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POTENTIALITIES OF MICRO-PACKED COLUMNS

SOME APPLICATIONS IN PETROLEUM CHEMISTRY

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SUMMARY

Packed columns of an internal diameter of 0.6–0.8 mm and lengths of up to 15 m were prepared. Theoretical plate numbers of the order of 50 000 at moderate inlet pressures were obtained. A homogeneous particle size was found to be essential. The columns are coiled and subsequently packed under pressure and vibration. A distinct advantage over the packed capillary columns according to HALASZ AND HEINE is that all types of support, coated with any stationary phase, may be used (*e.g.*, Porapak, Durapak, silanized glass beads). The packing may be prepared in large batches, ensuring reproducible columns. The small volume makes the use of expensive packings feasible. Sample size is such that direct injection presents no difficulties. A few applications to hydrocarbon mixtures are given.

INTRODUCTION

In high-resolution gas chromatography (GC), two basic types of columns are used: open tubular columns according to GOLAY[1], and packed capillary columns according to HALASZ AND HEINE[2,3].

Theoretically, open-tubular columns give the best separations. They combine high plate numbers with high permeability and a high production of plates per unit time. In practice, however, difficulties with injection and in the choice of stationary phases are encountered. Stream splitters are unsuitable for high-boiling compounds on account of the desirable fast injection. The quantitative results are unsatisfactory for samples with a wide boiling range. Also, the loss of sample associated with stream splitters is unacceptable in a number of cases (*e.g.*, steroids in body fluids).

Direct injection is still in the development stage[4–8]. Reproducible coating of open-hole tubular columns, especially glass columns, remains difficult[6–9]. The formation of a homogeneous film on the wall is the critical step. Packed capillary columns are prepared from glass only and the packing obtained is often irregular. The choice of supports is limited on account of the high temperatures to which they are subjected.

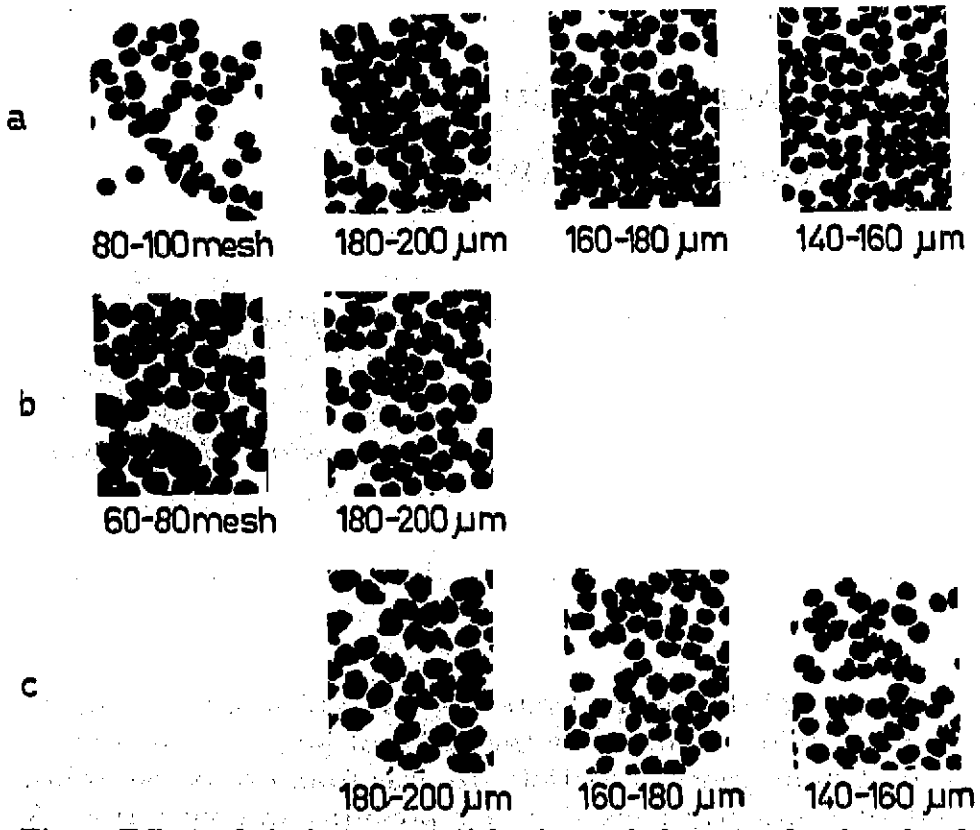

Fig. 1. Effect of sieving on particle size and shape. *a*, *b*: glass beads, GLC-110; *c*: Chromosorb W-AW.

