owing to their sorption properties, can be successfully used to solve some separation problems with better results than those obtained with standard adsorption materials. The copolymers of ethylvinylbenzene and divinylbenzene, introduced as gas chromatographic (GC) column packings by HOLLIS[1] (Porapak, Waters Associates, Inc., Framingham, Mass., U.S.A.) were used by us[2] in thin-layer chromatography (TLC) as well as liquid chromatography (LC) and are still the subject of systematic investigation[3] and practical utilization[4,5].

The use of non-polar Porapak Q in TLC for the separation of aromatic hydrocarbons, heterocyclics and higher phenols[3], as well as olefins, alicyclics and aromatics[5], revealed new separation possibilities and indicated areas of wider applicability of organic porous materials. The modification of the non-polar skeleton of the polymer by polar units produces copolymers that have specific sorption properties. The functional groups of the built-in monomeric units markedly alter the over-all sorption properties of the adsorbent.

Of the group of Porapak-type materials, the most polar one is Porapak T. The polar groups have a positive electrostatic field on the surface and thus determine the adsorption selectivity of the adsorbent, particularly towards molecules with localized multiple bonds. The extent of the interactions of Porapak T with a solute molecule depends on the electron-donor properties of the solute, as shown by GC measurements[6,7]. We shall show that the above interactions can be followed in an example of the separation of non-substituted aromatic hydrocarbons and their partially hydrogenated derivatives in a liquid–polymer system.

The separation of aromatic hydrocarbons has been accomplished by various chromatographic techniques, such as paper chromatography[8,9], TLC[10–13], LC[14] and GC[15,16]. A valuable contribution to the elucidation of the behaviour of both hydrogenated and non-hydrogenated aromatic hydrocarbons on Silica Gel G in TLC was made by PETROWITZ[17,18]. The results of his measurements indicate that the separation capability of the adsorption system used by him for the separation of aromatic hydrocarbons and their partially hydrogenated derivatives is not very high.

The present paper demonstrates the easy separation of aromatic hydrocarbons and their partially hydrogenated derivatives on Porapak T and discusses the relationship between the adsorption affinities of the substances and their structures.

EXPERIMENTAL AND RESULTS

The measurements on the thin layer as well as in the column were carried out with Porapak T (Waters Associates, Inc., Framingham, Mass., U.S.A.) with a particle size of 200–325 mesh (Batch No. 845).

Thin-layer chromatography

A suspension of Porapak T in propanol (2:5, w/w) was poured on to a dry glass plate, and the layer was spread to a thickness of 0.5–0.6 mm with a glass stick. The layer was dried at ambient temperature for 5 h and the drying was completed with an evaporation lamp applied from a distance of 15–20 cm for 15 min.

The model substances were aromatic hydrocarbons and their hydrogenated derivatives (Koch-Light Laboratories, Ltd., Colnbrook, Great Britain; Fluka AG, Buchs, Switzerland; Gesellschaft für Teerverwertung, Duisburg, G.F.R.; British Drug Houses, Ltd., London, Great Britain; Lachema, N.E., Brno, Czechoslovakia; Institute of Organic Synthesis, Pardubice-Rybitví, Czechoslovakia). The samples were dissolved in benzene and applied on to the layer, 1.5 cm from the lower edge of the plate and 1–1.5 cm from each other, with an injection syringe. The initial amount of the samples applied was in the range 10^{-7}–10^{-4} g, depending on the substance used and the type of detection. The development was carried out by the ascending technique at room temperature in an S chamber and was stopped when the solvent front reached a distance of 10–11 cm from the starting line. The four mobile phases used for the separation of the model substances were: light petroleum, tetrachloromethane, methanol and acetone (Lachema, N.E., Brno, Czechoslovakia). The time of analysis was determined by the solvent used and varied from 15 min for acetone to 50 min for tetrachloromethane. The angle of the slope of the plate was about 20° during development.

The substances were detected as fluorescing spots under a UV lamp (Chirana ZAR-7, Czechoslovakia). The non-fluorescent hydrogenated aromatics were sprayed with a saturated solution of tetracyanoquinonedimethane (Lachema, Institute of

Pure Chemicals, Brno, Czechoslovakia) in water-free acetonitrile (VEB Laboratorchemie, Apolda, D.D.R.), containing 0.12 g of tetracyanoquinonedimethane per 100 ml of solution, and were observed as dark spots on the background of light-green fluorescence of the reagent.

