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DEVELOPMENT OF POROUS-LAYER CAPILLARY COLUMNS

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SUMMARY

Procedures for preparing porous-layer capillary columns have been improved and their preparation with kaolin and graphitized carbon black coated with a variety of stationary phases is described. It is shown that an almost theoretical coverage can be achieved and that short columns with high efficiency can be realized. A number of separations (terpenes, essential oils, anilines, chlorocarbons, amines, alkylbenzenes isomers) are reported.

INTRODUCTION

Although most research on open-tubular columns has been devoted to the stabilization of the film on the glass or silica surface to produce coatings of a layer of constant thickness, a different approach has been the deposition on the glass walls of suspended particles in order to replace the original surface with a suitable layer. On the new layer, which does not suffer from the limitations of the glass or silica surface, the stationary phase is then spread. Columns prepared according to this procedure have been designated as porous-layer open tubular (PLOT) columns. A variety of these columns have been described according to the method of preparation and the materials used. Of these, PLOT columns made with kaolin and graphitized carbon black (GCB) have been most extensively investigated¹⁻⁴ and are capable of excellent performance. The two materials have different properties: the former yields a stable, thermally resistance layer upon which a variety of stationary phases can be coated, whereas the latter permits the transfer to capillary columns of the outstanding properties of GCB, extensively used in packed columns.

The preparation of these columns has been further exploited and a number of applications are presented in this paper.

EXPERIMENTAL AND RESULTS

Glass capillary columns were made from Duran glass by means of a Carlo Erba (Milan, Italy) Model GC DM6 drawing machine.

For the preparation of kaolin-coated capillary columns, a suspension of British kaolin was prepared by exposure to ultrasonic waves for 60 min of a mixture of 200 mg of kaolin, 35 cm³ of carbon tetrachloride, 15 cm³ of chloroform and 40 mg of free

fatty acid phase (FFAP), as a dispersing agent. A 2-cm³ volume of this suspension was made to flow forwards and backwards through the capillary columns, this operation being performed twice. After washing the columns twice with 10 ml of dichloromethane, they were dried and conditioned overnight at 400°C under a stream of nitrogen in order to dehydrate the kaolin. This treatment forms a stable layer with good mechanical properties and the columns are ready to be coated with the selected stationary phase.

Graphitized carbon black, a homogeneous non-porous material largely used in packed columns for its regular structure is commercially available from Supelco (Bellefonte, PA, U.S.A.) and can be used for the preparation of PLOT columns. Two procedures are described.

A suspension of GCB, prepared by exposure to ultrasonic waves for 40 min of a mixture of 20 cm³ of carbon tetrachloride, 5 cm³ of dichloromethane, 65 mg of Carbowax A and 7.5 mg of FFAP, was made to flow through the column. The suspension obtained was stable for several days, presumably owing to the action of FFAP. After being washed three times with 10 cm³ of dichloromethane, the column was dried and coated by a procedure similar to that suggested by Simons and Szepesy⁵. The column was filled with a solution of the selected stationary phase dissolved in dichloromethane, closed at both ends and kept at room temperature for 48 h. The solvent was then removed by passing nitrogen through the column and, after being conditioned overnight at a selected temperature, the column was ready for use.

Alternatively, a procedure can be used that involves exposure to ultrasonic waves of the suspension of GCB in a suitable solvent and then bringing the mixture almost to dryness. Next, the selected stationary phase is added with thorough mixing. A solvent is then added and the mixture is coated on the walls by making it flow forwards and backwards for about 10 min under nitrogen.

Special attention must be paid to the selection of the solvent used to prepare the GCB-stationary phase suspension, to prevent the dissolution of the stationary phase. For a GCB column for basic compounds, prepared with Versamide, the following procedure was followed: to 100 mg of GCB 2 cm³ of potassium hydroxide in methanol (0.06 *M*) were added and the suspension was exposed to ultrasonic waves. The solvent was then evaporated and a 12 mg/ml solution of Versamide in chloroform-1-butanol (1:1) added and stirred with the GCB suspension under a flow of nitrogen. The paste was then suspended in 1-butanol-dichloromethane (1:9), and the suspension was coated as described above.

