Journal of Chromatography, 299 (1984) 139–149
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

CHROM. 16,839

POLYIMIDE CAPILLARY COLUMN FOR GAS–LIQUID CHROMATOGRAPHY

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(Received April 3rd, 1984)

SUMMARY

A new principle and method have been developed for producing a high-efficiency WCOT column by forming a polyimide capillary tube of 1–5 μm wall thickness inside a supporting glass capillary (tube-in-tube system). This polyimide layer is chemically resistant, heat-proof (up to 450°C) and mechanically stable. Adsorption on the silica surface can be virtually eliminated using this polyimide column. The preparation of the column is simpler than usual because it is not necessary to use pre-treatment or deactivation procedures. The polyimide tube can be coated easily with polar and apolar stationary liquids by dynamic or static coating methods.

The wettability, thermal stability, character of interactions between Carbowaxes and the polymer surface and the adsorption effect of the polyimide tube were investigated. The performance of some polyimide capillary columns is demonstrated with different examples.

INTRODUCTION

Important aims in capillary gas chromatography are to overcome the excess sorption effects on the silica surface and to increase the wettability of the support. In practice, several physical and chemical processes are used in treating the surface and forming new non-silica surfaces, especially silylation with polar silylating reagents for deactivation of free silanol groups on the glass surface[1–3], etching the surface with different acids[4,5] and the utilization of various surface-active materials. However, the best results were obtained by covering the internal surface with a carbon layer[6–10] and by the formation of a barium carbonate layer, as suggested by Grob and Grob[11,12]. Significant progress was made through the introduction of quartz capillaries and fused-silica columns.

The unfavourable adsorption effect of glass or quartz surfaces can only be

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0021-9673/84/$03.00

eliminated, in our opinion, by the total elimination of the silica surface. This principle led us to construct a polyimide capillary column for utilization in gas–liquid chromatography[13,14].

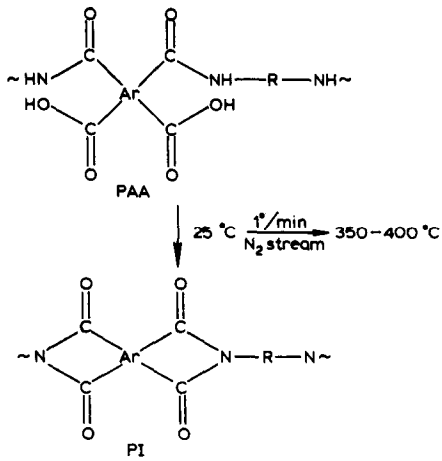
EXPERIMENTAL

Formation of polyimide capillary columns

Various polyimides have been utilized in gas chromatography. Scientific Glass Engeneering (SGE, North Melbourne, Australia) and Perkin-Elmer (Norwalk, CT, U.S.A.) use them to cover the outside of quartz capillaries. Mathews *et al.*[15] recommended some polyimides of relatively low melting point as stationary phases in high-temperature gas chromatography. The use of polyimides as capillary tubes seemed to be a favourable possibility for the elimination of the silica surface because of their outstanding heat stability and their good wettability by common stationary phases. However, the production of capillary columns of sufficient length and diameter from polyimides has not been achieved and, to our knowledge, it is impossible to prepare capillaries of this type without a support because the rheological character of the material does not permit long capillary tubes to be formed either before or after imidization. We therefore prepared a glass capillary in the traditional way and covered its inner surface with a 1–5 μm polyimide layer so that it completely covered the silica surface. This tube-in-tube system serves as a polyimide capillary and the cross-section of such a column is shown in Fig. 1.

The internal polyimide tube can be prepared in two steps: (1) preparation of a polyamide acid (PAA) layer and (2) its imidization.