The used Porapak T can be regenerated with methanol and acetone in a glass column. Both solvents were removed from the regenerated adsorbent by heating it under reduced pressure to 70°.

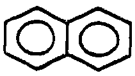
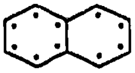
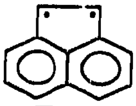
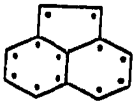
With light petroleum as the mobile phase, the separation efficiency of the layer was 125 theoretical plates for naphthalene ($R_F = 0.42$) and 450 for octahydrophenanthrene ($R_F = 0.71$). The shape of the spots of the model substances on Porapak T is slightly elliptical rather than circular (*cf.*, Fig. 1b). When evaluating the chromatograms, the centres of the spots were measured as the points of intersection of the axes of the ellipse.

For the sake of comparison, the chromatographic behaviour of partially hydrogenated aromatics was followed on reflecting silica-gel sheets (Silufol, Kavalier, N.E., Votice, Czechoslovakia). The sheets were not made up in any way before use. Table I gives the R_F values of 22 model substances, obtained with the above solvents on both adsorbents. The R_F values obtained are the averages of two to five replicate measurements.

ABLE I

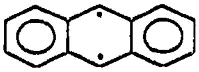
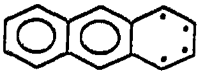
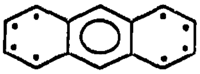
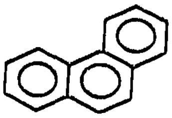
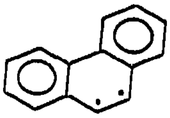
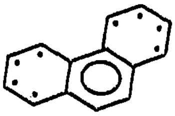
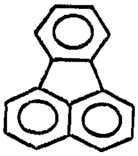
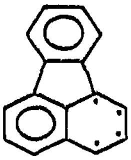
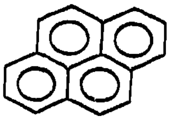
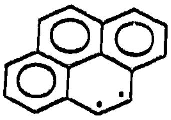
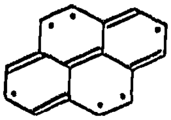
$_F$ VALUES OF MODEL AROMATIC HYDROCARBONS AND THEIR PARTIALLY HYDROGENATED DERIVATIVES ON PORA-K T AND SILICA GEL IN A LAMINAR ARRANGEMENT (TLC)

= Light petroleum; S_2 = tetrachloromethane; S_3 = methanol; S_4 = acetone.

ubstance	*Structure*	*Colour*	*Porapak T*				*Silica gel*	
			S_1	S_2	S_3	S_4	S_1	S_3
dene		Brown[a]	0.49	0.83	0.68	0.92	0.53	0.55
ydrindene		Yellow-brown[a]	0.62	0.96	0.68	0.90	0.60	0.39
aphthalene		Dark brown[a]	0.42	0.75	0.63	0.91	0.53	0.69
etralin		Brown-red[a]	0.72	0.89	0.68	0.91	0.63	0.62
ecalin		Light green[a]	0.90	0.97	0.76	0.93	–	–
cenaphthylene		Brown[a]	0.26	0.61	0.51	0.89	0.45	0.75
cenaphthene		Dark brown[a]	0.40	0.78	0.52	0.91	0.50	0.66
ecahydroacenaphthene		Light green[a]	0.94	0.94	0.73	0.94	–	–

(Continued on p. 480)

ABLE I *(continued)*

ubstance	*Structure*	*Colour*	*Porapak T*				*Silica gel*	
			S_1	S_2	S_3	S_4	S_1	S_3
nthracene		Violet^{b}	0.15	0.53	0.34	0.90	0.40	0.72
,10-Dihydroanthracene		Yellow-brown^{a}	0.26	0.77	0.59	0.93	0.40	0.76
,2,3,4-Tetrahydro-anthracene		Brown^{a}	0.46	0.86	0.47	0.90	0.50	0.67
ctahydroanthracene		Brown^{a}	0.73	0.95	0.55	0.91	0.60	0.66
henanthrene		Violet^{b}	0.17	0.63	0.38	0.90	0.33	0.71
,10-Dihydrophenanthrene		Brown^{a}	0.20	0.69	0.44	0.92	0.35	0.70
ctahydrophenanthrene		Brown^{a}	0.71	0.95	0.58	0.92	0.54	0.62
luoranthene		Blue-green^{b}	0.15	0.35	0.42	0.89	0.29	0.76
,2,3,4-Tetrahydrofluoranthene		Brown^{a}	0.29	0.53	0.50	0.91	0.32	0.74
etracene		Green^{b}	0.06	0.41	0.15	0.89	0.29	0.80
,12-Dihydrotetracene		Brown^{a}	0.13	0.66	0.30	0.91	0.30	–
yrene		Violet^{b}	0.11	0.37	0.37	0.89	0.33	0.72
ihydropyrene		Grey-blue^{b}	0.13	0.42	0.38	0.90	0.34	0.72
ym.-Hexahydropyrene		Brown^{a}	0.43	0.90	0.40	0.90	0.41	0.71