Silanized supports, glass beads, Porapak, Durapak and the like, cannot be used. Sample introduction is less of a problem here. In both types, the quantity of stationary phase is difficult to control.

The advantages of ordinary packed columns and to a large extent those of capillary columns may be combined in a new type of column that we shall call "micro-packed columns" and which has the following advantages: any support may be impregnated with any stationary phase in the desired quantity; the packing may be prepared in large batches to ensure reproducible properties; the number of theoretical plates is high; the pressure drop is not excessive; direct injection presents no difficulties; and the small volume allows the use of expensive packings (*e.g.*, Durapak, Dexil).

EXPERIMENTAL

Packing material

The reduction in diameter of ordinary packed columns succeeds only down to about 1 mm. The pressure drop is the limiting factor. We have found that significant improvements are obtained if carefully sieved fractions of support are used. The particle size distribution must be smaller than 20 µm. A comparison of sieved and non-sieved Chromosorb W (acid-washed) and silanized glass beads is given in Fig. 1. The sieved support shows a marked improvement in the regularity of packing, and the regularity increases with decreasing particle size.

TABLE I

REPRODUCIBILITY OF PACKING DENSITY

Column	*I.D. (mm)*	*Length (m)*	*Particle size of glass beads support (μm)*	*Packing on support*	*Weight of packing per m of column length (g/m)*
SS	1.0	6.0	140–160	PMPE	1.35
SS	1.0	6.0	140–160	PMPE	1.35
SS	1.0	6.0	140–160	PMPE	1.34
SS	1.0	6.0	140–160	PMPE	1.33
SS	1.0	6.0	160–180	PMPE	1.29
SS	1.0	6.0	160–180	PMPE	1.29
Glass	0.8	14.6	140–160	PMPE	0.66
Glass	0.8	14.6	140–160	SE-30	0.65
Glass	0.8	10.0	140–160	SE-30	0.65
Glass	0.6	26.0	140–160	PMPE	0.33
Glass	0.6	7.6	140–160	PMPE	0.33

Sieving also removes large particles that might block the capillary during packing. It was found that a ratio of particle diameter to column diameter of about 0.2–0.3 is the most favourable. Elimination of fines is achieved by sieving in a vacuum. Instead of sieving, flotation or sedimentation may be used depending on the density of the support. The latter techniques yield a very narrow range of particle size. It was found that specified mesh-size ranges of commercial supports were smaller than those obtained after sieving.

Preparation of micro-packed columns

An empty glass or metal tube of the desired dimensions is coiled and one end of the tube is plugged with 1–2 cm of glass wool. The other end of the tube is connected to a cylindrical container. The axis of the coil is horizontal and that of the container is vertical. The packing is introduced into the container and the latter is connected to a pressure line. The lower part of the container and almost the complete coil are placed in an ultrasonic bath so that the plugged end of the column is above the level of the bath. Vibration and pressure will transport the packing continuously into the