For the preparation of a PAA layer, the supporting glass (or metal) capillary has to be filled with PAA solution (solvents: N-methylpyrrolidone, N,N-dimethylacetamide, dimethylformamide). After equilibration of the system for 1 day at room temperature, the solution is removed slowly and a uniform PAA layer is formed. The excess of solvent is evaporated by a stream of dry nitrogen (or vacuum). Then slow heating (1°C/min) is applied up to 350–400°C and a continuous polyimide (PI) layer is formed in the following polycondensation reaction:



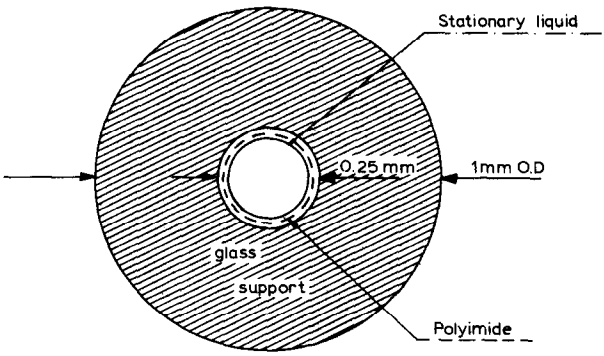


Fig. 1. Cross-section of a polyimide capillary.

In this work, the PAA used was prepared by polycondensation of pyromellic acid dianhydride and 4,4'-diaminodiphenyl ether. The thermal characteristics of this product and other derivatives were investigated in detail[16]. The above-mentioned careful heating programme is very important for slow evaporation of the water arising form the reaction without blistering the layer. By using different Ar or R groups the surfaces formed have different chemical and physical properties, so their wettability and heat stability can also be changed.

The adhesion of polyimide to the glass surface is very good especially if the layer is not thicker than 50 μm. Microscopic examinations showed that even thin layers of 1–10 μm show good adhesion and a fully continuous layer.

In order to determine the characteristics of the polyimide capillary column, the following experiments were carried out: (1) investigation of the wettability of the PI surface with common stationary liquids; (2) study of the chemical behaviour forwards acids, bases and organic solvents; (3) investigation of the interaction between Carbowaxes and PI with the help of "thermal evaluation analysis" (TEA) and IR spectrophotometry; (4) examination of thermal decomposition; and (5) study of the adsorption behaviour of PI.

Thermal analytical measurements

TEA and differential thermogravimetric (DTG) measurements were made on DuPont TEA and DuPont 990 systems, respectively. Pieces 1–5 mm long broken from a ready-made 10-cm capillary were used as samples.

Infrared spectrophotometry

A Varian FTS-14 instrument was used for measurements between 1550 and 4000 cm^{-1}.

Gas chromatography

Gas chromatographic analysis was performed using a Pye Model 105 gas chromatograph with home-made low dead-volume flame-ionization detector.

RESULTS AND DISCUSSION

To study the wettability of the polyimide surface, polyimide layers of about 20 μm thickness were prepared on microscopic slides. With the help of a heated objective table, the samples were thermostated 5–10°C above the minimum operating limit of the stationary phases examined. One droplet of a 1% stationary phase solution or the stationary phase alone was placed on each slides. For the twenty stationary phases of different polarity studied it was found that those which have a McReynold's constant of less than 500 for 1-butanol spread very well on the PI surface. The coverage by Carbowax 400 is poor but the estimated contact angle remains less than 30°. β,β'-Oxydipropionitrile and water did not wet the given surface (other polyimide layers containing polar R groups were also prepared and were wetted very well by even fully polar stationary liquids). Estimates based on the literature[5] suggest that the surface tension of the PI investigated may be between 30 and 40 dyn/cm.

The effect of various chemicals on polyimide layers on glass sheets: was studied by immersing the sheets in the liquid reagents. We found that the layer did not dissolve, swell or shrink and there was no change after immersion for 24 h in organic solvents such as *n*-hexane, benzene, carbon tetrachloride, chloroform, acetone, tetrahydrofuran, ethanol, phenol, pyridine or nitromethane. Strong bases cause them to deteriorate slowly and they dissolve in concentrated nitric acid. When left in hot water for a long period they start to shrink. However, polyimide capillaries are not

