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EVALUATION OF SMALL DIAMETER CAPILLARY COLUMNS FOR GAS CHROMATOGRAPHY

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SUMMARY

Glass and fused silica capillary columns of inner diameter 50–200 μm were compared for their chromatographic characteristics and their application to the analysis of complex mixtures. The results show that columns of small diameter can be usefully employed in gas chromatography despite some instrumental difficulties.

INTRODUCTION

Until recently, an increase in the efficiency of gas chromatographic capillary columns depended on the possibility of utilizing longer columns. In recent years, research has been focused on the inner diameter (I.D.) and the liquid film thickness (d_f). The decrease in these two parameters, which appear as squared terms in the mass transfer term (C) in the numerator of the Van Deemter equation, suggested the possibility of obtaining a large number of theoretical plates with relatively short columns.

Several workers have prepared capillary columns of I.D. <200 μm and obtained promising results[1–8]. Cramers[9] provided some technical considerations to explain the chromatographic behaviour of these columns. However, their use is limited because of their relatively small sample loading capacity.

This work was aimed at determining experimentally the chromatographic performance of columns of I.D. 50–200 μm and assessing whether the kind of capillary, glass or fused silica, affects the chromatographic performance.

EXPERIMENTAL

Glass capillary columns were prepared in our laboratory with a drawing machine manufactured by Carlo Erba (Milan, Italy) from Duran glass tubing of O.D. and I.D. 7 and 2 mm, respectively, for columns of I.D. >100 μm and from tubing of I.D. 1 mm for columns with I.D. $\leqslant 100$ μm. The tubing was previously washed with a cleaning solution consisting of concentrated sulphuric acid and 0.1 M potassium dichromate and then with distilled water and acetone.

Fused-silica columns were obtained from SGE (Melbourne, Australia). Both

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the glass and fused-silica columns, after washing with dichloromethane, were leached with 20% hydrochloric acid at 175°C overnight, followed by successive washing with 1% hydrochloric acid, water and acetone; they were then dehydrated under pure nitrogen at 300°C for 3 h[10–12].

The columns were silanized at 400°C with diphenyldichlorosilane (Fluka, Buchs, Switzerland)[13] for 3 h followed by washing with dichloromethane and then hexamethyldisilazane (Fluka) overnight. The pure silanizing agents were passed through the columns at a rate of *ca.* 2.5 cm/s.

After each silanization, deactivation was checked by performing gas chromatography at 60°C on a standard mixture including *n*-decane, *n*-undecane and *n*-dodecane, octanol, 2,6-dimethylphenol (2,6-DMP) and 2,6-dimethylaniline (2,6-DMA). After silanization, all columns were washed successively with toluene, methanol and pentane.

The stationary phase was deposited statistically together with dicumyl peroxide (DCUP) and changing the relative concentrations according to the I.D. as shown in Table I.

TABLE I

SOLUTION CONCENTRATIONS FOR COLUMNS OF 0.20 μm FILM THICKNESS

I.D. (μm)	*% (w/v) (SE-54/pentane)*	*% (w/w) (DCUP/SE-54)*
200	0.4	0.25
100	0.8	1.2
75	1.1	2.0
50	1.6	3.0

Both ends of the columns were closed by melting, and curing was performed with temperature programming from 50 to 170°C at 3°C/min; the final temperature was maintained for 30 min.

After curing and conditioning at 280°C under hydrogen, the columns were washed with methanol, dichloromethane and pentane. The columns were evaluated by performing chromatography at 90°C on the above standard mixture; the carrier gas was hydrogen.

Each chromatographic parameter reported in Table II was assessed at the minimum point of the Van Deemter curves; the mass transfer term C was obtained by plotting $h \cdot \bar{u}$ against u^2, where h is height equivalent to a theoretical plate and $\bar{u}$ is the linear velocity of carrier gas. Comparison of the capacity factors (k') of *n*-dodecane obtained from columns prepared with SE-54 only and from cross-linked columns indicated that the reaction gave a 60–70% yield, in agreement with the literature[2,14]. This comparison also served as a basis for evaluating the actual thickness of the liquid film (d_f). Gas chromatographic measurements were performed using DANI 3900 and 6500 and Hewlett-Packard 5890 gas chromatographs with Shimazu C-R 3 and HP 339 A integrators.