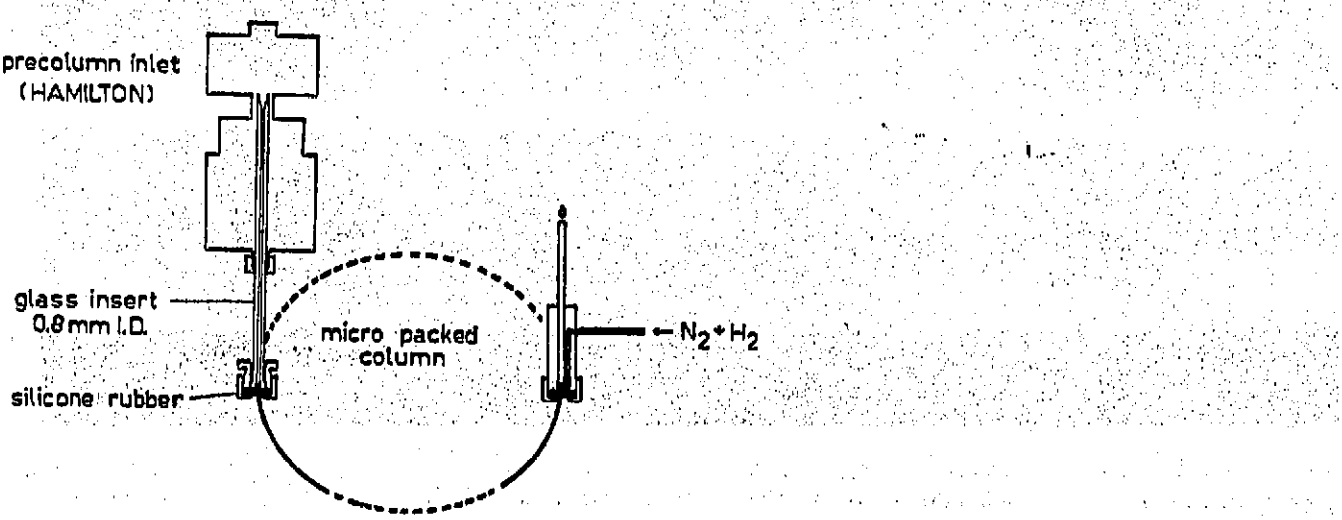

Fig. 2. Connection of micro-packed column to gas chromatographic system.

column. Care is taken to keep the pressure gradient across the packed part of the column about constant, to ensure a homogeneous packing density along the column.

At the start of the procedure, the increase in pressure should be very gradual so as not to blow out the plug. The final pressure depends on the material used but will be in the order of 0.4–2 atm per m of column length. The lower value applies to