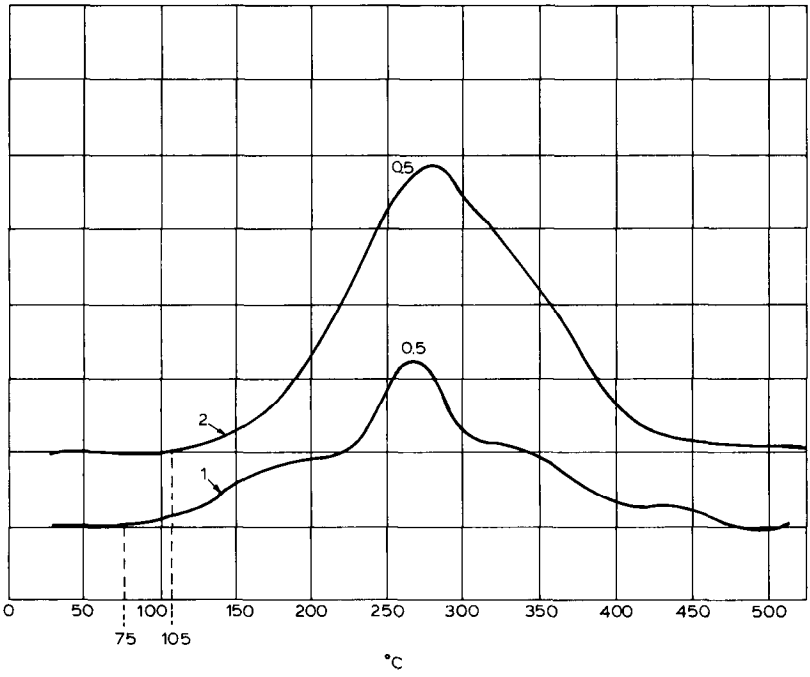


Fig. 2. TEA curves of Carbowax 400 on glass and polyimide surfaces. Heating rate, 32°C/min; flow-rate (nitrogen), 1.8 l/h. 1, Glass + Carbowax 400; 2, glass + PI + Carbowax 400.

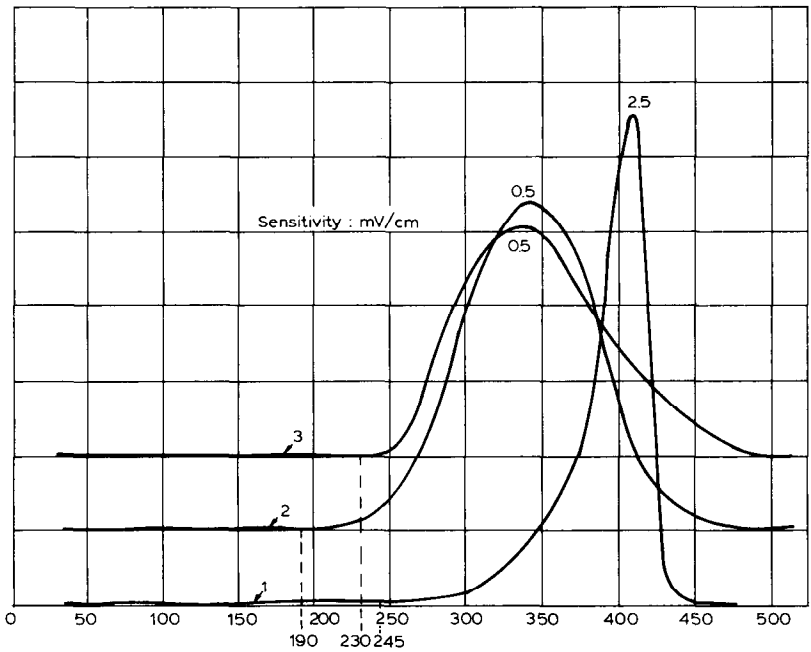


Fig. 3. TEA curves of Carbowax 4000 on glass and polyimide surfaces and of Carbowax 4000 particles. Conditions as in Fig. 2. 1, Carbowax 4000; 2, glass + Carbowax 4000; 3, glass + PI + Carbowax 4000.

