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Gas–liquid microcapillary columns precoated with graphitized carbon black

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ABSTRACT

Glass and fused-silica capillary columns (100 μm I.D.) were precoated with a very thin layer of graphitized carbon black and then coated with polar liquid phases. The layer of carbon black in the inner walls increased the wettability of the capillary columns and, consequently, a very uniform coating was obtained. The polymeric polar liquid phases were also more strongly retained on the carbon black, and these microcapillary columns showed a much higher temperature stability. Columns coated with free fatty acid phase, Carbowax 20M, 40M and 600M were prepared. The columns were tested with a mixture of polar compounds.

INTRODUCTION

Capillary columns with internal walls modified by a thin layer of graphitized carbon black (GCB) have been used in gas chromatography (GC) for a long time. They have been the object of many studies since they present very high efficiencies, are simple to prepare and because it is possible to change their selectivity by varying the stationary phase charge, thus allowing operations in both gas–liquid chromatographic and gas–solid–liquid chromatographic contexts [1–13].

Until now research has been carried out mainly with graphitized columns with an I.D. of 200–500 μm, although promising results have been obtained with columns of 150–160 μm I.D. [6,7]. Microcapillary columns (I.D. < 200 μm) are, as has recently been shown, characterized by a large number of theoretical plates (N) per metre and per second. Moreover, they present mass transfer resistance values (C) such as to allow analytical separation even at high linear velocity values. The main constraint on their use has been the insufficient rate of response of detectors and recorders, which may by now be largely regarded as outdated by modern equipment standards. At present, the only hindrance to their use is the sampling rate. In fact, when such high values per second for theoretical plates are reached ($N/s = 10^4$), with columns of 50 μm I.D. the sampling rate becomes a strongly limiting factor, especially for the separation of substances having low retention time [14–28].

This study describes the technique for preparing microcapillary columns precoated with Carbopack A, of 100 μm I.D., and then coated with polar stationary phases, reaching high efficiency. Some complex-mixture separations are reported.

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Moreover, particular attention has been devoted to the possibility of using these microcapillary columns for aromatic and aliphatic amines, given the promising results obtained on classical capillary columns precoated with GCB [29].

EXPERIMENTAL

Equipment

Two DANI gas chromatographs were used, Model 3900 and Model 6500 (Monza, Italy), equipped with a flame ionization detector and split injector with 1:500 split ratio, and connected to a Shimadzu CR3A integrator–recorder.

Preparation of microcapillaries

Glass capillaries with 100 μm I.D. were obtained from Duran glass tubes cleaned with a solution of sulphuric acid (96%)–0.1 *M* potassium dichromate for 48 h, washed extensively in water and acetone and then dried. After this treatment, the tubes were drawn using a Carlo Erba GCDM 60 drawing machine. The 100 μm I.D. glass capillaries thus obtained were washed in dichloromethane and dried under nitrogen flow. The fused-silica capillaries were supplied by SGE (Australia).

The columns were precoated with a solid support, Carbopack A (Supelco, Bellefonte, PA, U.S.A.), a GCB having a surface area of around 12 m^2/g. The dynamically deposited support increased the surface area with respect to the smooth capillary, increasing stationary phase wettability. This allowed a uniform deposit of the stationary phase to be obtained. Support depositing was carried out with a GCB suspension prepared with 50 mg GCB, 25 ml carbon tetrachloride, 25 ml dichloromethane and then exposing to ultrasonic waves for about 30 min. Approximately 2 ml of this suspension were made to flow at high speed (*ca.* 60 cm/s) through the capillary for four times in succession, each time reversing flow direction and waiting for solvent evaporation. The support layer of GCB obtained inside the capillary was then thermically treated with Carbowax 20M (C 20M). This pretreatment was carried out by statically depositing C 20M from a 0.2% solution in dichloromethane. After conditioning in a flow of hydrogen for about 10 min at a temperature of 240°C, the column was put into the oven at a temperature of 280°C for one night, after having sealed both ends under a flame. The column was cooled to room temperature and then washed with dichloromethante. Pretreatment with C 20M probably increases the wetability of capillary internal surface for polar stationary phases, deactivates the walls and makes the GCB surface uniform.

After undergoing this treatment, the column is statically coated with the stationary phase. Using a concentrated solution enabled the desired film thickness to be obtained. The columns were conditioned by programming the temperature to increase by 3°C min from 50°C to 240°C and keeping the column at the latter temperature for 90 min under hydrogen flow. Microcapillary columns were prepared using different stationary phases: C 20M, C 40M, C 600M and free fatty acid phase (FFAP). Assessment of GC parameters of the columns was carried out by GC of a mixture of *n*-octanol, 2,6-dimethylphenol (DMF) and 2,6-dimethylaniline (DMA) at 90°C. In the reported analysis hydrogen, as carrier gas, is used with a linear gas velocity of the values given in Table I.