Several stationary phases can be successfully applied on both materials, deposited in glass columns. With kaolin-coated capillary columns high efficiencies have been obtained with SP-2100 and 2340, SE-30, -52 and -54, Carbowax 1500 and 20M, FFAP and Pluronic. Apparently, the stable layer of dehydrated kaolin can be covered with almost any stationary phase. Only with Apiezon L did we meet some difficulties and the use of this phase, because of its aromatic structure, is not recommended. However, it must be pointed out that when kaolin columns must be coated with non-polar phases deactivation with a suitable agent improves their performance. The effect of silylating the kaolin coating with hexamethyldisilazane (HMDS) and with 1,3-diphenyl-1,1,3,3-tetramethyldisilazane (DPTMDS) in two columns subsequently coated with SP-2100 and SE-54 can be seen in Fig. 1 where the HETP value is plotted

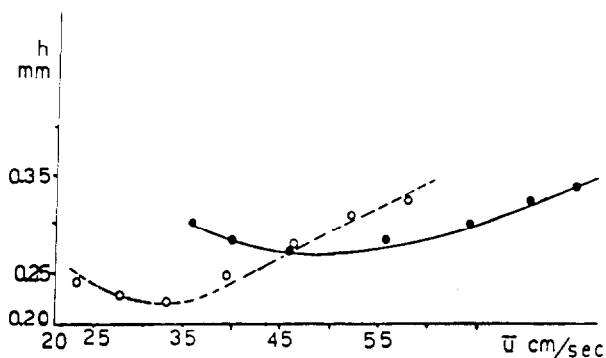


Fig. 1. Height equivalent to a theoretical plate (HETP, h) versus linear velocity (\bar{u}) for pentadecane on pre-coated kaolin silanized columns. Carrier gas hydrogen; temperature 120°C. Columns: ○, 17 m × 0.30 mm I.D., SE-30; ●, 22 m × 0.25 mm I.D., SE-54.

versus the linear gas velocity when hydrogen is used as the carrier gas. With both columns high coating efficiencies have been obtained, *ca.* 100% with the former and 95% with the latter.

GCB offers the unique feature of conferring upon capillary columns multilayer formation, a behaviour observed in packed columns. Thus, they may be operated as gas-liquid-solid or as gas-liquid columns, depending on the amount of the stationary phase. Good performance has been observed with Apiezon L, 1,2,3-tris(2-cyanoethoxy)propane (TCEP), Carbowax 1500 and 20M, Versamide, polyethyleneimine and FFAP.

Plots of HETP versus linear velocity indicate the high efficiency of these columns (Fig. 2). Only the silicone phases did not give satisfactory results on account of the poor wettability of the carbon surface.

Table I summarizes the main characteristics of various kaolin and GCB pre-coated columns in terms of the capacity ratio (k') and coating efficiency (η). It appears that the coating efficiency is in most cases better than 70% and that in some instances the theoretical value is almost reached. One of the main advantages of the procedure described is the ease of preparation. The performance of these columns is demonstrated in various examples. Fig. 3 shows the separation of 24 halogen- and nitro-

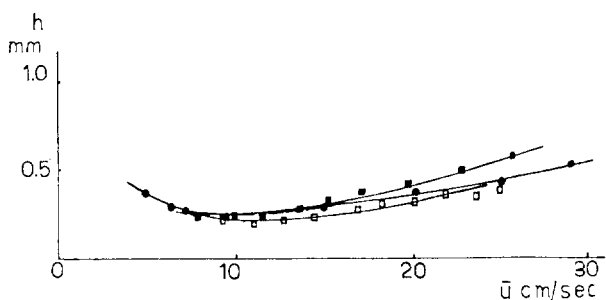


Fig. 2. h vs. \bar{u} for n -alkanes with various phase loads. Column: GCB pre-coated with Carbowax 20M (20–25 m × 0.25 mm I.D.). Carrier gas, nitrogen. Loading: □, 0.04; ■, 0.11; ●, 0.16 mg/m.