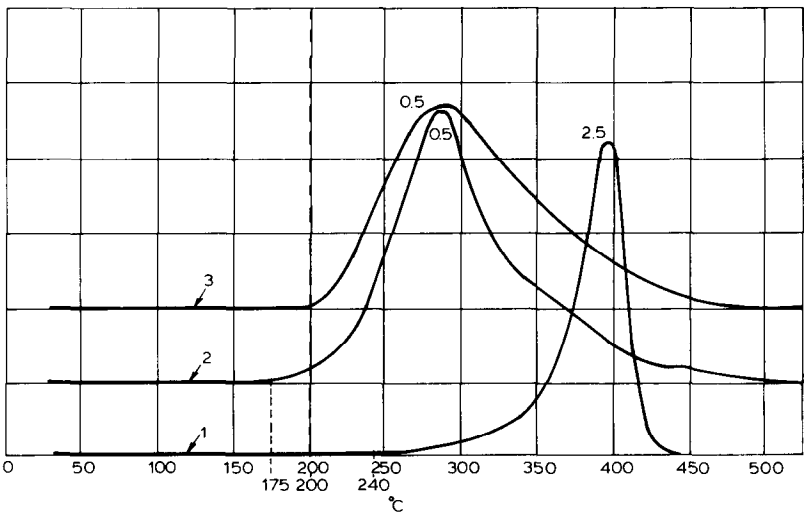


Fig. 4. TEA curves of Carbowax 20M on glass and polyimide surfaces and of Carbowax 20M particles. Conditions as in Fig. 2. 1, Carbowax 20M; 2, glass + Carbowax 20M; 3, glass + PI + Carbowax 20M.

exposed to such extreme attack in chromatography and consequently it can be said that after carbon layers the polyimide tube is the column material most resistant to chemical agents.

In addition to Van der Waals interactions between Carbowaxes and the PI surface, hydrogen-bridge structures were considered to be formed. The TEA and IR investigations seem to support this hypothesis. Figs. 2–4 show results of TEA measurements, which suggest a hydrogen-bridge interaction in the PI–Carbowax system. For comparisons the TEA curves of Carbowaxes on glass and the vaporization curves of pure Carbowax 400 and Carbowax 20M are shown. It can be seen that Carbowax 400 starts to evaporate 30°C, Carbowax 4000 40°C and Carbowax 20M 25°C higher than from the glass (borosilicate) surface, presumably owing to the stronger character of the interactions (1–5 mm long pieces of capillaries were used as samples).

Fig. 5 shows the Fourier-transform IR spectra of (a) a glass sheet covered with PI and (b) a PI resin sheet wetted with Carbowax 20M (in order to avoid the disturbing effect of glass the range above a wavelength of 1550 cm^{-1} was investigated). The bands at 1765 and 1720 cm^{-1} correspond to typical lines of carbonyl groups in this range. At the same position in spectrum (b) a broad, stretched line of lower intensity can be observed with a peak around 1700 cm^{-1}. The fact that the peak shifted towards shorter wavelengths and its intensity decreased suggests that the number of free carbonyl groups had significantly decreased owing to the formation of hydrogen bridges.

Fig. 6 shows the heat stability of PI capillaries. Two peaks can be seen: at around 610°C a rearrangement takes place in PI due to the loss of CO and CO_2, and at 650°C the remaining part of PI is oxidized at maximum speed (graphite is the

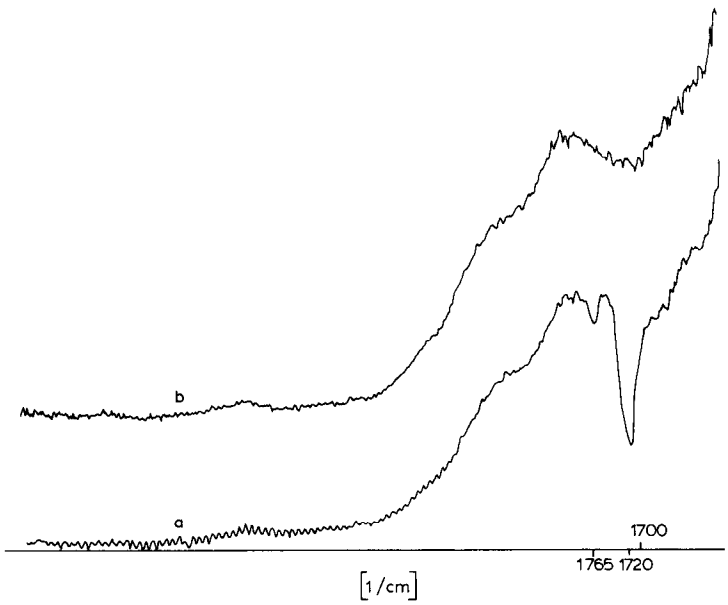


Fig. 5. Fourier-transform IR spectrum of a Carbowax 20M layer: (a) polyimide layer on a glass surface without Carbowax 20M and (b) with Carbowax 20M.