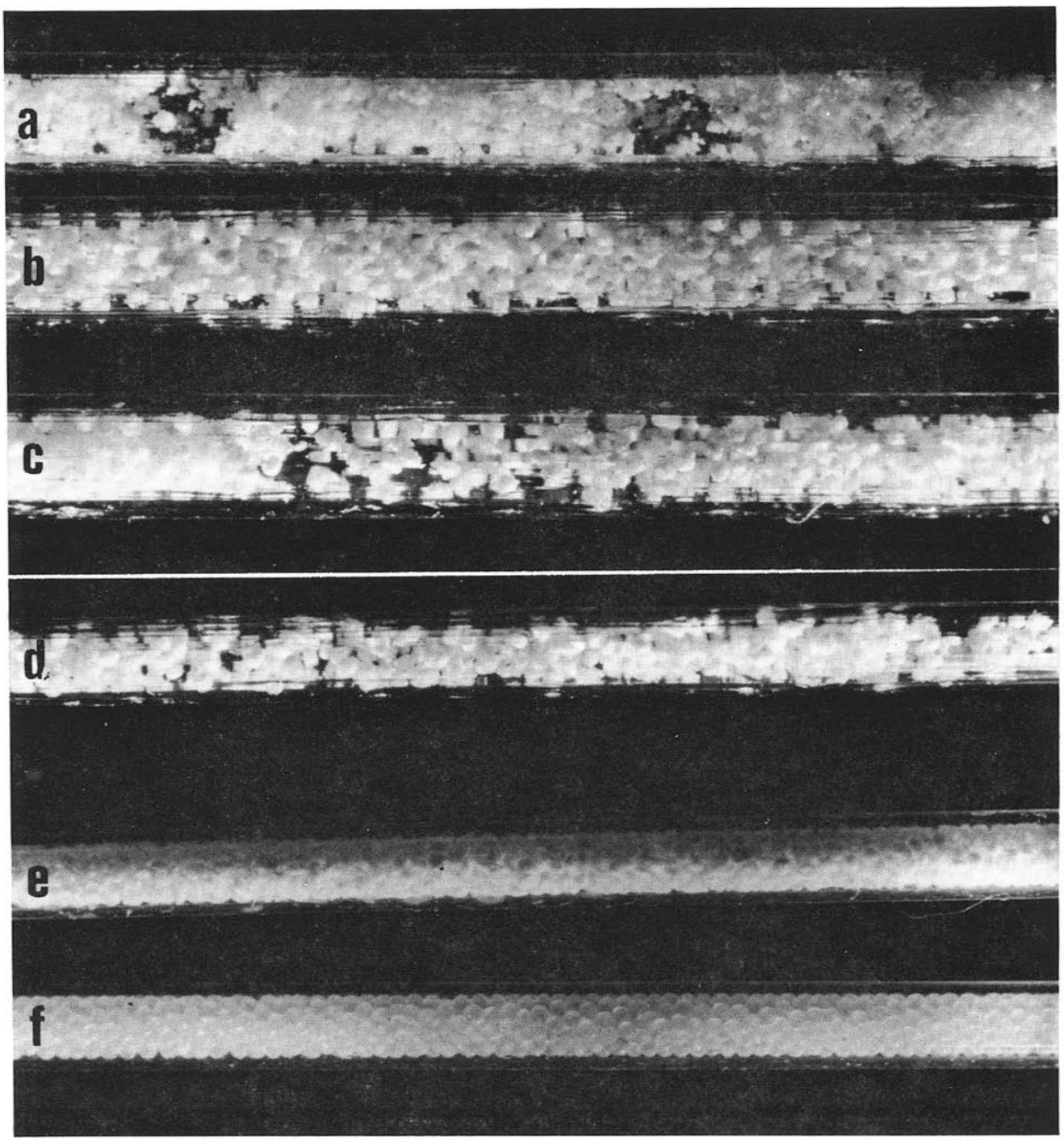

Fig. 3. Comparison of packed capillary (*a*, *b*, *c*, *d*) and micro-packed columns (*e*, *f*). *a*: Gas-Chrom S, 80–100 mesh; *b*, *c*, *e*: Chromosorb W-AW, 180–200 μm; *d*: Chromosorb W-AW, 80–100 mesh; *f*: glass beads, GLC-110, 180–200 μm.

Chromosorb and the higher to glass beads. With glass columns, the packing can be followed visually. In the case of metal columns, packing up to a constant weight should be carried out. The time necessary for packing is 1–2 min per m of column length. Table I shows the reproducibility of packing density.

Apparatus

A home-made gas chromatograph equipped with means for direct sample introduction and a stream splitter (Hamilton) was used in our measurements. Direct injection is illustrated in Fig. 2.

The inlet port was provided with a glass insert tube of 11 cm length and 0.8 mm I.D. One end of the insert used for the connection to the column was wider and conically shaped. The column was inserted about 2 mm into the cone.

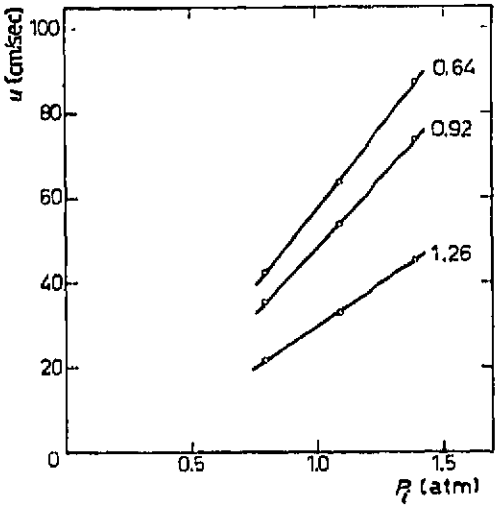

Fig. 4. Relationship between linear carrier gas velocity, u and inlet pressure, P_i for several column diameters expressed in mm (column length 1 m).

The seal was made by means of a silicone rubber ring. The outlet of the column protruded into the nitrogen + hydrogen stream for the flame-ionization detector. Since the flow rate was high (1 cm³/sec), the effective dead volume between column and detector was very small.

RESULTS AND DISCUSSION

Comparison of packed capillary columns and micro-packed columns

The packed capillary columns according to HALASZ AND HEINE[2,3] require a support of sufficient mechanical strength and great thermal stability to withstand the glass-drawing operation. This support, in most cases, cannot be coated in advance.