TABLE I

COLUMN CHARACTERISTICS (I.D. 100 μm)

C = Carbowax; FFAP = free fatty acid phase; DMA = 2,6-dimethylaniline, DMF = 2,6-dimethylphenol.

Column No.	Phase	Length (m)	D_f (μm)	k'	U_{opt} (cm/s)	H_{min} (mm)	N/s	UTE (%)	Test substance
1	C 20M	5.7	0.10	52.2	52.6	0.109	4830	87	DMA
2	C 20M	16.0	0.07	51.1	54.2	0.091	5960	100	DMA
3	C 40M	5.5	0.10	57.9	50.2	0.116	4330	82	DMA
4	C 40M	5.5	0.20	87.0	55.0	0.110	5050	87	DMA
5	C 40M	4.6	0.10	85.2	54.0	0.116	4660	81	DMF
6	C 40M	7.2	0.10	45.1	51.1	0.087	5870	100	DMA
7	C 600M	6.0	0.07	49.3	57.3	0.103	5560	93	DMA
8[a]	C 600M	15.0	0.07	49.3	56.6	0.094	6020	100	DMA
9[a]	C 600M	10.0	0.07	61.9	54.3	0.088	6130	100	DMA
10	FFAP	8.5	0.07	58.9	60.7	0.115	5280	82	DMF

[a] Fused silica.

RESULTS AND DISCUSSION

Fig. 1A and B shows the effects due to pretreatment with C 20M. The gas chromatograms were obtained at 90°C by injecting the mixture of DMF, DMA and *n*-octanol on two glass columns with stationary phase C 40M. The chromatogram in Fig. 1A was obtained on a column not pretreated with C 20M, while the one in Fig. 1B was obtained on a column pretreated with C 20M. As may be observed in Fig. 1A,

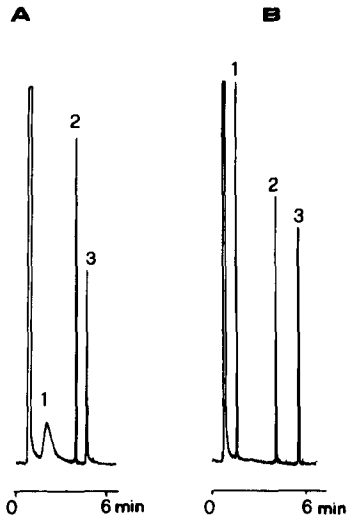

Fig. 1. Gas chromatograms of polar compounds on two columns: (A) not pretreated by C 20M; (B) pretreated by C 20M at 90°C. Peaks: 1 = *n*-octanol; 2 = DMA; 3 = DMF.

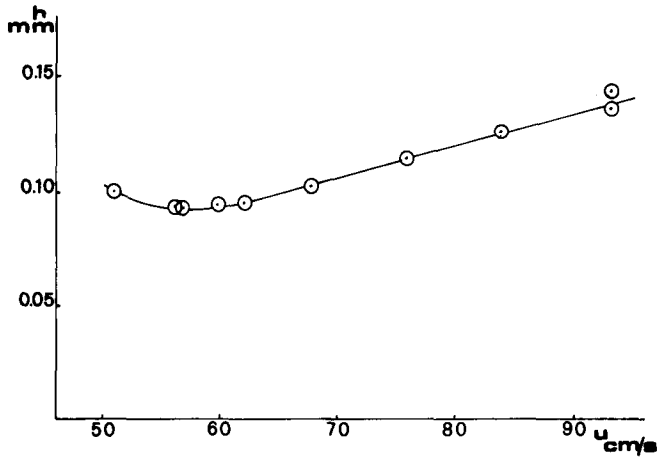

Fig. 2. Van Deemter plot of DMA at 90°C. Column 7 of Table I.

the octanol peak is considerably deformed and the DMF peak shows a slight tail. In Fig. 1B, all the peaks are symmetrical.

Table I shows the GC characteristics of some columns that were pretreated and coated with a polar stationary phase. Theoretical plate height (H_{min}), capacity ratio (k'), liquid film thickness (D_f), optimum linear velocity (U_{opt}), utilized theoretical efficiency (UTE%) and number of plates per second (N/s) are reported for each column. From the results in the table, all the columns show UTE values that lie between 82 and 100%, H_{min} values ranging from 0.08 to 0.116 mm, with optimum linear velocities between 50 and 60 cm/s and N/s values between 4400 and 6000.