TABLE I

CHROMATOGRAPHIC DATA OF KAOLIN (K) AND GRAPHITIZED (GCB) PRE-COATED COLUMNS

Phase	Length (m)	I.D. (mm)	T (°C)	Carrier gas	k'	Plates per metre	η (%)	Sample
K-SP2100*	14	0.25	175	N ₂	5.9	4500	96	Tetracosane
K-SP2100**	22	0.25	120	H ₂	7.5	4540	100	Pentadecane
K-SP2340*	14	0.35	120	N ₂	8.3	2400	73	Methyl margarate
K-SE 54**	17	0.30	120	H ₂	5.8	3700	95	Pentadecane
K-Carbowax 20M	16	0.30	120	N ₂	7.0	3000	79	<i>o</i> -Chloroaniline
K-Carbowax 1500	16	0.30	80	N ₂	5.3	2900	74	<i>o</i> -Nitrophenol
K-FFAP	13	0.35	170	N ₂	13.1	2950	92	Capric acid
K-FFAP	13	0.30	200	H ₂	42.1	3420	87	Stearic acid
K-FFAP	14	0.24	200	H ₂	48.0	3800	86	Stearic acid
GCB-FFAP	10	0.40	100	N ₂	14.8	2170	79	Octadecane
GCB-Apiezon L	14	0.50	120	N ₂	14.0	2000	91	Octadecane
GCB-SP2100	10	0.40	100	N ₂	2.9	2560	79	Eicosane
GCB-Carbowax 20M	10	0.25	110	N ₂	17.7	4160	96	Octadecane
GCB-Carbowax 20M	7.8	0.19	110	N ₂	15.5	5000	85	Octadecane
GCB-Carbowax 20M	9.0	0.14	110	N ₂	18.5	6250	81	Octadecane

* Deactivated with PEG 1500.

** Perylanized.

containing hydrocarbons with a boiling range between 130 and 320°C on a 16-cm kaolin-pre-coated Carbowax 20M column. By operating with temperature programming, separation of all components of the mixture is achieved in about 40 min.

An interesting separation of oxy and bicarboxylic acids, such as lactic, glycolic, succinic, glutaric, aspartic and fumaric acids, without derivatization is shown in Fig.

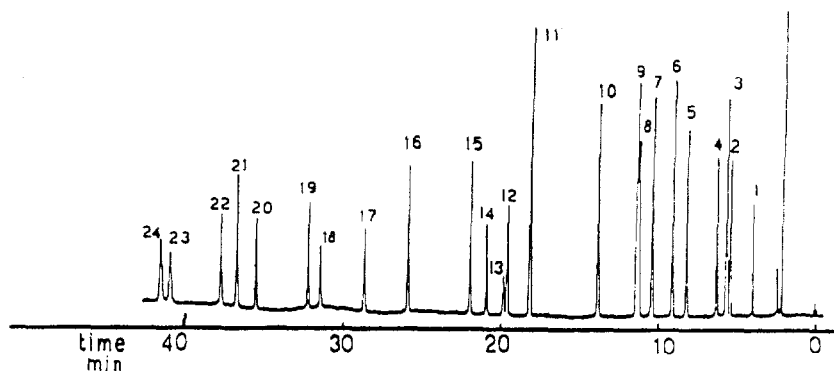


Fig. 3. Gas chromatogram of halogenated and nitro-aromatic hydrocarbons on a 16-m kaolin column coated with Carbowax 20M. Peaks: 1 = chlorobenzene; 2 = *o*-chlorotoluene; 3 = *m*-chlorotoluene; 4 = bromobenzene; 5 = 1,3-dichlorobenzene; 6 = 1,4-dichlorobenzene; 7 = 1,2-dichlorobenzene; 8 = 2,4-dichlorotoluene; 9 = 2,6-dichlorotoluene; 10 = 3,4-dichlorotoluene; 11 = nitrobenzene; 12 = *o*-nitrotoluene; 13 = 1,2,4,5-tetrachlorotoluene; 14 = *m*-nitrotoluene; 15 = *p*-nitrotoluene; 16 = *o*-chloronitrobenzene; 17 = 2,5-dichloronitrobenzene; 18 = hexachlorobenzene; 19 = *p*-nitroanisole; 20 = 2,6-dinitrotoluene; 21 = 1,3-dinitrobenzene; 22 = 2,4-dinitrotoluene; 23 = 2,4-dinitrochlorobenzene; 24 = 1,2-dinitrobenzene.