TABLE II

GAS CHROMATOGRAPHIC CHARACTERISTICS OF THE COLUMNS

No.	*I.D.* *(μm)*	*Length* *(m)*	d_f *(μm)*	k' $(C_{12}H_{26})$	$\bar{u}$ *(cm/s)*	h_{min} *(μm)*	*h/I.D.*	*n/s*	*TZ/m*	*η*	$C \cdot 10^5$ *(s)*
1	200	6	0.14	10.2	35.0	171	0.86	2050	3.7	100	28
2[a]	200	13	0.14	10.3	37.0	173	0.87	2230	2.6	100	27
3	180	18	0.13	10.3	36.7	161	0.81	2280	2.4	100	21
4[a]	100	7	0.19	27.5	39.5	99	0.99	3980	4.9	93	15
5	100	7	0.22	31.6	40.5	99	0.99	4090	5.0	94	12
6[a]	100	4.5	0.22	32.1	41.0	115	1.15	3550	5.3	81	17
7	75	6.3	0.09	17.0	44.7	86	1.15	5210	5.5	86	9
8	75	5.7	0.15	29.8	44.0	91	1.20	4880	5.3	82	13
9	75	7.0	0.16	30.5	41.7	81	1.10	5140	5.0	87	12
10	75	6.0	0.24	35.0	42.1	98	1.30	4340	5.5	71	15
11	75	6.5	0.35	66.3	41.0	94	1.25	4380	5.4	75	27
12	50	6.0	0.13	37.0	43.6	56	1.12	8720	7.1	83	9
13	50	4.7	0.13	35.1	46.9	47	0.95	10 300	8.2	100	10

[a] Fused-silica columns.

RESULTS AND DISCUSSION

Fig. 1 shows the Van Deemter curves for *n*-dodecane ($C_{12}H_{26}$) obtained from four columns with I.D. decreasing from 200 to 50 μm; it clearly shows the increase in efficiency resulting from the decrease in I.D. The larger dispersion shown by the curve for the column of smallest I.D. can be attributed to the difficult introduction of the sample into the column at a rate sufficient to maximize its resolving power.

The results in Table II indicate that when the I.D. decreases the column efficiency increases (h_{min} from 171 to 56 μm) for columns having approximately the same d_f and length (6 m) such as Nos. 1 and 12; at the same time, the peak capacity per metre of column length (TZ/m) increases from 3.7 to 7.2; the same is true for the separation speed, n/s, which increases from about 2000 for larger diameter columns to 8000–10 000 for smaller diameter columns. The capacity factor, k', increases from about 10 (column of 200 μm I.D.) to over 35 (for 50 μm I.D. columns). This increase in k' is due, as expected, to the increased phase ratio ($V_f/V_m = 2\,d_f/r$); assuming d_f to be constant, it is inversely related to the capillary radius, r. However, this effect does not imply an increased analysis time; to achieve a given separation with smaller diameter columns it is possible to employ shorter columns or operate at a higher linear flow-rate, as is shown by the decrease in the C term, which falls from $28 \cdot 10^{-5}$ s for 200 μm I.D. columns to about $10 \cdot 10^{-5}$ s for columns of smaller I.D. with the same d_f. The coating efficiency (η) is quite good for almost all columns.

Table II also shows how the thickness of the liquid film affects the microcolumn efficiency (see columns 7–11 of 75 μm I.D.). In fact, when d_f increases from 0.09 to 0.35 μm, h_{min} increases from 86 to 94 μm whereas n/s decreases from 5200 to 4300 and TZ/m remains virtually unchanged.