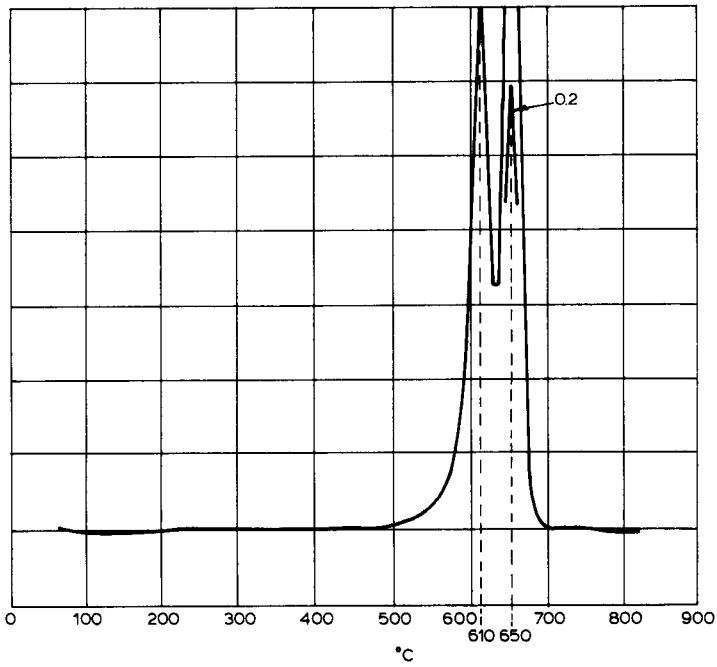


Fig. 6. Polyimide DTG curve. Heating rate, 10°C/min; flow-rate (air) 10 l/h.

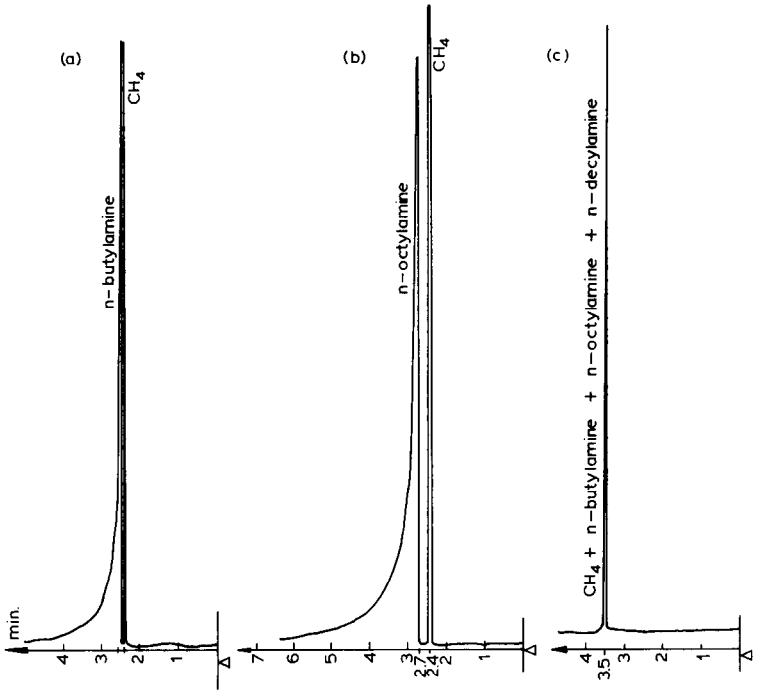


Fig. 7. Chromatograms of methane and some alkylamines obtained with an empty glass capillary column (a and b) and a polyimide capillary (c). Columns, 45 × 0.5 mm I.D.; 120°C.