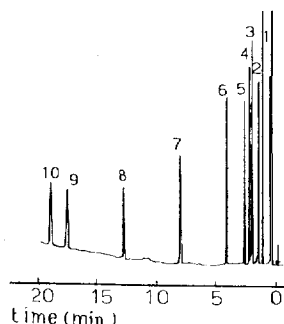
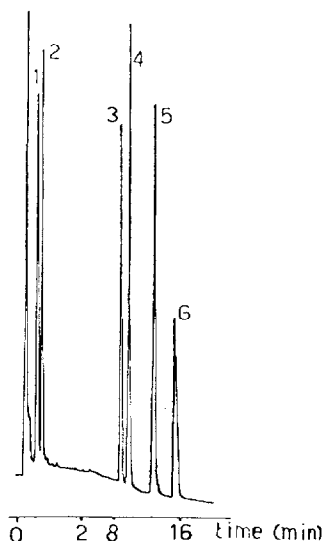


Fig. 4. Gas chromatogram of oxy- and bicarboxylic acids at 200°C on a kaolin-FFAP column (12 m). Carrier gas, hydrogen; \bar{u} = 110 cm/sec. Peaks: 1 = lactic; 2 = glycolic; 3 = succinic; 4 = glutaric; 5 = aspartic; 6 = fumaric acid.

Fig. 5. Gas chromatogram of high-boiling amines on a kaolin-Carbowax 20M column (16 m). Carrier gas, hydrogen. Temperature, programmed from 180 to 260°C at 3°C/min. Peaks: 1 = 2-phenylenediamine; 2 = 4-phenylenediamine; 3 = 3-phenylenediamine; 5 = 2-nitroaniline; 5 = 1-naphthylamine; 6 = 3-nitroaniline; 7 = nitroaniline; 8 = N-phenyl-2-naphthylamine; 9 = benzidine; 10 = *o*-tolidine.

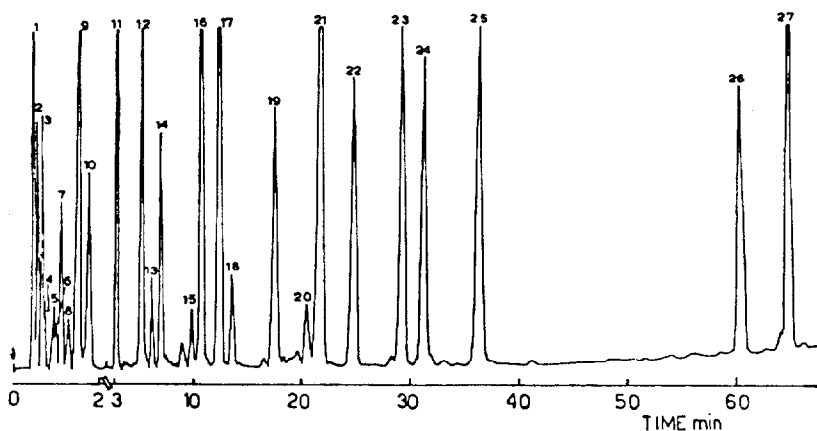


Fig. 6. Gas chromatogram of a terpene mixture on a kaolin-Carbowax 1500 column (7 m). Carrier gas, hydrogen. Peaks: 1 = α -pinene; 2 = camphene; 3 = β -pinene; 4 = sabinene; 5 = myrcene; 6 = α -terpinene; 7 = limonene; 8 = 1,8-cineole; 9 = γ -terpinene; 10 = *p*-cymene; 11 = 3-octyl acetate; 12 = 3-octanol; 13 = neryl oxide; 14 = camphor; 15 = β -caryophyllene; 16 = bornyl and linalyl acetate; 17 = linalool; 18 = 4-terpinenol; 19 = neral; 20 = borneol; 21 = geraniol and α -terpineol; 22 = geranyl acetate; 23 = citronellol; 24 = nerol; 25 = geraniol; 26 = eugenol; 27 = thymol.