In any case, the moderate decreases in efficiency observed in the d_f range examined allows columns with a relatively high phase load to be employed and the sample

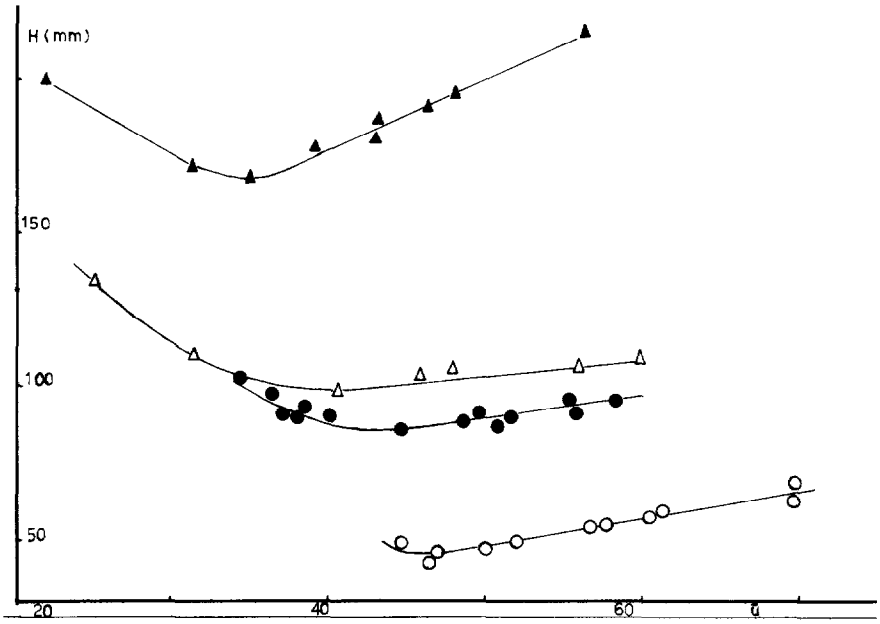

Fig. 1. Van Deemter plots: *n*-decane at 90°C, hydrogen as carrier gas. Column No.: ▲, 1; △, 5; ●, 7; ○, 13.

load to be kept within acceptable values. The *C* term is affected by an increase in d_f only at higher values (see columns 10 and 11). The values reported in Table II show that capillary columns with similar d_f and I.D. have equivalent properties, regardless of the kind of capillary (glass or fused silica).

Table III reports the retention indices for octanol, 2,6-DMP and 2,6-DMA determined using the same columns as in Table II. These values, which change by

TABLE III

RETENTION INDICES

Column No.	*n-Octanol*	*2,4-DMP*	*2,4-DMA*
1	1070	1106	1163
2[a]	1073	1109	1167
3	1076	1113	1170
4[a]	1072	1109	1167
5	1078	1111	1169
6[a]	1075	1111	1169
7	1073	1110	1167
8	1073	1109	1167
9	1071	1109	1166
10	1074	1111	1168
11	1076	1113	1170
12	1075	1113	1170
13	1078	1112	1169

[a] Fused-silica columns.

only a few units, show that the type of capillary and the various methods employed have only a very limited influence on the column polarity.

Some chromatographic determinations are presented in order to evaluate the performance of these columns. Columns of different I.D. were compared: with the same number of theoretical plates; with comparable lengths; and with comparable linear carrier gas flow-rates ($\bar{u}$).

Gas chromatograms obtained from two different columns with the same polycyclic aromatic hydrocarbon (PAH) standard are shown in Fig. 2. The two columns, of different length (23 and 7 m), had the same number of theoretical plates (about 74 000) and I.D.s of 300 and 100 μm, respectively. The two chromatograms were obtained isothermally at 240°C using hydrogen as the carrier gas with $\bar{u}$ = 40 cm/s for the first column and 60 cm/s for the second in order to obtain roughly the same number of plates. The separations were equivalent but the analysis time was 25 min with the first and less than 10 min with the second column.

Fig. 3 shows chromatograms obtained from columns having the same length, with I.D. 200 and 100 μm, analysing the same petit grain essential lemon oil and using for the second column a higher linear carrier gas flow-rate to obtain a similar analysis time (the temperature programme was the same for both columns). The column of smaller I.D. shows a better separation, especially for the peaks marked with asterisks.