The micro-packed columns make no special demand on the support (except for homogeneity of particle size) and the latter can be coated in advance. The great difference in regularity and density of both types of column can be seen in Fig. 3. A soft packing in the case of packed capillary columns gives rise to holes (Fig. 3,*a*). Also in the case of packed capillary columns, sieving improves the quality of the

TABLE II

CHARACTERISTICS OF MICRO-PACKED AND PACKED CAPILLARY COLUMNS

L = length; d_c = diameter of column; p = pressure; k = capacity ratio; $H_{opt.}$ = optimum height of a theoretical plate; $u_{opt.}$ = optimum carrier gas velocity; n = plate numbers; P.I. = performance index; T = temperature.

Columns	L (m)	d_c (mm)	p (atm.)	k	$H_{opt.}$ (mm)	$u_{opt.}$ (cm/sec)	n	n/t (sec^{-1})	P.I.	T (°C)
Micro-packed[10]										
A. Support: glass beads, GLC-110 (180–200 μm) Stationary phase: 0.05% (dehydroepiandrosterone)	14.3	0.8	4	4.8	0.32	11.5	44500	61	8.4	240
B. Support: as A Stationary phase: 0.05% SE-30 (Pregnanediol)	14.3	0.8	4	7.4	0.34	11.8	42600	44	8.7	220
Packed capillary[11]										
C. Support: Chromosorb W (115–160 μm) Stationary phase: squalane (heptane)	7	0.55	2.7	6.0	0.65	40	10800	88	13.3	50
D. Support: Chromosorb W (160–200 μm) Stationary phase: squalane (heptane)	21.5	0.55	3.8	6.4	1.0	20	21500	27	28.6	50
E. Support: Chromosorb W (200–250 μm) Stationary phase: squalane (heptane)	17.5	0.55	2.2	6.8	2.0	17	8800	11	95.2	50

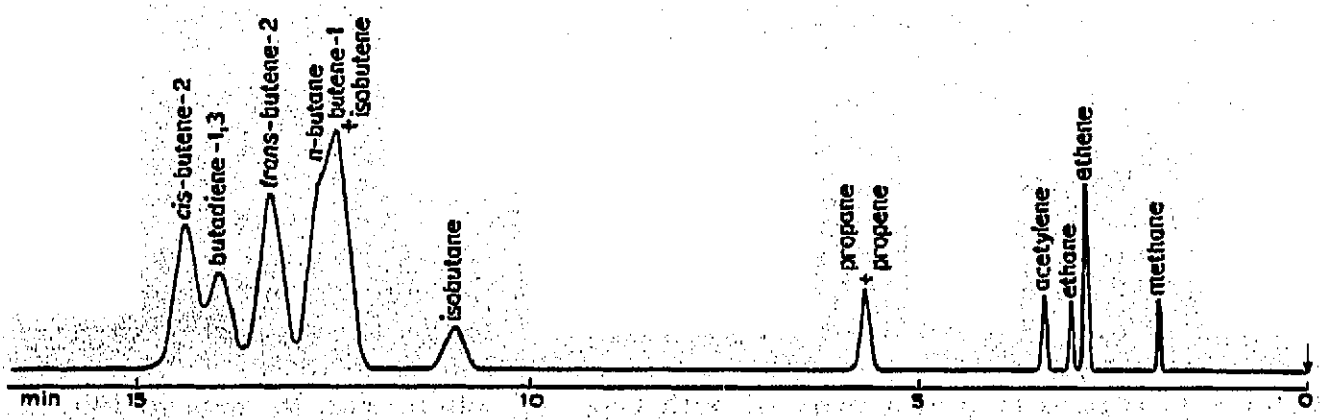

Fig. 5. Analysis of hydrocarbon mixture with micro-packed column. Porapak N, 180–200 μm, L = 5 m, I.D. = 0.8 mm, T = 150°, P_i = 2.0 atm, $n_{opt.}$ (at 1.5 atm) = 12,500 for butadiene-1,3 (k = 7.2).

