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A STUDY OF THE SHAPE OF CHROMATOGRAPHIC BANDS IN PREPARATIVE GAS CHROMATOGRAPHIC COLUMNS

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SUMMARY

In preparative gas chromatography it has been observed that the maximum flow-rate and concentration of a component occur in the centre of the column. The reasons for such phenomena are discussed. Some procedures for decreasing the HETP of large diameter columns are described.

INTRODUCTION

At present, preparative gas chromatography is being transformed into a semi-industrial method for obtaining pure substances. The use of columns with diameters of 100 mm and greater is becoming more common. It is known that efficiency decreases with an increase in column diameter, the principal reason for which is thought to be the unequal velocity of movement of the component over different portions of the column cross-section. This inequality of rates has been observed experimentally in a number of investigations. The nature of the velocity profile and its causes, however, have not yet been ascertained. The view of GIDDINGS AND FULLER¹ is that the main cause of the inequality in the rates of movement of the component is the inequality of the carrier gas flow-rates. The latter, in turn, is due to a non-uniform distribution of the sorbent particles over the column cross-section. This phenomenon is explained by the fact that when the packing is poured into the column, the coarser particles accumulate near the column walls, and the smaller particles about its axis. Such a distribution of particles according to size along the column section was observed by GIDDINGS AND FULLER¹, PIPKER² and BEREZKIN AND RASTYANNIKOV³. With such a distribution of particles, the rates of flow of the carrier gas and the components must decrease from the walls towards the column axis. Such a profile of flow-rates of the carrier gas has been found by HUYTEN *et al.*⁴ as well as by BEREZKIN AND RASTYANNIKOV³. At the same time, some papers have been published in which a profile has been described of rates of movement of the component having a reverse shape, the maximum rate being observed at the centre of the column. Such a rate distribution was discovered by LIPPMAN AND LUIGA⁵ and an analogous rate profile was observed by HUPE *et al.*⁶.

The object of the present investigation was to study the rate profile of the component and the carrier gas across a column section of large diameter with different procedures for packing the column; the distribution of the packing particles according to size was also studied.

EXPERIMENTAL

The experiments were carried out on a column 140 mm in diameter and 1 m long, packed with 0.5–1.0 mm Spherochrom with 15% of dinonyl phthalate. Into the upper removable cone of the column were welded some tubes that terminated with thin capillaries 0.3–0.4 mm in diameter (Fig. 1). The gas flow could be passed along these capillaries from different points along the column. The resistance offered by the capillaries to the flow approximately corresponds to the resistance of the upper layer of the packing.

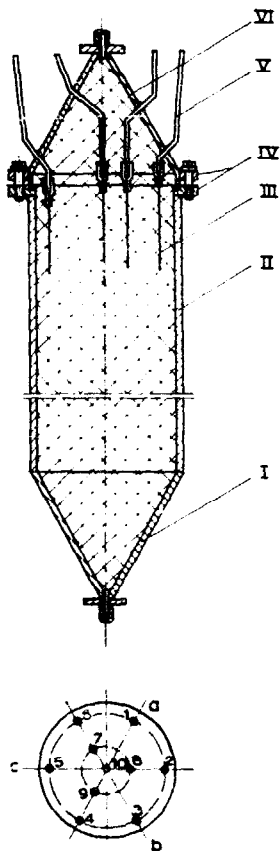


Fig. 1. Schematic diagram of the column with the capillaries (1–10). I = inlet cone; II = column; III = capillary; IV = flanges; V = outlet port; VI = outlet cone.

The main flow of gas from the column was removed through the upper port, while only an insignificant part of the flow was removed through the capillaries. This enabled the disturbance of hydrodynamics and a possible redistribution of the flow to be minimized.

The column was packed without the upper cover. The packing was poured in and compacted to a level corresponding to the position of the lower edges of the capillaries. After the core of the column had been set in place, subsequent packing

of the remaining portion of the column and the outlet cone was made through the upper port. To the capillaries were connected two thermal conductivity detectors, of which one was permanently connected with the central capillary, and the other with one of those at the periphery. The chromatograms from the two detectors were recorded by two potentiometers, which enabled the variation of the concentration with time at two points on the column cross-section to be obtained in one run. The experiments were carried out at room temperature. A 2-ml volume of *n*-pentane was injected through the evaporator. The profile of the carrier gas flow-rates was determined by eluting helium through the column. It was possible to heat the column to a higher temperature with a band heater coiled on the external wall of the column. At the same time as the concentrations were measured, the temperature change due to the band passing through the bed of sorbent was also measured by means of thermocouples inserted into the column through tubes in the cover and fixed on the capillaries. The readings of the thermocouples were recorded as thermopeaks on electronic potentiometers with a 0.1 mV scale.

