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Chromatographic characteristics of capillary packed columns with increased pressure drop

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ABSTRACT

The use of high-efficiency columns in gas chromatography, with an increased resistance to the carrier gas, necessitates an increase in the column inlet pressure. This approach has resulted in the realization of relatively efficient chromatographic processes involving columns with inlet pressures × xe25 bar. Long chromatographic columns are characterized by efficiencies as high as 20 000 real theoretical plates, whereas short columns may increase the number of analyses per unit time.

INTRODUCTION

The development of micropacked capillary columns is of some interest as they possess several advantages compared over open-tubular columns. First, micropacked columns are characterized by larger capacities and consequently longer column lifetimes, *e.g.*, when samples containing practically non-eluted components are analysed. Second, large sample volumes can be analysed, therefore decreasing the detection limits of the components. Finally, a high specific effeciency can be achieved (the specific efficiency of micropacked columns is about 10 000–30 000 theoretical plates per metre), giving the prospect of obtaining efficiency using shorter columns.

The increase in the total efficiency of packed chromatographic columns and the number of analysis that can be performed in a given time is usually restricted by the high pressure of the carrier gas at the column inlet. Thus, Huber *et al.* [1] used a column packed with the 30–35-μm fraction of Spherosil, the inlet pressure being 10 bar. The total efficiency was 15 000 theoretical plates.

However, an increased carrier gas pressure complicates the injection of a sample into columns packed with fine sorbents. In a previous study [2] with silica gel (20 μm) we obtained efficiencies of 10 000–30 000 theoretical plates. In those experiments the column inlet pressure was 25 bar and the sample was injected into the chromatograph through a specially designed gas syringe. It should be noted that the injection procedure was complicated when the pressure exceeded 5–10 bar.

The use of an injection valve seems to be more promising in this situation. Such a valve enabled Ghijsen *et al.* [3] to inject samples into micropacked columns at a

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[a] Author deceased.

carrier gas pressure of 43 bar, the diameter of the column packed with a gas–liquid chromatographic sorbent being 1.2 mm. One of possible solutions involves the use of an injection valve wideley used in liquid or supercritical fluid chromatography.

Despite the above minor drawbacks, capillary columns packed with fine sorbents are promising for future applications. The principal advantages of these columns are a reduced wastage of carrier gas and sorbent, high efficiency and an increased number of analyses in a given time.

EXPERIMENTAL

The experiments were carried out using fused-silica capillaries with an outer polymer coating producing in the U.S.S.R. [4] and France (Quarz et Silice, Courbevoie). These capillaries were packed with the sorbents by vibration at increased gas pressure. The sorbent was fixed on either side by a binder permeable to the carrier gas [5,6].

We used four columns: (1) aluminium oxide (40–50 μm), 113 cm × 0.32 mm I.D.; (2) Silasorb 600 (LC), 20 μm (Lachema, Brno, Czechoslovakia) (25 m × 0.25 mm I.D.; (3) as (2), 254 cm × 0.32 mm I.D.; (4) as (2), 59 cm × 0.25 mm I.D.

Injection of samples above 25 bar was realized using an injection valve designed by the Special Design Bureau of the Institute of Organic Chemistry (U.S.S.R. Academy of Sciences, Moscow, U.S.S.R.). At pressures below 25 bar we used a flow splitter and the sample was injected using a gas syringe.

We used a model LKhM-8MD chromatograph equipped with a flame ionization detector (Khromatograf Plant, Moscow, U.S.S.R.).

Carbon dioxide served as the carrier gas. Various gases and vapours of C_1–C_7 hydrocarbons were used as sorbates.

RESULTS AND DISCUSSION

Carbon dioxide was used as the carrier gas as it has a relatively low viscosity of *ca.* $148 \cdot 10^{-6}$ P, whereas those of nitrogen and helium are $175 \cdot 10^{-6}$ and $194 \cdot 10^{-6}$ P, respectively [7].

Fig. 1 compares the characteristics of the capillary packed columns in systems equipped with an injection valve capable of operating at elevated pressures and with a "conventional" flow splitter, plotted as height equivalent to a theoretical plate (HETP) against carrier gas velocity. Parameters reflecting column efficiency such as the total number of theoretical plates (N), the minimum value of the HETP ($H_{\min}$), the A and C terms of the Van Deemter equation and the maximum inlet pressure ($P_{\max}$) are given in Table I for the two injection procedure.

The data in Fig. 1 and Table I show that injection of a sample using an injection valve at elevated pressures does not decrease the total number of theoretical plates and the specific efficiency in comparison with the conventional flow-splitting technique.