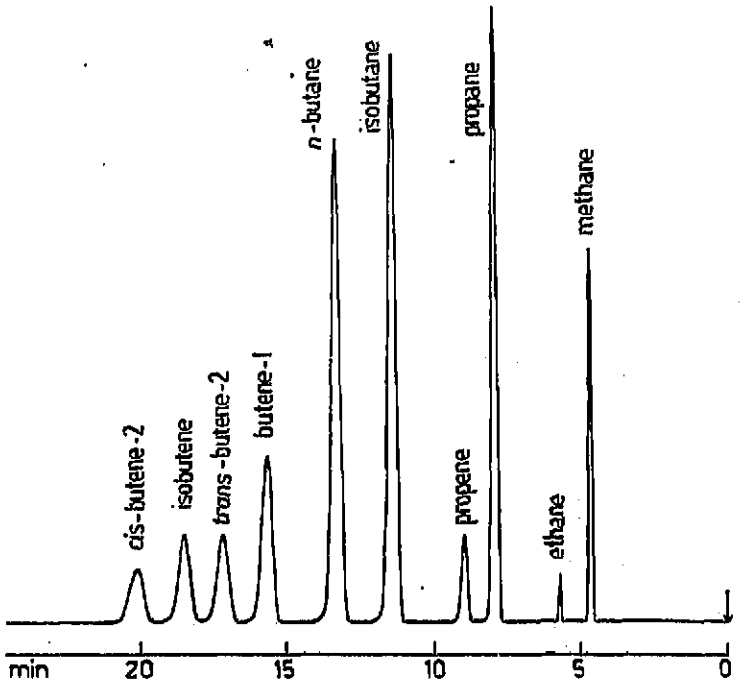

Fig. 6. Analysis of hydrocarbon mixture with micro-packed column. Spherosil (66 m^2/g)/10% squalane, 100–200 μm, L = 5 m, I.D. = 0.8 mm, T = 70°, P_i = 3.2 atm, $n_{opt.}$ (at 1.7 atm) = 10,200 for n-butane (k = 2.9).

packing (Fig. 3,*b* and *d*). The use of a glass rod inside the tube during packing before the drawing operation results in a looser packing (compare Fig. 3,*b* and *c*). The use of a narrow sieve fraction in micro-packed columns results in very homogeneous packings (Fig. 3, *e* and *f*).

Optimum plate numbers were 3500 per m for glass beads and 3000 for Chromosorb W even for columns of 15 m length.

The relation between linear gas velocity and pressure drop for several column

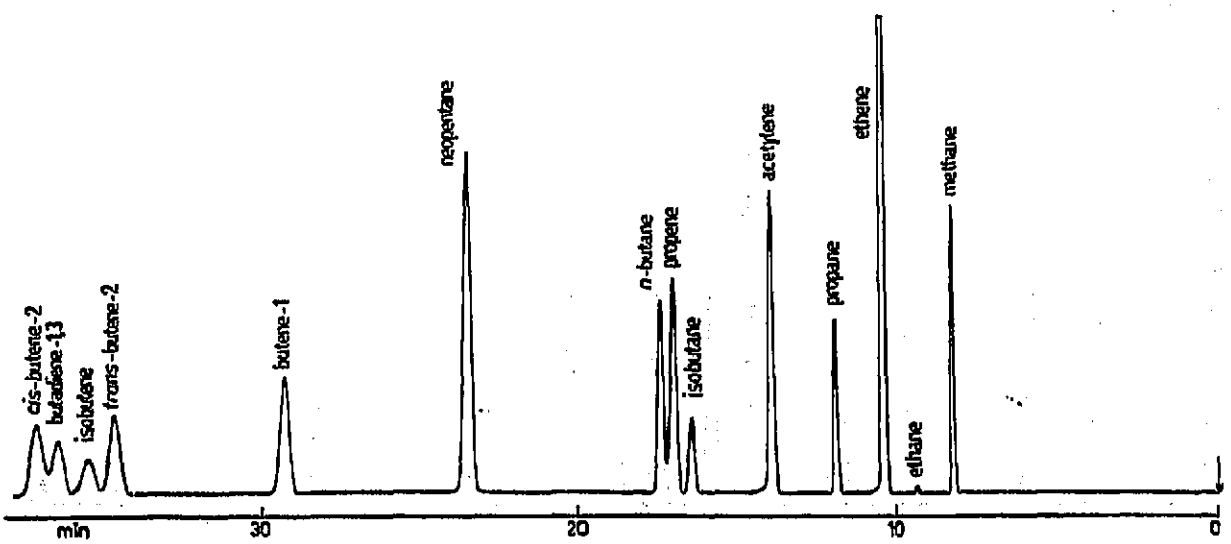

Fig. 7. Analysis of hydrocarbon mixture with micro-packed column. Porasil C/phenyl isocyanate, 180–200 μm, L = 15 m, I.D. = 0.8 mm, T = 70°, P_i = 3.5 atm, $n_{opt.}$ (at 3.6 atm) = 46,000 for butadiene-1,3 (k = 4.4).