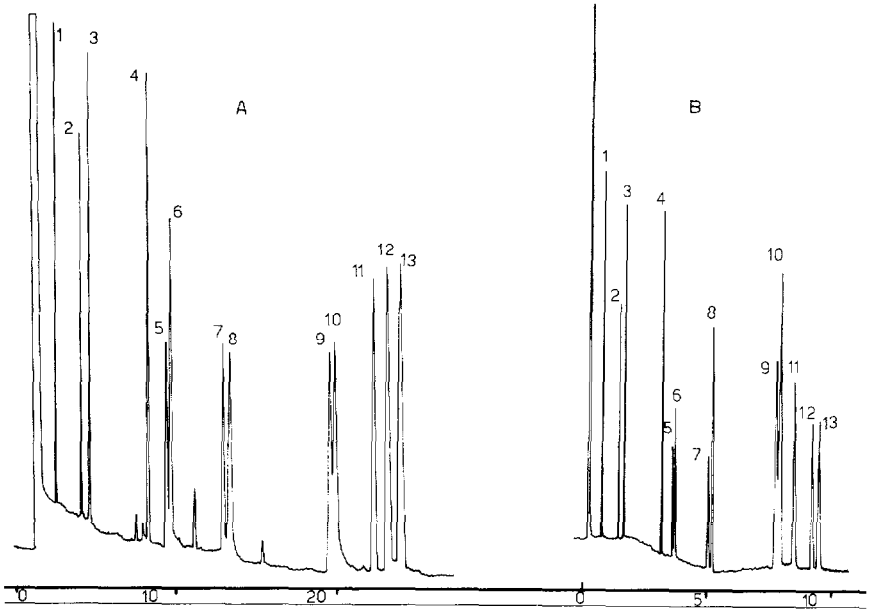

Fig. 2. Gas chromatograms of a standard PAH mixture at 240°C: (A) column length = 23.2 m, I.D. = 300 μm, $\bar{u}$ = 39 cm/s; (B) column length = 7.0 m, I.D. = 100 μm, $\bar{u}$ = 62 cm/s. Peaks: 1 = phenanthrene; 2 = fluoranthene; 3 = pyrene; 4 = benzo[*ghi*]fluoranthene; 5 = benzoanthracene; 6 = chrysene; 7 = 2-methylchrysene; 8 = 4-methylchrysene; 9 = benzo[*h*]fluoranthene; 10 = benzo[*k*]fluoranthene; 11 = n-C_{28}; 12 = benz[*e*]pyrene; 13 = benz[*a*]pyrene.