To increase the column inlet pressure, a cylinder of liquefied carbon dioxide was used as a pressure source, the equilibrium pressure being 73 bar (room temperature) [7].

The velocity at the outlet of column 2 (silica gel, 20 μm) equipped with a

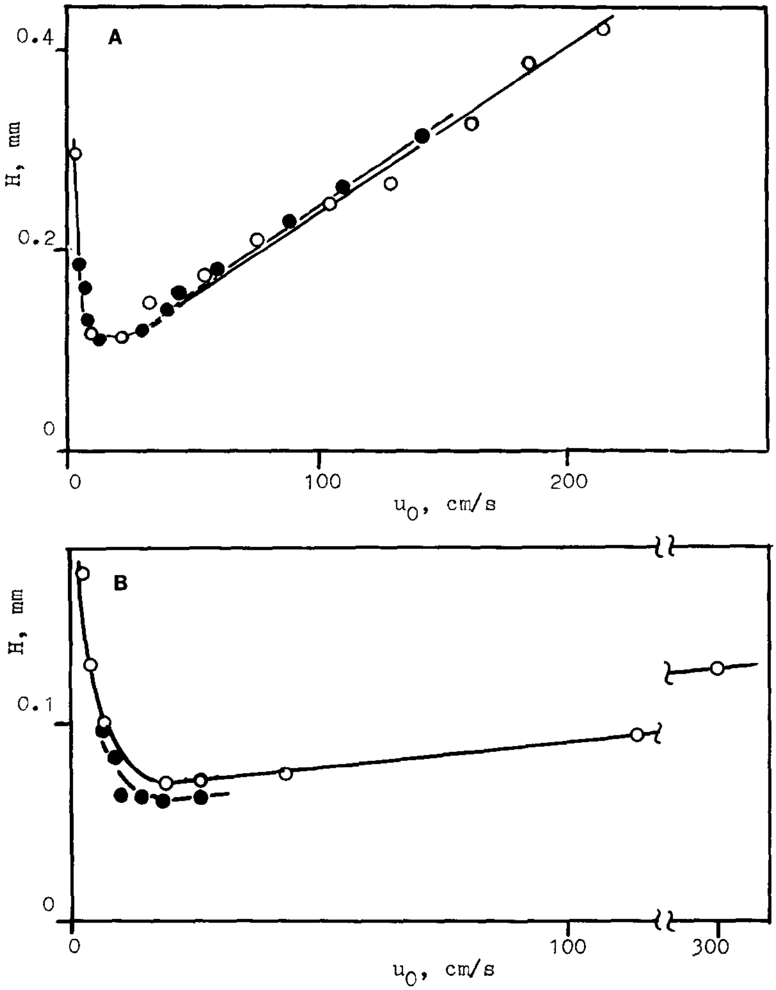

Fig. 1. Dependence of HETP (*H*) on the carrier gas velocity at the column outlet, u_0. Carrier gas, CO_2; temperature, 50°C. (A) Column 1, 113 cm × 0.32 mm I.D.; sorbent, Al_2O_3; sample, *n*-pentane. (B) Column 2, 25 cm × 0.25 mm I.D.; sorbent, silica gel; sample, *n*-hexane. Mode of injection: (●) high-pressure injection valve; (○) syringe injection into a flow splitter.

restrictor (maximum pressure *ca.* 25 bar) was 115 cm/s (Fig. 1B) at a pressure of 27.2 bar, whereas direct connection of the injection valve to liquid gas tank increased the velocity to 295 cm/s.

It should be noted that the high-efficiency capillary packed column showed a slightly increased HETP value with an increase in the carrier gas velocity, caused by an increase in the pressure at the column inlet. Thus, inlet pressures of 14.7, 27.2 and 73 bar with column 2 resulted in an increase in the carrier gas velocity to 25, 115 and 295 cm/s, respectively. As Fig. 1B indicates, this led to a corresponding increase in the HETP (0.062, 0.094 and 0.127 mm, respectively). One can deduce from Table I that this is due to the low value of the resistance to mass transfer term, *C*. We should also

TABLE I

EFFICIENCY CHARACTERISTICS OF CAPILLARY PACKED COLUMNS 1 AND 2 WITH DIFFERENT SAMPLE INLETS, (IV) INJECTION VALVE AND (S) SYRINGE INJECTION INTO A SAMPLE SPLITTER, AT 50°C

Column No.	Sorbent	Sample	Sampler	No. of theoretical plates	H_{min} (mm)[a]	Van Deemter term		P_{max} (bar)
						C (s)	A (mm)	
1	Al_2O_3	*n*-Pentane	IV	10 300	0.110	0.00016	0.083	25
			S	10 300	0.110	0.00015	0.082	14.2
2	Silasorb	*n*-Hexane	IV	3 900	0.065	0.000027	0.063	27.2
			S	4 150	0.061	–	0.060	17

[a] Optimum carrier gas pressure for columns 1 and 2 = 5 and 12 bar, respectively.