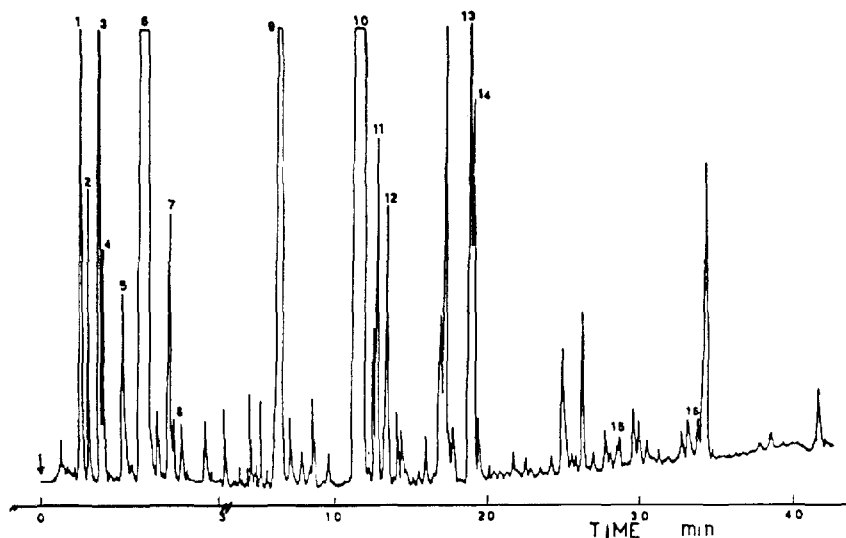


Fig. 7. Gas chromatogram of lavender essential oil on a kaolin-Pluronic 64 column (9 m). Carrier gas, hydrogen. Temperature, programmed from 40°C at 1°C/min. Peaks: 1 = α -pinene; 2 = camphene; 3 = β -pinene; 4 = sabinene; 5 = myricene; 6 = 1,8 cineole; 7 = γ -terpinene; 8 = *p*-cymene; 9 = camphor; 10 = linalool; 11 = 4-terpineol; 12 = linalyl acetate; 13 = borneol; 14 = α -terpineol; 15 = nerol; 16 = geraniol.

4. It was obtained on a 12-m kaolin-pre-coated FFAP column in about 15 min.

Fig. 5 shows the gas chromatogram of a mixture of high-boiling amines with a boiling range between 256 and 400°C. The chromatogram was obtained in about 20 min on a Carbowax 20M kaolin-pre-coated column.

The analysis of essential oils is difficult on account of the large number of components with a wide boiling range. Usually, they are analysed by using long columns, which require long analysis times. The high efficiency obtained with PLOT columns gives remarkable analytical results by operating with short column at fairly low temperature. A typical example is the analysis of an artificial mixture of terpenes,

TABLE II

CAPACITY RATIOS OF TERPENES ON GCB-PRE-COATED COLUMNS OF THE SAME DIAMETER WITH DIFFERENT CARBOWAX 20M LOADS

Terpene	Carbowax 20M load (mg/m)			
	0.04	0.08	0.12	0.16
<i>d</i> -Camphor	0.83	1.73	3.58	4.48
Decanal	0.95	1.81	3.60	4.15
α -Terpineol	2.28	5.33	11.02	13.18
Citronellyl acetate	2.55	4.22	10.70	12.90
Dihydrocarvacrol	2.97	7.36	16.12	18.38
Neryl acetate	3.55	7.02	15.34	17.87

likely to be found in most essential oils. The chromatogram shown in Fig. 6 was obtained on a 7-m column by injecting the sample at 50°C and then programming the temperature at 1°C/min. Almost all terpenes are separated, with the exception of bornyl and linalyl acetate and of α -terpineol and geraniol, the highest temperature reached being 120°C. Essential oils can thus be analysed. Fig. 7 is a chromatogram of lavender oil obtained on a kaolin-pre-coated 9-m Pluronic column by operating at a temperature below 80°C, which is a protection against thermal decomposition. It is worth mentioning that on account of their high load capacity columns with a small diameter can be used.

The most interesting feature of GCB-pre-coated columns is that they may be operated in the gas-liquid-solid and gas-liquid modes, depending on the amount of stationary phase. A practical procedure for classifying a GCB-pre-coated column and for evaluating its behaviour in terms of multilayer deposition consists in obtaining a chromatogram of a mixture of xylene isomers. Because adsorption on the graphite faces of the polyhydral particles of GCB is non-specific, separation of isomeric species occurs as a result of geometric differences between molecules. The order of elution of the isomers from the GCB naked surface is *m*-, *o*-, *p*-xylene. On gradual addition of a stationary phase, the *para*-isomer is less retained and the elution order becomes *m*-, *p*- and *o*-xylene⁶⁻⁸. Further increases in stationary phase decrease retention time, and the elution order becomes *p*-, *m*-, *o*-xylene. The latter corresponds to gas-liquid chromatographic (GLC) behaviour, whereas the former may be attributed to gas-liquid-solid chromatography (GLSC).

