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SANDWICHED COLUMNS IN GAS-LIQUID CHROMATOGRAPHY

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SUMMARY

Sandwiched capillary columns consisting of one or more carbon threads inserted in a glass capillary and coated with a stationary phase have been prepared and the dependence of the performance characteristics on the capillary diameter and on the number of carbon threads has been investigated. Van Deemter equation constants, gas and liquid phase mass transfer resistance terms, performance indices and performance parameters have been calculated. A comparison between sandwiched columns and other types of columns shows that regarding permeability, performance index, performance parameter and loading capacity, the former have intermediate values between open tubular and classical packed columns. The advantage of the sandwiched columns with respect to packed capillary columns lies in the ease of their preparation and the lower pressure drop corresponding to a minimum plate height. Large columns with more than a hundred threads offer no advantage over classical packed columns.

INTRODUCTION

Sandwiched capillary columns are the latest type of column to be introduced in gas chromatography. So far they have been used only as adsorption columns[1]. This investigation deals with the performance of these columns in gas–liquid partition chromatography.

The solid support in a sandwiched column is represented by any material available as a thread and consists therefore of a bundle of fibres, inserted in a glass capillary.

With regard to their geometrical features, these columns differ from any other type of column and consequently have different chromatographic properties.

A sandwiched column of ideally regular structure would be a good approximation to a column consisting of a bundle of parallel capillaries. A regular structure requires that no free space should be left between the surface of the threads and the wall of the capillary and that the fibres should be in a uniformly loose contact with each other. With respect to classical open tubular columns, this structure affords the possibility of using larger quantities of liquid phase without at the same time increasing the film thickness. On the other hand, sandwiched columns could be expected to offer

a higher permeability as compared with classical columns packed with a granular support having a particle size similar to the diameter of the fibres.

The present investigation deals with the influence of geometrical characteristics on the performance of liquid coated sandwiched columns. A comparison is made with other columns, such as classical packed, open tubular and packed capillary columns, on the basis of data reported in the literature[2,3].

EXPERIMENTAL

The sandwiched columns were prepared according to the method described by LIBERTI et al.[1]. The carbon yarn designated WYG from Union Carbide had the following characteristics: diameter of a filament: 7.5 μ, specific surface: 1 m^2/g, weight of yarn: 0.00375 g/m.