[a] Fluorescence extinction.
[b] Fluorescence.

High-pressure liquid chromatography

The separation of the model substances was carried out on a column 500 mm long and of 2 mm I.D., packed with 0.853 g of Porapak T and operated at room temperature. The flow-rate of the mobile phase, *n*-hexane, was 0.3 ml/min. The dead volume of the column was 1.6 ml. The pressure shocks produced by the piston pump (MC-300, Mikrotechna, N.E., Prague, Czechoslovakia) were eliminated by the damping system described by LOCKE[10]. The detection was carried out with a modified UV analyzer (67005/V, The Development Workshops of the Czechoslovak Academy of Sciences, Prague, Czechoslovakia), having a built-in mercury discharge lamp as the source of UV radiation and limiting filters for taking up a wavelength of 2537 Å. Amounts of 10^{-6}–10^{-4} g of the solute, dissolved in benzene, were injected on to the column with a Hamilton 7005 syringe (Whittier, Calif., U.S.A.).

The results of the measurements are given in Table II in the form of the ratios of the retention times of the substances being examined to that of naphthalene.

TABLE II

RELATIVE RETENTION TIMES, t'_R, OF SOME AROMATIC HYDROCARBONS AND THEIR PARTIALLY-HYDROGENATED DERIVATIVES ON PORAPAK T IN A COLUMNAR ARRANGEMENT (LC)

Naphthalene = 1.000.

Substance	t'_R	*Substance*	t'_R
Indene	0.59	Phenanthrene	2.68
Hydrindene	0.25	9,10-Dihydrophenanthrene	1.44
		Octahydrophenanthrene	0.87
Naphthalene	1.00		
Tetralin	0.86	Fluoranthene	3.69
		1,2,3,4-Tetrahydrofluoranthene	1.47
Acenaphthylene	1.91		
Acenaphthene	1.10	Tetracene	5.33
		5,12-Dihydrotetracene	3.67
Anthracene	2.33		
9,10-Dihydroanthracene	1.18	Pyrene	3.31
1,2,3,4-Tetrahydroanthracene	0.82	Dihydropyrene	2.24
Octahydroanthracene	0.21	*sym.*-Hexahydropyrene	0.83

DISCUSSION

In order to compare the chromatographic behaviours of the model substances on Porapak T as a function of their structures, the partially hydrogenated aromatic hydrocarbons selected were arranged into structurally similar groups. Each of the groups contains a basic aromatic and at least one hydrogenated derivative of it.

Table III shows the relative increments of the R_F values of partially hydrogenated hydrocarbons, related to the R_F value of the basic aromatic of the structural group. The relative increment expresses the extent of the change in adsorption affinity of the basic hydrocarbon due to its partial hydrogenation and is given by $[(R_F)_{ha} - (R_F)_a]/(R_F)_a$, where $(R_F)_{ha}$ is the R_F value of a partially hydrogenated aromatic hydrocarbon and $(R_F)_a$ is the R_F value of the basic aromatic of the particular group.