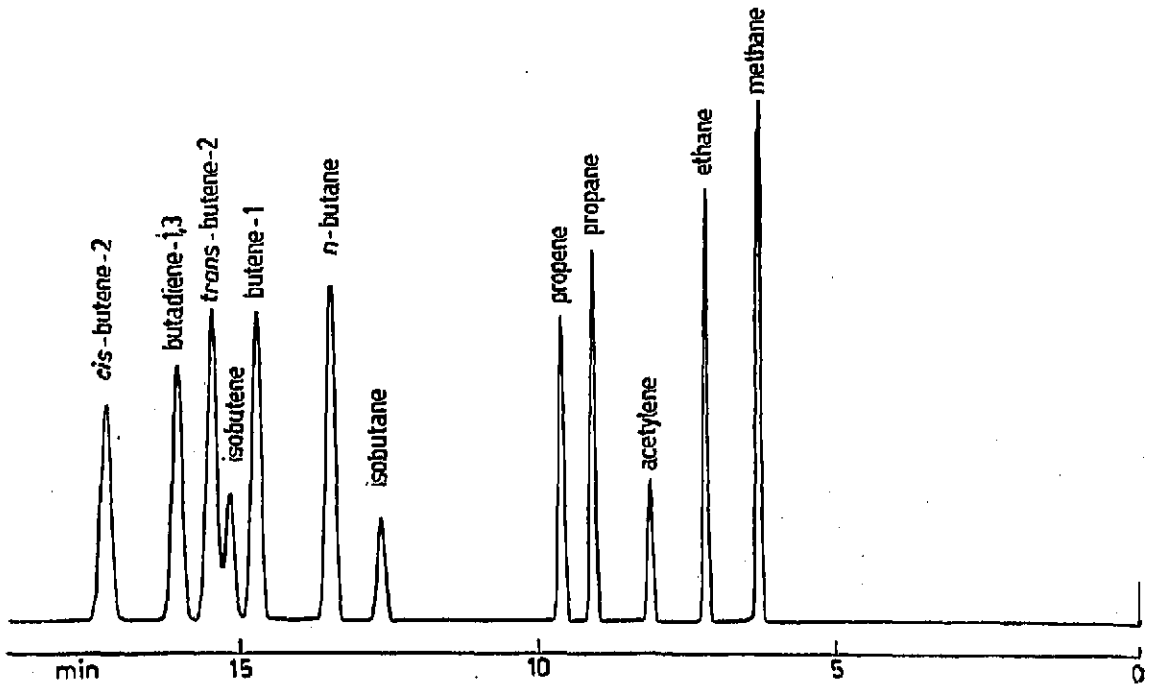

Fig. 8. Analysis of hydrocarbon mixture with micro-packed column. Porasil C/OPN, 180–200 μm, L = 15 m, I.D. = 0.8 mm, T = 70°, P_i = 3.5 atm, $n_{opt.}$ (at 3.5 atm) = 42,000 for butadiene-1,3 (k = 2.7).

diameters is given in Fig. 4. A reduction in the internal diameter fortunately makes possible the use of longer columns. A number of column characteristics for both types of column are given in Table II. The performance index (P.I.) in poise is given by[1]:

$$\text{P.I.} = 31.2 \frac{H^2_{\text{min.}}}{u_{\text{opt.}}} \cdot \frac{k+1}{k} \cdot \frac{\Delta p}{L}$$

where $H_{\text{min.}}$ = minimum height of a theoretical plate; $u_{\text{opt.}}$ = optimum carrier gas velocity (cm/sec); k = capacity ratio; Δp = pressure drop (dyne/cm²); and L = column length (cm).