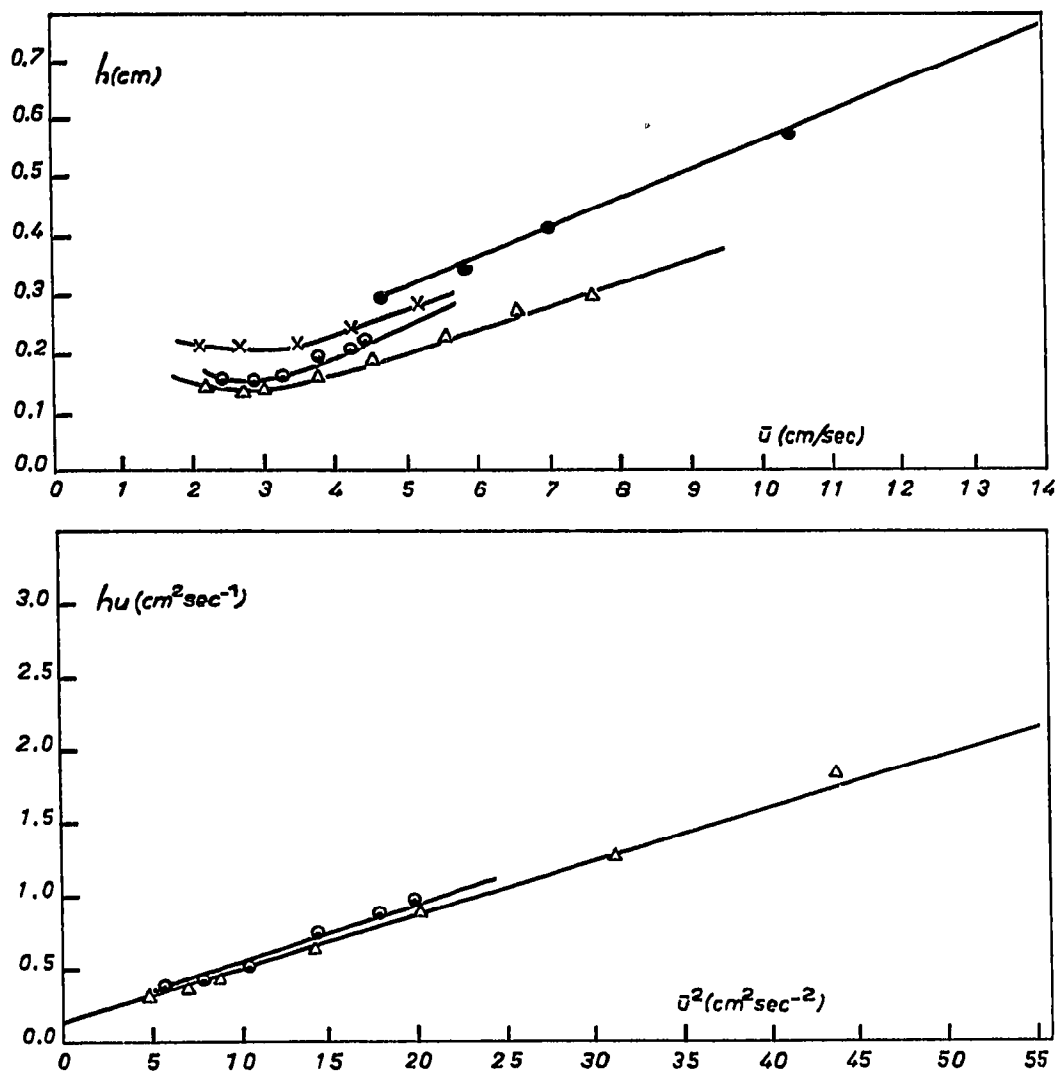A 1.5% solution of squalane, dissolved in pentane, was passed through the

Fig. 1. Plots of h vs. $\bar{u}$ and $h\bar{u}$ vs. $\bar{u}^2$ for n-octane on sandwiched columns. Carrier gas. N$_2$ ● column No. 1; × column No. 2; △ column No. 3; ◑ column No. 4.