It is evident from Tables I–III that the elution order of the model substances of the individual groups is the same on both adsorbents when the non-polar solvents

TABLE III

RELATIVE INCREMENTS OF THE R_F VALUES OF PARTIALLY HYDROGENATED AROMATIC HYDROCARBONS

Substance	*Porapak T*			*Silica gel*	
	S_1	S_2	S_3	S_1	S_3
Hydrindene	0.265	0.157	0.000	0.132	−0.291
Tetralin	0.714	0.187	0.079	0.189	−0.101
Decalin	1.143	0.293	0.206	–	–
Acenaphthene	0.538	0.279	0.020	0.111	−0.120
Decahydroacenaphthene	2.615	0.541	0.431	–	–
9,10-Dihydroanthracene	0.733	0.453	0.735	0.000	+0.056
1,2,3,4-Tetrahydroanthracene	2.067	0.623	0.382	0.250	−0.069
Octahydroanthracene	3.867	0.792	0.618	0.500	−0.083
9,10-Dihydrophenanthrene	0.176	0.095	0.158	0.061	−0.014
Octahydrophenanthrene	3.176	0.508	0.526	0.636	−0.127
5,12-Dihydrotetracene	1.166	0.610	1.000	0.034	–
1,2,3,4-Tetrahydrofluoranthene	0.933	0.514	0.190	0.103	−0.026
Dihydropyrene	0.182	0.135	0.027	0.030	0.000
sym.-Hexahydropyrene	2.909	1.432	0.081	0.242	−0.014

(S_1 and S_2) are used. However, on Porapak T, the differences in retention acquire values that are of interest from the analytical point of view, and the regularities are apparently of general applicability.

With linearly fused non-hydrogenated aromatics, the R_F values on Porapak T decrease markedly in the sequence naphthalene, anthracene, tetracene (naphthalene: $S_1 = 0.42$, $S_2 = 0.75$; tetracene: $S_1 = 0.06$, $S_2 = 0.41$). When eluting with non-polar solvents, the R_F values of structurally similar members of the groups increase non-linearly on both adsorbents with increasing hydrogenation of the molecule. However, the mutual differences in their adsorption affinities, expressed by the relative increments of the R_F values, are again substantially more favourable on Porapak T than on silica gel (Table II and Fig. 1). The hydrogenation of even one double bond in the molecule leads to a substantially lower adsorption, as compared with the basic aromatic, on Porapak T in non-polar solvents. In contrast to the values obtained with silica gel[17], this effect is so large that it is feasible to separate even mixtures

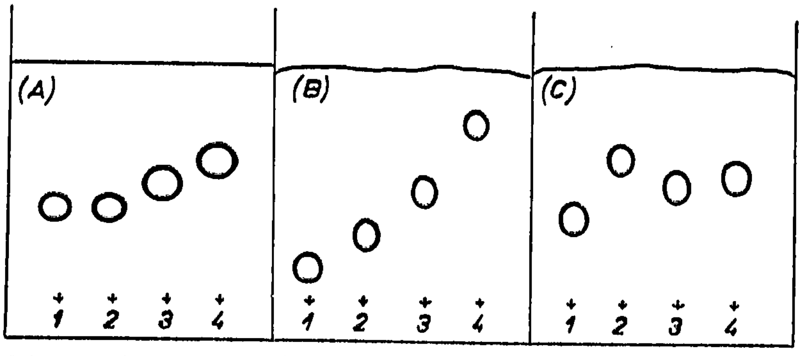


Fig. 1. TLC of anthracene (1), 9,10-dihydroanthracene (2), 1,2,3,4-tetrahydroanthracene (3) and octahydroanthracene (4). (A) silica gel–light petroleum ether; (B) Porapak T–light petroleum ether; (C) Porapak T–methanol.

such as indene–hydrindene and acenaphthene–acenaphthylene on Porapak T in non-polar systems. Hence, the adsorption affinity of aromatic hydrocarbons and their hydrogenated derivatives towards Porapak T is determined, for a given type of solvent, by the polarizability of the molecules, caused primarily by the presence of free π electrons. The parts of molecule which do not have π electrons play a substantially minor part in the over-all sorption. For instance, the R_F values of substances in the system Porapak T–light petroleum are as follows: molecules with 10 π electrons: naphthalene 0.42, acenaphthene 0.40, 1,2,3,4-tetrahydroanthracene 0.46, *sym.*-hexahydropyrene 0.43; molecules with 6 π electrons: tetralin 0.72, octahydroanthracene 0.73, octahydrophenanthrene 0.71. Therefore, as the contribution to adsorption due to the induction forces decreases, the effect of the dispersion interactions increases. With non-polar solvents, the degree of hydrogenation of aromatics also enhances the solvation effect. Molecules that have a smaller number of polarizable π electrons are extracted more easily from the adsorptive surface into the liquid mobile phase, and thus have higher R_F values. It is therefore possible to estimate quite accurately from the adsorption behaviour of structurally different substances the position of a partially hydrogenated aromatic on the thin layer.