The importance of multilayer formation and its impact on the separation of different mixtures can be observed by examining the behaviour of some pairs of terpenes with different geometry. They were chromatographed on GCB-pre-coated Carbowax 20M columns with different amounts of stationary phase (Table II). By increasing the stationary phase load the order of elution is reversed as columns 1 and 2 operate in the GLSC mode, whereas columns 3 and 4 show GLC behaviour.

GCB-pre-coated columns yield excellent performance; an example is the sepa-

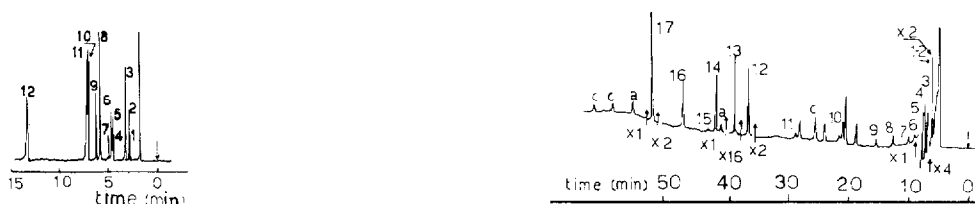


Fig. 8. Gas chromatogram of halogenated amines on a GCB-Carbowax 20M column (25 m). Carrier gas, nitrogen; temperature 130°C. Peaks: 1 = *o*-chloroaniline; 2 = 2-chloro-5-methylaniline; 3 = *o*-bromoaniline; 4 = *m*-chloroaniline; 5 = *p*-chloroaniline; 6 = 3-chloro-2-methylaniline; 7 = 4-chloro-2-methylaniline; 8 = 2,4-dichloroaniline; 9 = 2,5-dichloroaniline; 10 = *p*-bromoaniline; 11 = *m*-bromoaniline; 12 = *p*-iodoaniline.

Fig. 9. Gas chromatogram of caramel aroma trapped in water and analysed on an FFAP column. Temperature: isothermal for 7 min, then programmed at 2°C/min up to 150°C. Peaks: 1 = acetone; 2 = methyl acetate; 3 = ethyl acetate; 4 = methanol; 5 = ethanol; 6 = ethyl propionate; 7 = valeraldehyde; 8 = 1-propanol; 9 = 1-butanol; 10 = 1-pentanol; 11 = 1-hexanol; 12 = acetic acid; 13 = furfural; 14 = propionic acid; 15 = isobutyric acid; 16 = methylfurfural; 17 = isovaleric acid; a = unidentified acid; c = unidentified carbonyl compound.

ration of halogenated amines, carried out under isothermal conditions on a GLSC column (0.04 mg/m Carbowax 20M) (Fig. 8).

An interesting application is the use of these columns for aroma evaluation. Because in this instance a variety of compounds must be analysed, a multi-purpose column is desired. Fig. 9 shows the gas chromatogram of a caramel aroma, trapped in water and analysed on an FFAP column. The main components are ethyl acetate, methanol, ethanol, acetic acid and furfural, and the minor ones are acetone, methylfurfural, valeraldehyde and propionic acid.

CONCLUSION

PLOT columns have a wide range of applications and offer a number of attractive features. They are easily manufactured, as their preparation does not involve critical steps. Excellent performance is obtained by using short columns with a large variety of stationary phases. They exhibit good efficiency. Depending on the amount of stationary phase very versatile columns can be prepared as they may be operating in adsorption as well as in the GLC modes.

REFERENCES

- 1 G. Goretti, A. Liberti and G. Nota, *Chromatographia*, 8 (1975) 486-490.
- 2 G. Goretti, A. Liberti and G. Pili, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 1 (1978) 143-148.
- 3 G. Goretti, F. Geraci and M. V. Russo, *Chromatographia*, 14 (1981) 285-288.
- 4 G. Goretti, A. Liberti, M. V. Russo and J. Laencina Sanchez, *J. Chromatogr.*, 245 (1982) 109-113.
- 5 J. Simons and L. Szepesy, *J. Chromatogr.*, 119 (1976) 495-504.
- 6 I. Halász and Cs. Horváth, *Anal. Chem.*, 36 (1964) 2226-2229.
- 7 G. Goretti, A. Liberti and G. Nota, in C. L. A. Harbourn (Editor), *Gas Chromatography 1968*, Institute of Petroleum, London, 1969, pp. 22-30.
- 8 M. F. Gonnard, C. Vidal-Madjar and G. Guiochon, *J. Chromatogr. Sci.*, 12 (1974) 839-943.