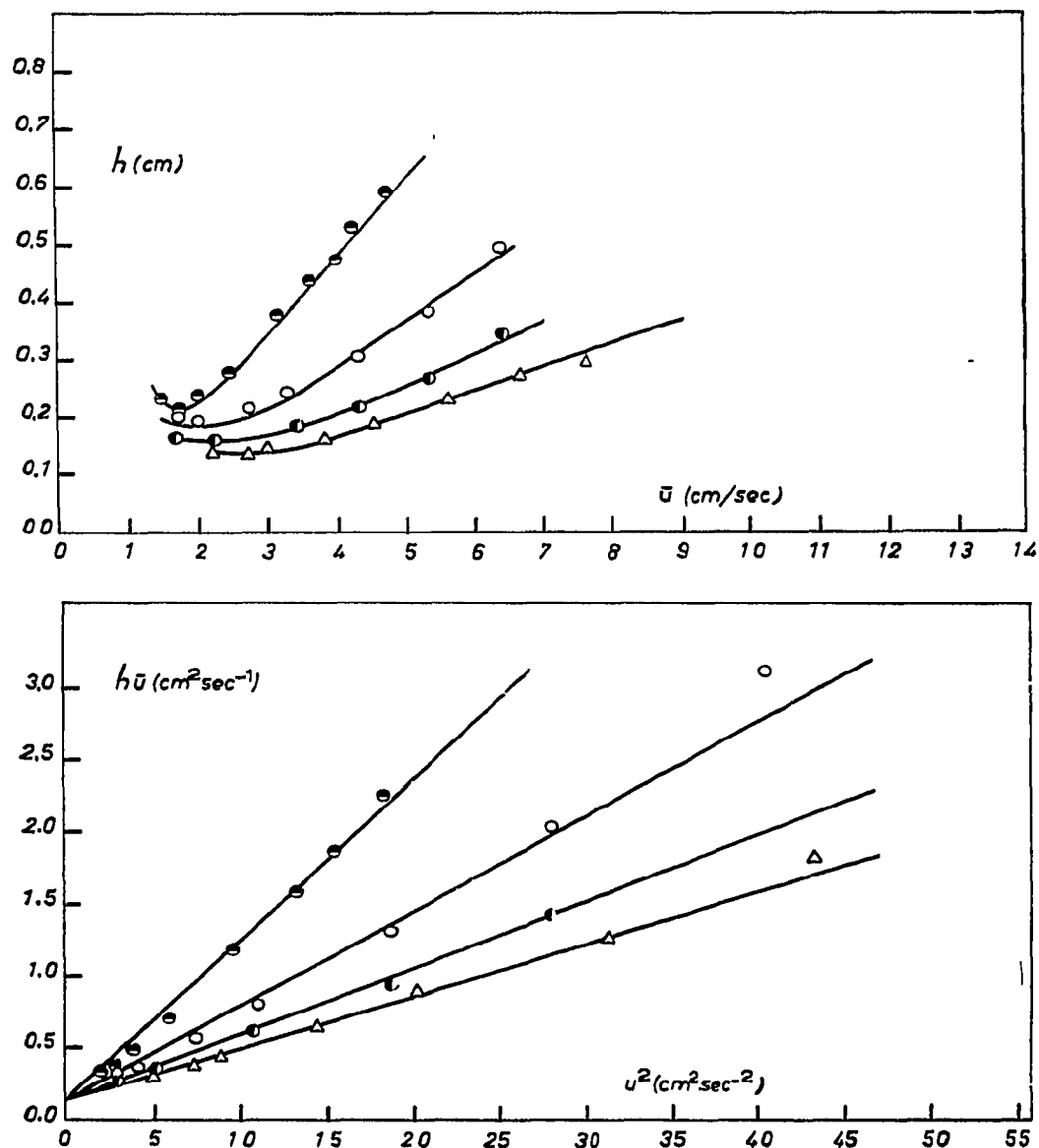
Fig. 2. Plots of h vs. $\bar{u}$ and $h\bar{u}$ vs. $\bar{u}^2$ for n-octane on sandwiched columns. Carrier gas: N_2 △ column No. 3; ◗ column No. 5, ○ column No. 6; ◖ column No. 7.