In systems with polar solvents, the separation of aromatic hydrocarbons and their hydrogenated homologues is impaired by the competitive effect of the mobile phase. The high R_F values of all the substances investigated in the system Porapak T–acetone indicate a preferential role of solute–solvent interactions over the intermolecular solute–porous polymer interaction. There is also a consistent difference in the behaviour of aromatic hydrocarbons and their hydrogenated derivatives in the systems silica gel–methanol and Porapak T–methanol. The elution sequence of the substance is reversed and this is due to the differences in the polarities of the adsorbents in methanol.

The anomalous behaviour of 9,10-dihydroanthracene on both Porapak T and silica gel with methanol as solvent is interesting. 9,10-Dihydroanthracene is always eluted, within its group, with the highest R_F value (Fig. 1c). The peculiarities in its adsorption properties in the system Silica Gel G–*n*-hexane were observed earlier by PETROWITZ[17], with the distinction that 9,10-dihydroanthracene in its group (anthracene–9,10-dihydroanthracene–octahydroanthracene) was the most adsorbed substance. We have not observed this effect, in non-polar solvents, either with Porapak T or with our silica gel. After the work of PETROWITZ, the anomalous adsorption behaviour of the molecules of 9,10-dihydroanthracene is associated with their non-planar spatial arrangement. However, the decrease in the effective cross-section of the molecule of 9,10-dihydroanthracene due to the distortion of its flatness[17] should, under any circumstances, result in lower sorption. Indeed, in accordance with the supposed role of the intermolecular actions of inductive and dispersion forces, 9,10-dihydroanthracene, which has 12 free π electrons, is eluted on Porapak T in a non-polar solvent system between anthracene (14 π electrons) and 1,2,3,4-tetrahydroanthracene (10 π electrons). On the contrary, the transition from non-polar light petroleum to polar methanol facilitates the release of aromatics from the polymer and, at the same time, decreases the solubility of more hydrogenated molecules. In compliance with this, all the partially hydrogenated aromatics displayed lower relative increments of the R_F values, except for 9,10-dihydroanthracene and 5,12-dihydrotetracene. In these sorption systems, the molecules with a spatial arrange-

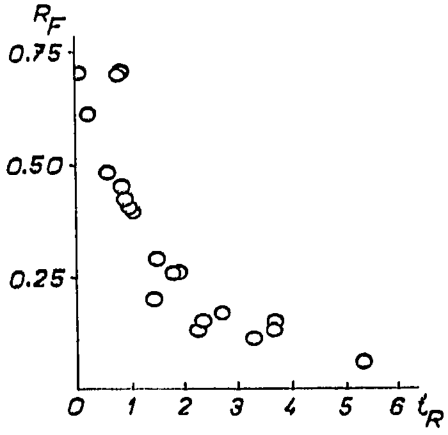


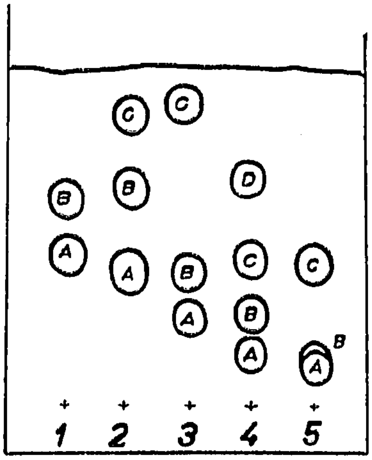
Fig. 2. Correlation of the R_F values (TLC) and relative retention times, t'_R, (LC) of some aromatic hydrocarbons and their hydrogenated derivatives in the systems Porapak T–light petroleum (TLC) and Porapak T–n-hexane (LC).

ment similar to that of 9,10-dihydroanthracene are solvated more easily by methanol, which facilitates the extraction of the former from the adsorptive surface into the liquid mobile phase.

Aromatic hydrocarbons and their hydrogenation derivatives are, within the individual groups, eluted in the same order on both layers and columns. The R_F values obtained by measurements on thin layers can be correlated with the values of the corresponding retention times calculated from the results measured in high-pressure liquid chromatography (Fig. 2).