In addition to the study of the zone front, the height equivalent to a theoretical plate (HETP) was also measured. For this purpose, a thermal conductivity detector was connected to the outlet port of the column, and part of the gas flow was diverted to this detector by a three-way pipe.

The size distribution of the particles along the column section was determined by screen analysis.

RESULTS

Fig. 2 shows typical chromatograms recorded when the detectors were connected to capillaries located at different distances from the column axis. Based on these chromatograms, the boundaries of the front and rear of the zone corresponding to a definite concentration were plotted. The maximum concentration line will be used below as a characteristic of the zone shape. It can be seen from Fig. 2

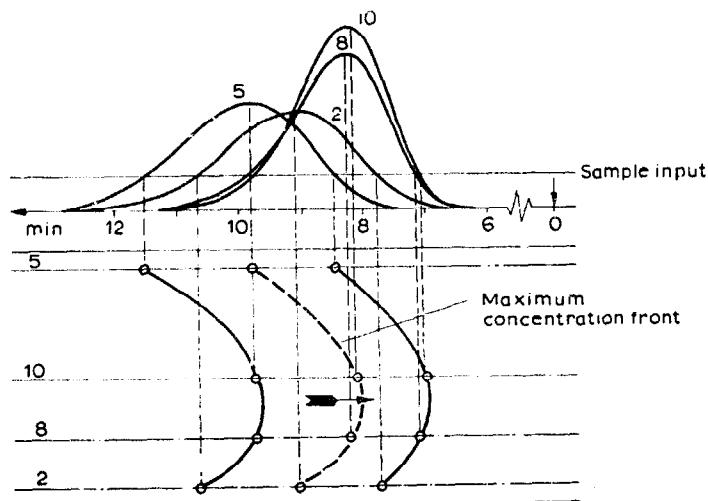


Fig. 2. Plot of zone fronts from chromatograms obtained on capillaries 2, 5, 8 and 10.

that the highest velocity and concentration are observed in the centre of the column. Fig. 3 shows the shape of the zone plotted from the peak maxima for three groups of capillaries located in three annular sectors a, b, c (Fig. 1) at 120° relative to each other. All three profiles coincide, although there is a certain asymmetry for some of them.