column. The solvent was evaporated slowly at room temperature by passing air through the column and subsequently nitrogen at 50°. Columns prepared with a more dilute solution of squalane gave rise to peak tailing, indicating interference due to adsorption phenomena on the solid surface.

All the columns showed a considerably increased efficiency after heating them at 200° and maintaining a slow stream of nitrogen through them for 2 h. In the course of this operation the amount of stationary phase did not vary significantly; however, a slight decrease of permeability could be observed. These effects can be attributed to a more uniform redistribution of the stationary phase on the support surface and to the expansion of the bundle of filaments constituting the yarn.

Two series of columns were prepared. In the first series, columns were prepared
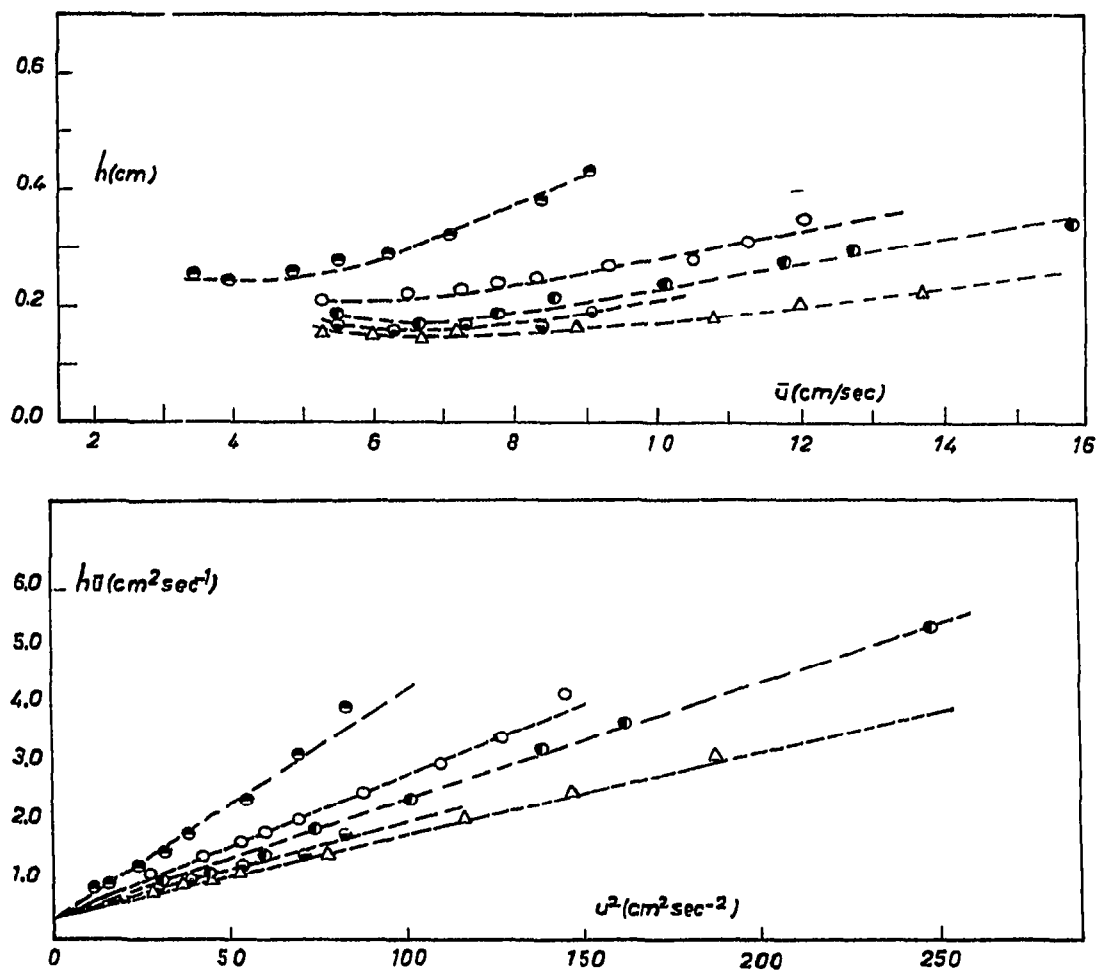
Fig. 3. Plots of h vs. $\bar{u}$ and $h\bar{u}$ vs. $\bar{u}^2$ for n-octane on sandwiched columns. Carrier gas: H_2. △ column No. 3; ◕ column No. 4; ◑ column No. 5; ○ column No. 6; ◒ column No. 7.

containing one thread of carbon and the internal diameter of the glass capillary was varied. In the second series, the columns were prepared in such a way as to maintain the permeability constant, by increasing the internal diameter of the column together with the number of the threads.

A hydrocarbon mixture containing n-pentane, n-hexane, n-heptane and n-octane was run on each column. The samples were taken from the vapour phase of the mixture and a small quantity of methane was added to each sample. The methane peak was used for the evaluation of the dead volume. All measurements were made at 50°, using nitrogen and hydrogen as carrier gas. The apparatus was a Carlo Erba Fractovap model C gas chromatograph. HETP values for n-heptane and n-octane were determined and h vs. $\bar{u}$ curves were plotted for all columns (Figs. 1, 2 and 3).

The constant terms A, B and C of the VAN DEEMTER equation for n-octane were determined graphically from the h–$\bar{u}$ plots (Figs. 1a, 2a, 3a) and where the term A was 0, from the $h\bar{u}$–$\bar{u}^2$ plots (Figs. 1b, 2b, 3b). The mass transfer resistance terms in the gas and in the liquid phase, C_g and C_l were determined on the basis of plate height measurements made with two carrier gases (hydrogen and nitrogen).