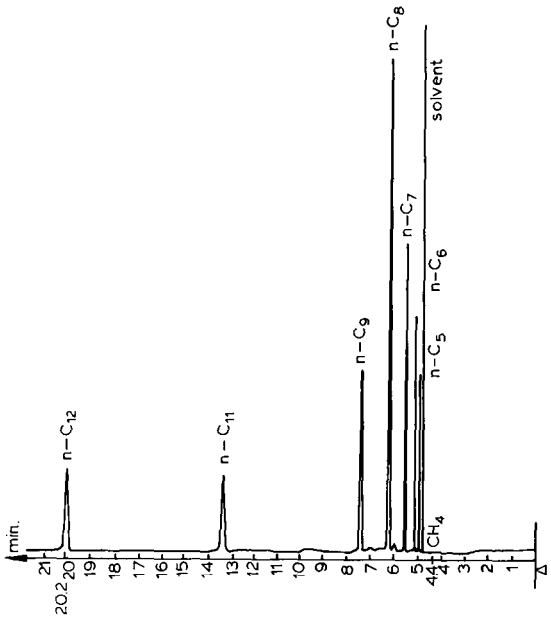


Fig. 8. Chromatogram of a hydrocarbon mixture on an OV-101 polyimide capillary column (20 m × 0.5 mm I.D.). Column temperature, 122°C; carrier gas (nitrogen) pressure, 25 kPa; flow-rate, 7.6 cm/sec.

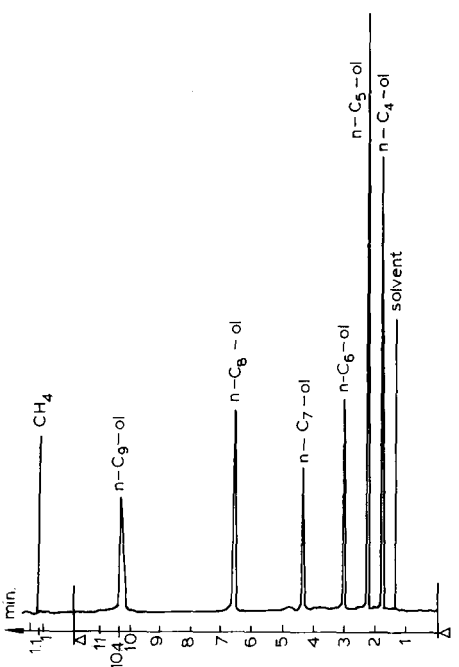


Fig. 9. Chromatogram of an alcohol mixture on a Carbowax 20M polyimide capillary (20 m × 0.5 mm I.D.). Column temperature, 122°C; nitrogen pressure, 37 kPa; flow-rate, 30.3 cm/sec.

TABLE I

CHARACTERISTICS OF DYNAMICALLY COATED PI CAPILLARY COLUMNS

Column length, 20 m; I.D., 0.5 mm.

Parameter	*OV-101* (n-C_{12})	*Carbowax 20M* (n-C_9OH)
k'	3.6	8.5
N	72,583	43,264
N/m	3626	2163
TZ	26 (C_{11}–C_{12})	25 (C_9OH–$C_{10}OH$)
η	70.7%	100%