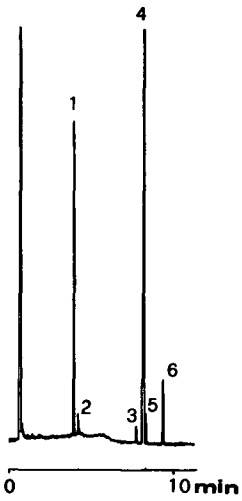

Fig. 3. Olive oil analysis on column 3 of Table I (C 20M), fatty acid methyl esters. Peaks: 1 = palmitic; 2 = palmitoleic; 3 = stearic; 4 = oleic; 5 = elaidinic; 6 = linoleic acid. Temperature 180°C.

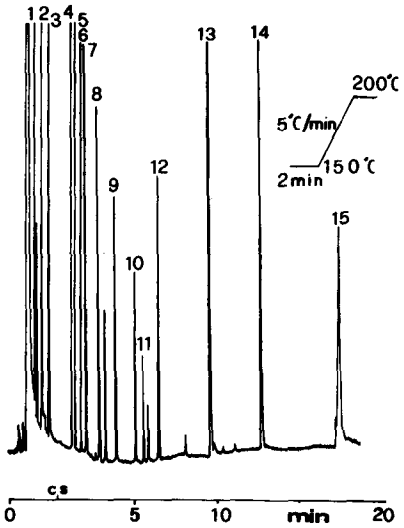

Fig. 4. Gas chromatogram of free fatty acid mixture. Column 9 of Table I. (FFAP) Peaks: 1 = acetic; 2 = propionic; 3 = butyric; 4 = valeric; 5 = caproic; 6 = heptanoic; 7 = caprylic; 8 = pelargonic; 9 = capric; 10 = undecenoic; 11 = undecylenic; 12 = lauric; 13 = myristic; 14 = palmitic; 15 = stearic acid.

Fig. 2 shows the Van Deemter curve obtained on column, 7 of Table I at a temperature of 90°C. Note that, even if linear velocity is considerably increased, efficiency still remains high. In fact, the mass transfer term (C) of this column is $15 \cdot 10^{-5}$ s. The temperature stability of these columns is higher than that of the columns coated with the same phases without GCB precoating and is similar to that obtained with the same bonded phases [30].

Some examples of complex mixture analysis carried out on these microcapillary

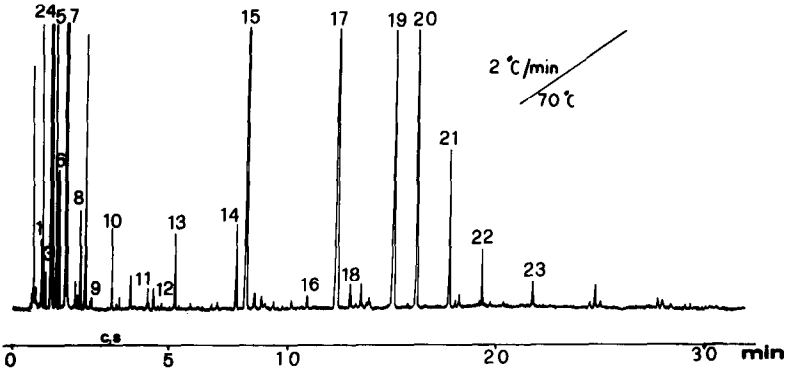

Fig. 5. Lemon petit grain oil, column 7 of Table I (C 600M). Peaks 1 = α-thujene; 2 = α-pinene; 3 = camphene; 4 = β-pinene; 5 = sabinene; 6 = myrcene; 7 = limonene; 8 = γ-terpinene; 9 = p-cymene; 10 = methyleptanone; 11 = nonanal; 12 = 3-octanol; 13 = citronellal; 14 = linalool; 15 = β-caryophyllene; 16 = humulene; 17 = neral; 18 = α-terpineol; 19 = geranial; 20 = neryl acetate; 21 = geranyl acetate; 22 = nerol; 23 = geraniol.