RESULTS AND DISCUSSION

These values are reported together with the constants for the Van Deemter equation and with the geometrical characteristics of the columns in Table I. The following method was employed for the calculation of C_g and C_l terms. According to the Golay equation we have for the same column, but for two different carrier gases:

$$h_{N_2} = \frac{B_{N_2}}{u} + C_{g,N_2} + C_l u \qquad (1)$$

$$h_{H_2} = \frac{B_{H_2}}{u} + C_{g,H_2} + C_l u \qquad (1a)$$

Since the difference between B_{N_2} and B_{H_2}, as well as between C_{g,N_2} and C_{g,H_2}, is only caused by the difference of the diffusion coefficients, we can write:

$$B_{H_2} = c B_{N_2}$$

and

$$C_{g,H_2} = \frac{C_{g,N_2}}{c}$$

Then

$$h_{H_2} = \frac{c B_{N_2}}{u} + \frac{C_{g,N_2}}{c} + C_l u \qquad (2)$$

B_{N_2} and B_{H_2} as well as C_{N_2} ($= C_{g,N_2} + C_l$) and C_{H_2} ($= C_{g,H_2} + C_l$) were determined graphically from the $h\bar{u}$–$\bar{u}^2$ plots, and the ratio of B_{H_2}/B_{N_2} yielded c. Knowing C_{N_2}, C_{H_2} and c, we are able to resolve the system:

$$C_{N_2} = C_{g,N_2} + C_l$$

$$C_{H_2} = \frac{C_{g,N_2}}{c} + C_l$$

and thus obtain the values of C_{g,N_2} and C_l.

The amount of stationary phase was calculated for each column from measurements made at 80° by comparing the retention volumes of n-octane with the values reported by McReynolds[4].

Values of the film thickness d_l and the volume ratio of the phases V_g/V_l were calculated from the weight of the stationary phase, the specific weight of squalane and the surface of the carbon thread.

All these data are collected in Table II. The same table also contains calculated values of permeability, P., the capacity ratio k' for the four hydrocarbons, the height equivalent for an effective plate H, the performance index $P.I.$ and the performance parameter PP, all calculated for n-octane, at the minimum of the $h\bar{u}$– curve.

The load capacity of the sandwiched capillaries was examined on two columns, No. 3 and No. 7, by injecting increasing quantities of a mixture of hydrocarbons, containing 28.3% of n-hexane, 35.4% of n-heptane and 36.3% of n-octane. The samples were introduced by means of a 10 μl Hamilton microsyringe and the quantities of n-heptane and n-octane passing through the column were calculated from the volume

TABLE I

GEOMETRICAL CHARACTERISTICS AND VAN DEEMTER EQUATION CONSTANTS OF SANDWICHED COLUMNS

Column No.	I.D. (mm)	Length (m)	Number of threads	Carrier gas N_2				Carrier gas, H				
				A (cm)	B (cm²/sec)	C (sec)	C_g (sec)	A (cm)	B (cm²/sec)	C (sec)	C_g (sec)	C_i (sec)
1	0.43	14.0	1	0.07	0.05	0.0470	—	—	—	—	—	—
2	0.37	15.0	1	0.07	0.10	0.0520	—	—	—	—	—	—
3	0.35	11.5	1	0.00	0.13	0.0360	0.0345	0.00	0.40	0.0136	0.0115	0.0021
4	0.32	10.0	1	0.00	0.13	0.0400	0.0367	0.00	0.40	0.0155	0.0122	0.0033
5	0.45	7.5	2	0.00	0.13	0.0469	0.0408	0.00	0.40	0.0197	0.0136	0.0061
6	0.55	10.4	3	0.00	0.13	0.0690	0.0675	0.00	0.40	0.0240	0.0227	0.0015
7	0.69	9.4	5	0.00	0.13	0.1116	0.1091	0.00	0.40	0.0385	0.0364	0.0025

TABLE II

DATA AND RESULTS OBTAINED WITH VARIOUS SANDWICHED COLUMNS

Column No.	Permeability P · 10^{-7} cm^2	Squalane (mg/m)	V_g/V_l	Liquid film thickness (mμ)	k'				H_{min} (cm)	u_{min} (cm/sec)	ΔP_{min} (atm)	P.I. (poise)	P P (nC$_8$–nC$_7$) (atm/sec)
					nC$_5$	nC$_6$	nC$_7$	nC$_8$					
	84.5	0.93	105.6	30.6	0.37	1.04	2.80	7.50	—	—	—	—	—
	25.2	0.68	95 8	27.1	0.45	1.20	3.30	8.92	0.265	2.62	0.32	115	0.44
	8.6	0.90	65.3	29.6	0.58	1.56	4 31	11.45	0.167	2.70	0.70	146	0.68
	4.6	1.31	43.6	44 0	0.70	1.74	5.30	14.36	0.177	2.86	1.30	334	0.47
	8.3	1.92	54.3	31.5	0.76	2.10	5.83	15.50	0.188	2.25	0.40	202	1.17
	7.2	2.96	45.2	32.0	0.80	2.20	6.20	16.60	0.218	2.03	0.60	333	1.97
	4.5	5.59	38.6	37.3	1.08	3.00	8.00	21.55	0.230	1 73	0.70	587	4.39