CONCLUSIONS

It is apparent from the results that the sorption properties of Porapak T pre-



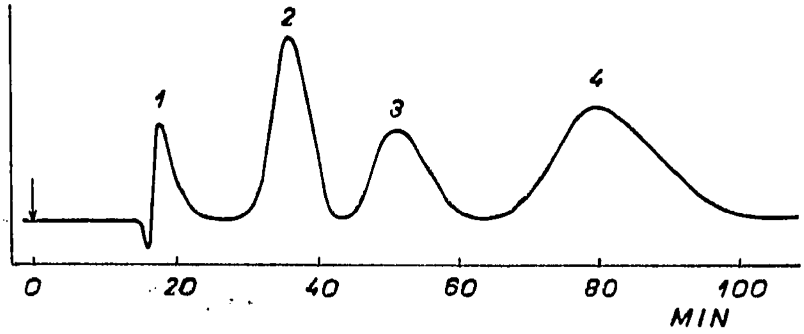


Fig. 3. TLC separation of mixtures of aromatics and their hydrogenated derivatives in the system Porapak T–light petroleum. 1: Indene (A), hydrindene (B); 2: naphthalene (A), tetralin (B), decalin (C); 3: acenaphthylene (A), acenaphthene (B), decahydroacenaphthene (C); 4: anthracene (A), 9,10-dihydroanthracene (B), 1,2,3,4-tetrahydroanthracene (C), octahydroanthracene (D); 5: pyrene (A), dihydropyrene (B), *sym.*-hexahydropyrene (C).

Fig. 4. LC separation on Porapak T of a mixture of octahydrophenanthrene (2), 9,10-dihydrophenanthrene (3) and phenanthrene (4), dissolved in benzene (1). Flow-rate of n-hexane mobile phase, 0.15 ml/min.

determine the use of this material for the selective separation of substances with different molecular polarizabilities. It is a new material suitable for analytical separations as well as preparations, by both the TLC and LC techniques, of pure aromatics hydrogenated to a different degree (Figs. 3 and 4). It is obvious that this finding is of general applicability and will be useful also for substituted aromatic molecules and their hydrogenated analogues.

A disadvantage of organic porous polymers is, up to now, a lower reproducibility of the individual production batches[20].

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REFERENCES

1 O. L. HOLLIS, *Anal. Chem.*, 38 (1966) 309.
2 J. JANÁK, *Chem. Ind. (London)* (1967), 1137.
3 J. JANÁK AND V. KUBECOVÁ, *J. Chromatogr.*, 33 (1968) 132; 48 (1970) 92.
4 M. KREJČÍ, R. VESPALEC AND M. ŠIREC, *J. Chromatogr.*, 65 (1972) 333.
5 J. JANÁK, Z. JAGARIĆ AND M. DRESSLER, *J. Chromatogr.*, 53 (1970) 525.
6 F. M. ZADO AND J. FABEČIĆ, *J. Chromatogr.*, 51 (1970) 37.
7 K. SAKODINSKY AND L. MOSEVA, *Chromatographia*, 1 (1968) 483.
8 T. M. SPOTSWOOD, *J. Chromatogr.*, 2 (1959) 90; 3 (1960) 101.
9 E. MALÝ, *J. Chromatogr.*, 7 (1962) 422.
10 R. H. WHITE AND J. W. HOWARD, *J. Chromatogr.*, 29 (1970) 108.
11 M. KÖHLER, H. GOLDER AND R. SCHIESSER, *Z. Anal. Chem.*, 206 (1964) 430.
12 F. GEISS, H. SCHLITT, F. J. RITTER AND W. M. WEIMAR, *J. Chromatogr.*, 12 (1963) 469.
13 N. KUCHARCZYK, J. FOHL AND J. VYMĚTAL, *J. Chromatogr.*, 11 (1963) 55.
14 G. J. CLEARY, *J. Chromatogr.*, 9 (1962) 204.
15 M. H. ABRAHAM AND R. E. MARKS, *J. Chromatogr.*, 13 (1964) 344.
16 A. J. SOLO AND S. W. PELLETIER, *Anal. Chem.*, 35 (1963) 1584.
17 H. J. PETROWITZ, *Chem.-Ztg.*, 88 (1964) 235; 90 (1966) 627.
18 H. J. PETROWITZ, in G. B. MARINI-BETTÒLO (Editor), *Thin-Layer Chromatography*, 1964, p. 132.
19 J. C. LOCKE, *J. Gas Chromatogr.*, 5 (1967) 202.
20 M. DRESSLER, R. VESPALEC AND J. JANÁK, *J. Chromatogr.*, 59 (1971) 423.