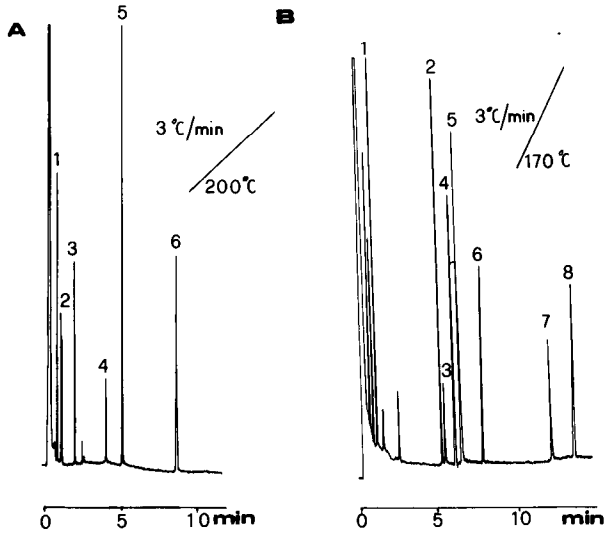

Fig. 6. Gas chromatograms of high-boiling amines on column 3 of Table I. Peaks: (A) 1 = *o*-phenylenediamine; 2 = *p*-phenylenediamine; 3 = *o*-nitroaniline; 4 = *m*-nitroaniline; 5 = 4-biphenylamine; 6 = *p*-nitroaniline; (B) 1 = 4-metroxyphenyl-1,2-ethylaminopropane; 2 = N,N-dimethyl-1,2-diphenylmethoxyethylamine; 3 = N-methyl-3,3-diphenylpropylamine; 4 = ketocaine; 5 = N-methyl-1,2-diphenylmethoxyethylamine; 6 = cyclizine; 7 = 2-diphenylmethoxyethylamine, 8 = adiphenine.

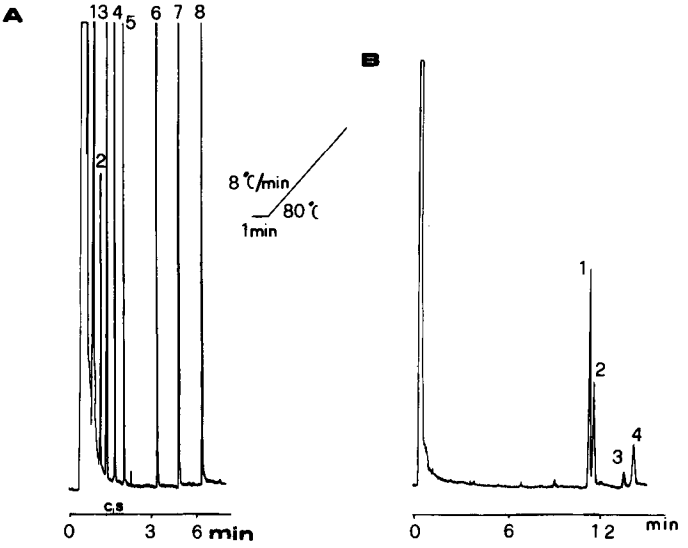

Fig 7. Gas chromatogram of aliphatic amines on column of Table I Peaks: (A) 1 = dipropylamine; 2 = pentylamine; 3 = dibutylamine; 4 = heptylamine; 5 = octylamine; 6 = decylamine; 7 = undecylamine; 8 = dodecylamine; (B) 1 = ephedrine; 2 = ψ-ephedrine; 3 = norephedrine; 4 = ψ-norephedrine. Temperature 125 °C.

columns are reported. Fig. 3 shows the chromatogram obtained by analysing a mixture of fatty acid methyl esters, prepared by transesterification of an olive oil. Analysis was carried out with a C 20M column (column 2 in Table I) and with analysis time under 10 min. Fig. 4 shows the results obtained using a column of FFAP (Table I, column 10) in analysing a mixture of free acids ranging from acetic acid to stearic acid. In particular, it is possible to observe the separation (saturated–unsaturated) of undecenoic acid from undecylenic acid. Fig. 5 shows a typical example of essential oil analysis. The chromatogram was obtained by analysing an essential oil of lemon petit grain on column 7 (Table I).

Fig. 6 and 7 show four examples of amine analysis carried out on two C 40M columns: column 3 with $D_f = 0.1$ μm and column 4 with $D_f = 0.2$ μm. Both columns may be used to analyse amines, but the lower phase charge of column 3 allows a reduction in the analysis times of high-boiling amines, while the greater phase charge makes column 4 more suitable for analysing low-boiling amines. Fig. 6 shows two analyses of high-boiling amines carried out on column 3, the first aromatic (A) and the second (B) of aliphatic type. In contrast, Fig. 7 shows to analyses of amines carried out on column 4. Fig. 7A is a mixture of aliphatic amines from pentyl to dodecylamine. Fig. 7B is a separation of ephedrines carried out isothermally at 125°C.

From the above, it is possible to note that all the columns present good efficiency with symmetrical peaks. Thus, it can be concluded that, even with reduced-diameter columns, GCB precoating does not reduce the typical characteristics of these microcapillary columns, namely high efficiency, low analysis times and lower operating temperatures, compared with classical capillary columns.

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