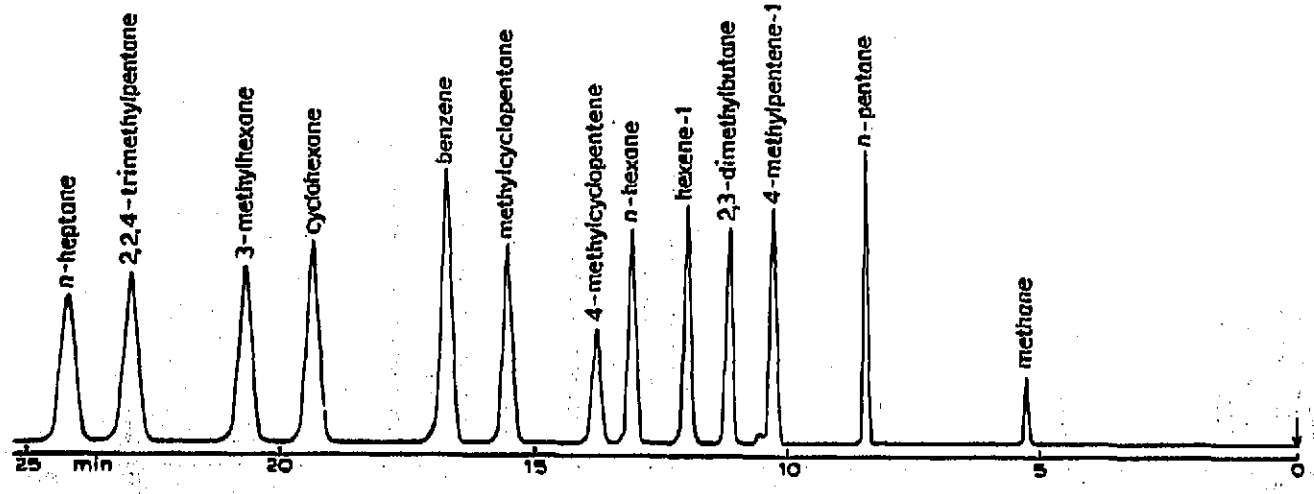

Fig. 9. Analysis of hydrocarbon mixture with micro-packed column. Chromosorb W, acid-washed/5% squalane, 180–200 μm, L = 15 m, I.D. = 0.8 mm, T = 70°, P_i = 3.5 atm, $n_{opt.}$ (at 3.9 atm) = 33,500 for n-heptane (k = 4.6).

The performance index has a minimum value of 0.1 when helium is used as the carrier gas, but higher values are usually obtained. In the case of packed columns, the performance index ranges between 20 and 2000.

The separation obtained when the micro-packed columns are applied to a mixture of low-boiling saturated and unsaturated hydrocarbons is illustrated in Figs. 5–8. The peak symmetry with materials such as Porasil is such that they can be applied to trace analysis (*e.g.*, quality control of ethylene).

The separation of saturated, unsaturated and aromatic hydrocarbons is illustrated in Fig. 9.

REFERENCES

1 M. J. E. Golay, in D. H. Desty (Editor), *Gas Chromatography 1958*, Academic Press, New York and London, 1958.
2 I. Halasz and E. Heine, *Nature*, 194 (1962) 971.
3 I. Halasz and E. Heine, *Anal. Chem.*, 37 (1965) 495.
4 C. A. Cramers and M. M. van Kessel, *J. Gas Chromatogr.*, 6 (1968) 577.
5 P. S. H. Kuppens, *Chem. Weekbl.*, 65, No. 36 (1969) 7.
6 K. Grob and G. Grob, *J. Chromatogr. Sci.*, 7 (1969) 584 and 587.
7 K. Grob, *Helv. Chim. Acta*, 51 (1968) 718.
8 M. Novotný and K. Tesařik, *Chromatographia*, 1 (1968) 332.
9 M. Novotný, L. Blomberg and K. D. Bartle, *J. Chromatogr. Sci.*, 8 (1970) 390.
10 C. A. Cramers, J. A. Rijks and P. Boček, *Clin. Chim. Acta*, 34 (1971) 159.
11 C. Landault and G. Guiochon, *Chromatographia*, 1 (1968) 119.