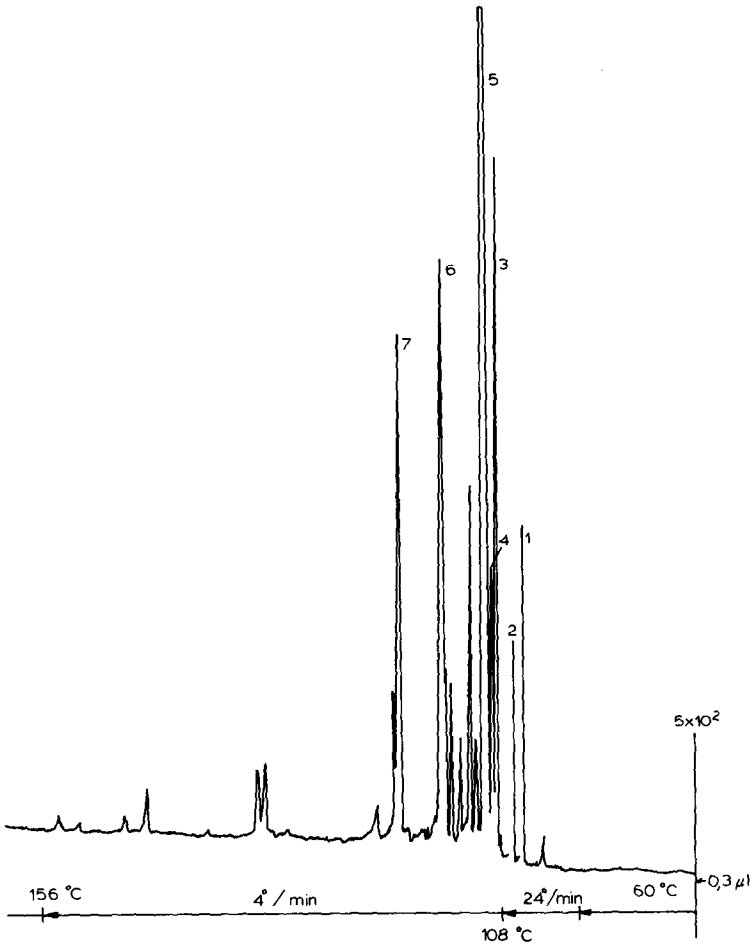


Fig. 10. Chromatogram of the volatile oil fraction of *Tagetes signata* treated with cold NaOH. The polyimide capillary column (12 m × 0.25 mm I.D.) contained SE-30 as the stationary phase with a film thickness of 0.4 µm. Temperature programme: 60°C for 3 min, increased linearly at 24°C/min for 2 min, then at 4°C/min to 156°C. Main components: 1 = β-pinene; 2 = myrcene; 3 = limonene; 4 = β-phellandrene; 5 = 2-methylbutadienyl 3-methylbutyl ether; 6 = *l*-menthol; 7 = tagetone.

TABLE II

CHARACTERISTICS OF A STATICALLY COATED SE-30 PI CAPILLARY COLUMN

Parameter	*n*-C_{10}	*n*-C_{11}
k'	11.7	16.6
N	89,400	87,468
N/m	7450	7289
TZ	20.6	20.6
η	60%	60%

end-product in an oxygen-free atmosphere). As shown in Fig. 6, thermal decomposition starts only above 450–460°C.

By studying the adsorption characteristics of the inner surface of PI capillaries using a test mixture containing butyl-, octyl- and decylamine it was found that this mixture of amines gives only a single, symmetrical peak with the same retention time as methane. In contrast, these compounds can adsorb strongly on a glass surface, and consequently an asymmetric peak shape and poor separation are observed (Fig. 7). This test method gives the possibility of establishing whether a free, uncovered silica surface was left in the column, and at the same time the narrow symmetrical amine peaks show negligible adsorption on PI. It was found that a PI tube with a wall thickness as low as 1 μm covers the support surface (the wall thickness was calculated based on the amount of PAA remining in the column).

Some examples

Figs. 8 and 9 show chromatograms of *n*-alkane and synthetic alcohol mixtures on OV-101 and Carbowax 20M PI columns coated by the dynamic method. Table I summarizes the most important parameters such as the capacity ratio (k'), number of theoretical plates (N), number of theoretical plates per metre (N/m), the separation number (TZ) and the coating efficiency (η) used for the evaluation of the performance characteristics of the columns.

In accordance with general practical experience, much more efficient columns can be prepared by the static coating method. Fig. 10 shows a chromatogram of a plant oil (extract of *Tagetes signata*) as an example on a 12 m × 0.25 mm I.D. SE-30 PI column with a calculated SE-30 film thickness of 0.4 μm. The main characteristics of this column are given in Table II.

CONCLUSIONS

The results show that a polyimide layer can be used to prepare an efficient "tube-in-tube" capillary column system. A polyimide tube with a wall thickness 1 μm is sufficient to cover the supporting glass surface and give an entirely smooth surface free from undesirable adsorption effects. This surface is resistant to chemicals and does not dissolve or swell in organic solvents. Because of its medium surface tension and its polar and apolar functional groups it can also be wetted very well by polar and apolar stationary liquids. PI can be used over a wide temperature range

because of its good heat stability (its decomposition starts only above 450°C). Only 0.1–0.2 mg/m of PAA is needed for its preparation, so it is inexpensive and can easily be made in the laboratory. It should also be emphasized that the supporting glass capillary does not need any special treatment, and consequently it is very easy to prepare a column.

Some further surface investigations are required in order to obtain additional data on the polyimide surfaces (*e.g.*, electron microscopy). We also plan to investigate the performance of columns wetted with different stationary liquids. It is to be expected that as a consequence of interactions with a non-silica surface the McReynold's constants of some stationary phases will be different from those obtained on Chromosorb supports or on the capillary columns used so far.

ACKNOWLEDGEMENTS

The authors thank Dr. V. Izvekov for obtaining the IR spectra, Dr. J. Kömives for the thermal analytical measurements and A. Kurtán for valuable technical assistance.

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