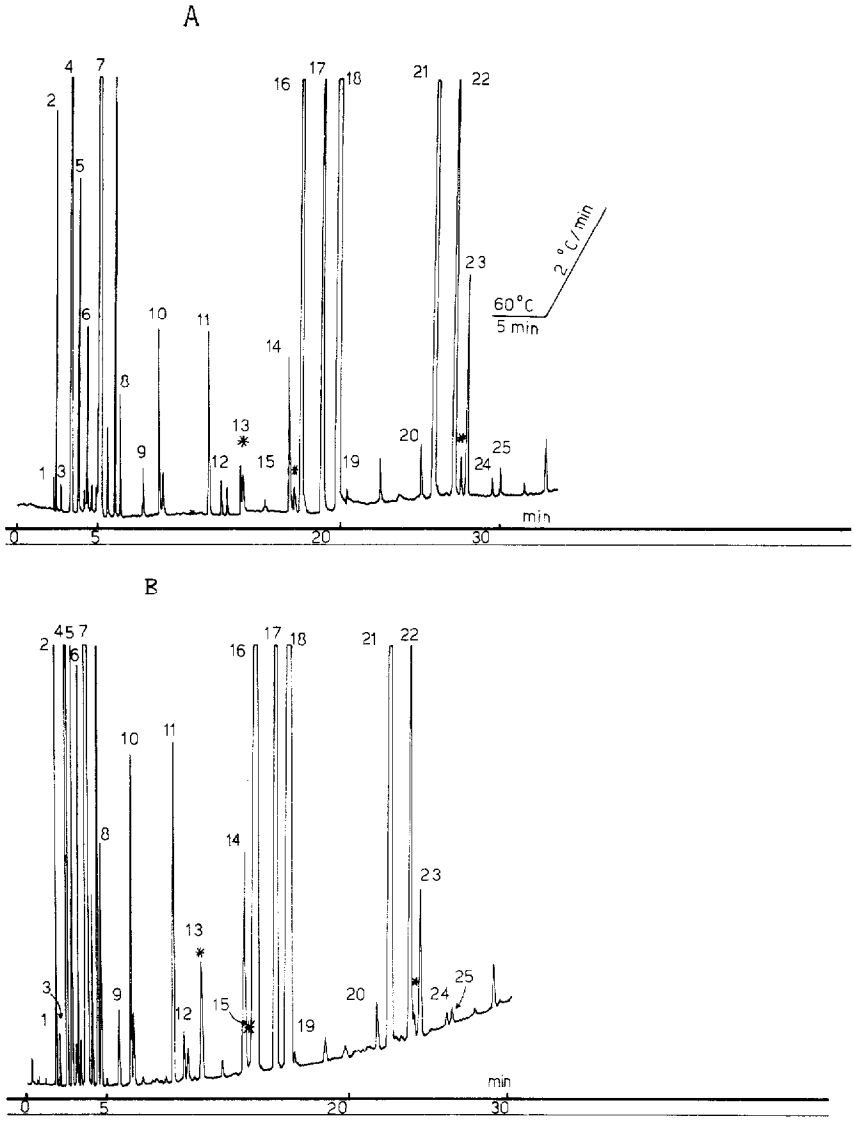

Fig. 3. Gas chromatograms of petit grain essential lemon oil on 7-m columns: (A) I.D. = 100 μm, $\bar{u}$ = 60 cm/s; (B) I.D. = 200 μm, $\bar{u}$ = 45 cm/s. Peaks: 1 = α-thujene; 2 = α-pinene; 3 = camphene; 4 = β-pinene + sabinene; 5 = myrcene; 6 = *p*-cymene; 7 = limonene; 8 = γ-terpinene; 9 = terpinolene; 10 = linalool; 11 = citronellal; 12 = 4-terpinolene; 13 = α-terpineol; 14 = nerol; 15 = citronellol; 16 = neral; 17 = linalyl acetate; 18 = geraniol; 19 = bornyl acetate; 20 = citronellyl acetate; 21 = neryl acetate; 22 = genaryl acetate; 23 = β-cariophyllene; 24 = bergamotene; 25 = humulene.

Fig. 4 shows chromatograms obtained by analysing Aroclor 1232 using columns of I.D. 100 and 50 μm; the temperature programme and linear carrier gas flow-rate (100 cm/s) were the same in each instance. The separations were roughly the same but the analysis time with the second column was 19 min compared with 27 min

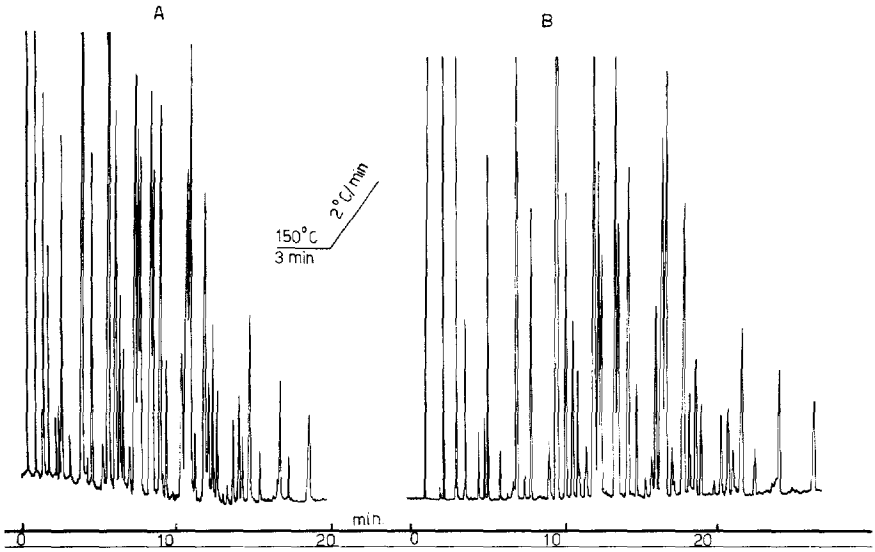

Fig. 4. Gas chromatograms of Aroclor 1232 on two columns: (A) length = 4.7 m, I.D. = 50 μm, $\bar{u}$ = 99 cm/s; (B) length = 7.0 m, I.D. = 100 μm, $\bar{u}$ = 101 cm/s.

for the first column; as a consequence, the elution temperature of the last peak is also markedly lower for the second column (about 180°C) than for the first (200°C).

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