injected, the split ratio, the composition and the density of the mixture. The base width of the peaks was determined by measuring the distance between the intersections of the base line and the tangents drawn to the inflexion points of the peak. Fig. 4 shows a plot of peak base width vs. quantity of hydrocarbon. The variation of the base width was chosen as the characteristic value indicating column overloading because neither the peak width at half height nor the number of theoretical plates showed any significant variation even when peak broadening became quite apparent.

Comparing columns 1, 2, 3 and 4 in Table II, all containing a single thread inserted in glass capillaries of different diameter, it can be seen that the permeability decreases with decreasing internal diameter according to Poiseuille's law. At the same time the ratio V_g/V_l also decreases, which explains the increasing values of the capacity ratio.

The height equivalent to an effective plate attained for each column a minimum in the region of 2.6–2.8 cm/sec of linear velocity of carrier gas. The data in Table II also demonstrate the decrease of the height of an effective plate with decreasing
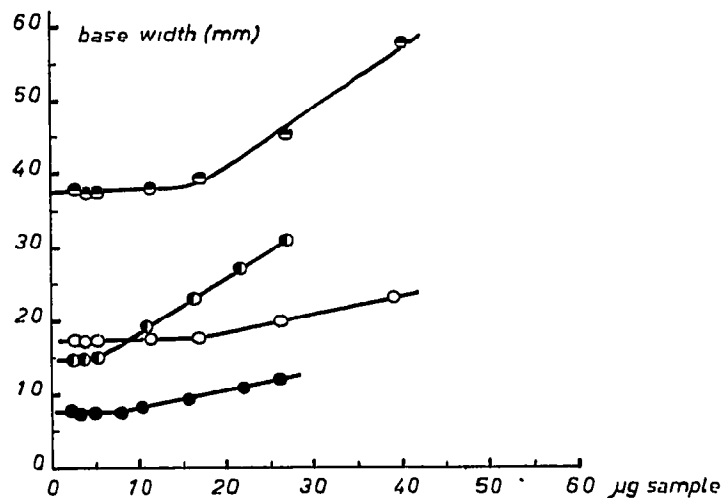

Fig. 4. Plots of peak base width vs. sample quantity. ● n-octane on column No. 7; ◐ n-octane on column No. 3. ○ n-heptane on column No. 7; ● n-heptane on column No. 3.

internal diameter and the increase of the pressure corresponding to the minimum plate height.

Comparing the data of columns 2, 3 and 4 in Table II, it can be seen that the pressure corresponding to the minimum plate height varies almost like a geometrical progression. The height of an effective plate, on the other hand, displays a considerable decrease when passing from column 2 to column 3, while the decrease is less significant when passing from column 3 to column 4. Consequently column 3 seems to represent a favourable compromise with respect to column efficiency and permeability.

Performance indices and performance parameters of all sandwiched columns have values intermediate between open tubular columns and classical packed columns. They might be considered and classified as regularly packed capillaries. This statement is supported by values of the constant terms of the Van Deemter equation, reported in Table I. The term A is o, and B becomes almost independent of the column diameter, as soon as the capillary becomes narrow enough to straighten the thread and to make the filament packing smoother.

If the threads are not slightly compressed by the wall of the capillary, the structure and the orientation of the thread become less regular, which is a possible explanation for the increment in term A for columns 1 and 2.

Another series of experiments served for the examination of columns prepared with more than one carbon thread. The columns were prepared in such a way as to maintain nearly constant the ratio of the internal diameter to the number of threads thus obtaining columns all having a similar permeability.