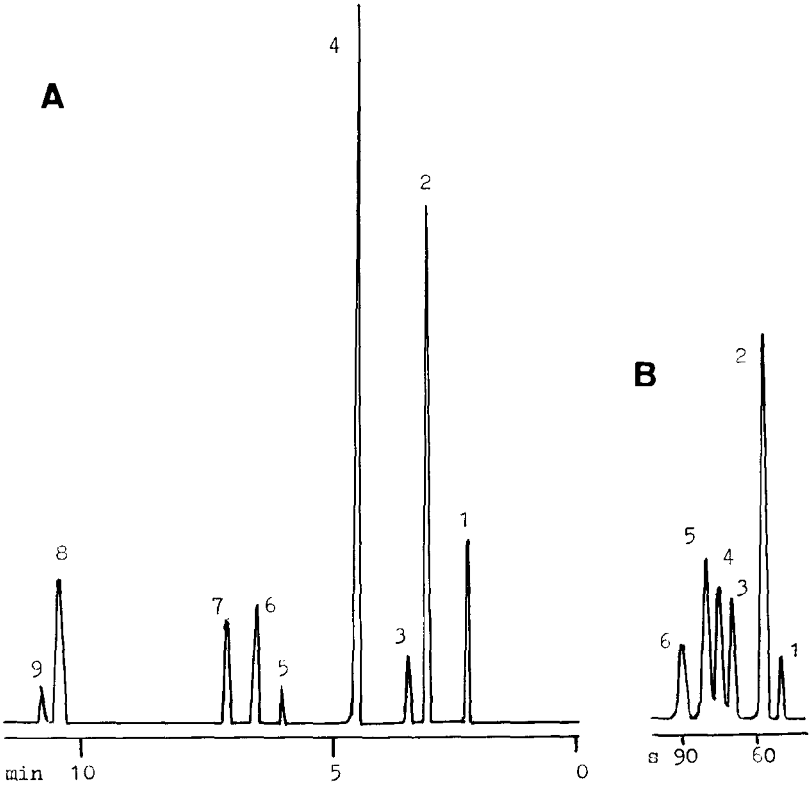

Fig. 2. Separation of light hydrocarbons. (a) Column 3 (254 cm × 0.32 mm I.D., silica gel, 20 μm); temperature, 52°C. Peaks: 1 = methane; 2 = ethane; 3 = ethene; 4 = propane; 5 = propene; 6 = isobutane; 7 = *n*-butane; 8 = *n*-pentane; 9 = isobutene. (b) Column 4 (59 cm × 0.25 mm I.D., silica gel, 20 μm); temperature, 80°C. Peaks: 1 = *n*-pentane; 2 = tetramethylbutane; 3 = 2,2-dimethylbutane; 4 = 2,3-dimethylbutane; 5 = *n*-hexane; 6 = cyclohexane.

point out that the value of the eddy diffusion term (A) is small, which demonstrates a satisfactory packing of the sorbent particles in the capillary column.

A gas chromatograph with a high inlet pressure can improve the overall efficiency with an increase in the column length and by operating at elevated pressures. The experiments were carried out using column 3 (sorbent, Silasorb 600) having a length of 254 cm (Fig. 2A). Its total efficiency was significantly higher than that of column 1 (113 cm), *i.e.*, 30 000 *vs.* 10 300 theoretical plates. The value of $P_{\max}$ for column 3 was about 73 bar.

The capillary packed column with an increased length operating at a high carrier gas pressure permitted the separation time to be decreased in comparison with the optimum carrier gas velocity. Thus, when column 2 was replaced with column 4 and the carbon dioxide pressure was increased from 11.9 bar to the pressure of the liquid gas tank, the retention time of *n*-hexane decreased from 168 to 80 s and the total efficiency increased from 3600 to 5400 theoretical plates.

Fig. 2B shows the chromatogram of a hydrocarbon mixture (up to C_6) using column 4 at a pressure close to that of the liquid gas tank. The total analysis time was about 1.5 min, whereas the use of the open-tubular column resulted in a total analysis time of 2–3 min.

CONCLUSIONS

Capillary packed columns with microparticulate adsorbents are characterized by a high efficiency and only a small dependence of the efficiency on the carrier gas velocity. Apparatus designed for supercritical fluid chromatography can be used with high-efficiency capillary columns packed with microparticulate sorbents.

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