A comparison of columns 3, 5, 6 and 7 shows that the minimum heights of an effective plate for n-octane show slightly increasing values as well as performance indices and performance parameters, while the carrier gas velocities corresponding to H_{min} slightly decrease when the number of threads increases.

An examination of the Van Deemter equation constants shows that there is only a slight alteration in the regularity of the packing, the term A being o, and B constant for all these columns. The term C shows a pronounced increase on increasing the number of threads.

As shown by the data of Table I, the rather high values of C are mainly due to C_g, the mass transfer resistance in the gas phase, while C_l is much lower and nearly constant for columns 3, 6 and 7, in spite of the increasing quantity of liquid phase. The higher value of C_l in column No.5 is very probably due to the irregular distribution of the liquid phase in this column.

The increment of the gas phase mass transfer resistance term seems to be a limiting factor in increasing the number of threads. Even the column with 5 threads showed a rapidly decreasing separation efficiency at a carrier gas velocity higher than that corresponding to the minimum of the $h-\bar{u}$ curve. In fact, columns consisting of 120 and 180 threads inserted in a tube of 4 mm I.D. showed very poor separation efficiency, the column of 180 threads having a permeability of $20 \cdot 10^{-7}$ cm^2.

An examination of the graphs in Fig. 4 shows that the critical sample quantity causing column overloading is somewhat larger than 7 μg for the column with one thread and about 17 μg for the column with five threads which are doubtlessly larger quantities than those for classical capillary columns.

In Table III some characteristics of the sandwiched columns are reported together with those of other types of columns (data taken from refs. 2 and 3) for the sake

TABLE III

COMPARATIVE DATA FOR VARIOUS TYPES OF COLUMNS

Column type	Reference	Column length (m)	H_{min} (mm) n-heptane	ΔP_{min} (atm)	$\Delta P/l$ (atm/m)	Squalane mg/m	P (10^{-7} cm²)	V_g/V_l	k'
classical packed	2	4	1.11	2.11	0.50	337 6	1.94	22.6	18.4
classical packed	3	2	1.59	0 98	0 49	185.4	2 1	54 2	7.8
packed capillary	2	7	0.89	2.7	0.39	2.6	7 9	48.0	6 0
packed capillary	2	21.5	1.37	3.8	0.18	1.8	14.0	89.6	6.4
packed capillary	2	17.5	2 54	2.2	0 13	2 2	28 5	89.0	6 8
packed capillary	3	10.0	2.53	0.75	0 07	0.25	18 5	267 0	1 6
open tubular	2	140.0	1.37	3.9	0 03	0 26	124.5	150 0	2 7
sandwich No. 2		15.0	3.00	0.32	0 02	0.68	25.2	95.8	3.3
sandwich No. 3		11.5	2 04	0.60	0.05	0 89	8 6	65.3	4.2
sandwich No. 4		10.0	1.86	1.30	0.13	1.31	4.6	43.6	5.4
sandwich No 5		7.5	2.27	0.40	0.05	1.92	8.2	54.3	5 6
sandwich No. 6		10.4	2.51	0.60	0 06	2.96	7.2	45.2	6.2
sandwich No. 7		9 4	2.7	0 70	0.07	5 59	4 5	38 6	8 0

of comparison. These values are the minimum height of an effective plate for n-heptane, the pressure gradient of the column, the amount of the stationary phase contained in one meter of the column, the ratio V_g/V_l and the permeability. All these reported values correspond to the minimum of the $h-\bar{u}$ curve.

A comparison of these data demonstrates that the sandwiched columns have an intermediate value of V_g/V_l, ranging between that of the classical packed columns and the packed capillary columns, and a permeability comparable with that of the latter type.

The amount of the stationary phase is of the same order of magnitude as that of a packed capillary, i.e. it is higher than the quantity contained in an open tubular column. Also with respect to efficiency, they are comparable to the packed capillaries but require a lower pressure in the zone of the minimum plate height, providing the possibility of preparing and using columns of considerable length without the use of inconveniently high pressures.

The advantages of the sandwiched columns coated with a liquid phase may be summarized by underlining the ease of their preparation, their rather good separation efficiency even with a low pressure gradient, and the possibility of coating them with a rather high amount of stationary phase.

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