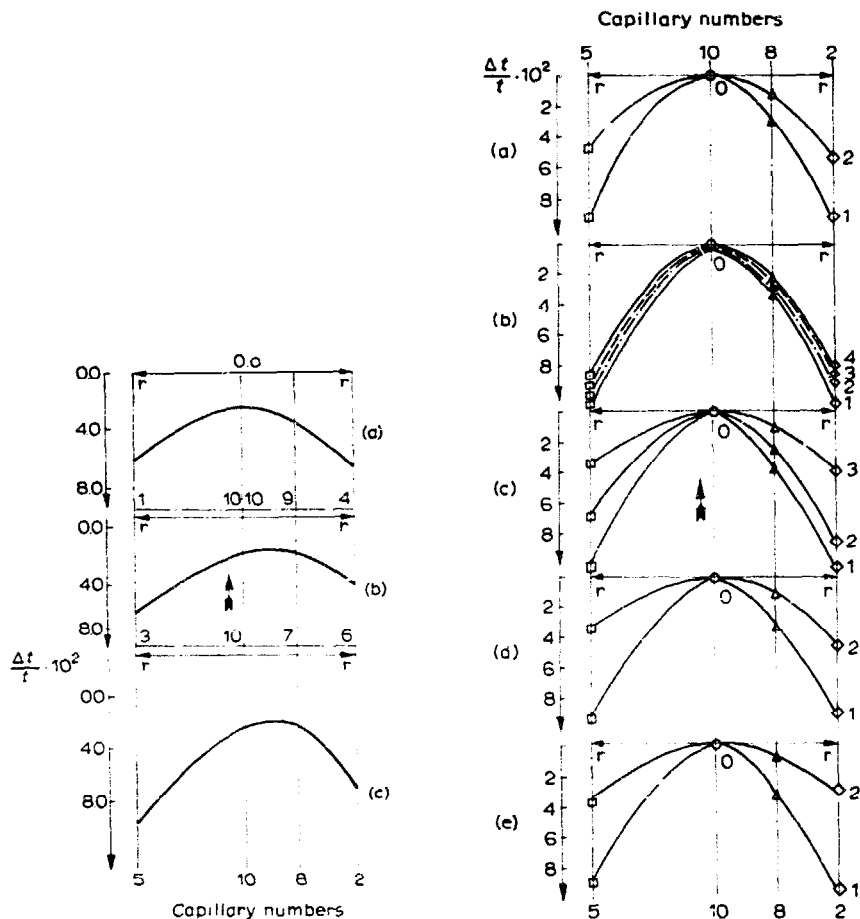


Fig. 3. The shape of the zone for three groups of the capillaries (a, b and c).

Fig. 4. The influence of the different factors upon the zone shape for capillaries 2, 5, 8 and 10. (a) Inlet cone packed without the disc (1) and with disc (2); (b) different *n*-pentane doses: (1) 20 ml, (2) 10 ml, (3) 5 ml, (4) 2 ml; (c) different methods of packing: (1) tapping 200 times, (2) tapping 50 times, (3) filling without compacting; (d) different methods of packing: (1) tapping 200 times, (2) vibrating; (e) the zone shape of *n*-pentane (1) and helium (2)

In Fig. 3, as well as in Fig. 4, the distance of that particular capillary from the column axis is plotted on the abscissa, and the relative delay $\Delta t/r = (t_p - t_c)/t_c$ is plotted on the ordinate, where t_p is the retention time of the peak maximum measured for the capillary on the periphery, and t_c is that for the central capillary.

The zone profiles shown in Figs. 2 and 3 were obtained by using the following procedures of packing the column. The column was entirely filled with the packing

and then tapped 200 times against a wooden plate. As in these experiments the inlet cone of the column was filled with the packing, it was justifiable to assume that the component rate profile was due to the effect of the inlet cone in which the path along the axis was shorter than that along the walls. The pressure gradient in the former case is also greater, which should result in an additional increase in the carrier gas flow-rate along the centre of the column.

To eliminate the influence of the above effects over the packing filling the lower cone, a disc was introduced, the diameter of which was less than that of the column. As a result, the gas flow could pass only along the annular clearance near the column wall. The existence of the disc makes the path along the column axis the longest; however, this did not influence the profile of the zone, although it did make it less convex (Fig. 4a). Similar results were obtained when the cone was packed with glass wool. The use of the disc and of glass wool resulted in a decrease in the HETP of the column. Hence the profile of the zone observed is determined firstly by the properties of the packing bed. The influence of the heat effects related to the evolution of the heat of sorption must be negligible with the amounts of sample used. This was confirmed by the fact that an increase in the sample size of *n*-pentane from 2 to 20 ml did not change the profile of the zone (Fig. 4b).

We tried to ascertain the influence exerted upon the profile of the zone by the method used to compact the packing, and also to relate this profile to the HETP of the entire column and the distribution of the packing particles according to size along the column section. The column was first filled without compacting the packing, then the packing was compacted by tapping the column 50 and 200 times, and finally the column was subjected to vibration. The compaction of the packing was therefore continuously increasing. After each compaction of the packing, the front of the zone and the HETP were measured. The results in Figs. 4c and d show that the more compact the packing, the sharper is the zone profile, although the profile is virtually absent with loose packing; in some experiments with a loose packing, a profile was obtained that was even concave in the direction of movement. After the vibration of the column the profile became flatter, which can be explained by a subdivision of particles according to size: with loose packing and tapping, the fraction composition of the packing was virtually uniform (Table I), but after vibration the coarser particles accumulated chiefly near the column walls, which promoted the formation of an even profile of the zone.

It can be assumed that the distribution of concentrations observed at the column outlet does not entirely correspond to the rate profile because of the effect of radial diffusion. As the packing becomes more compact, radial diffusion is decreased and with the same rate profile the distribution of concentrations becomes more convex. In order to ascertain the effect of radial diffusion upon the distribution of concentrations, *n*-pentane was eluted in different carrier gases, namely, nitrogen, helium and mixtures of these gases in different proportions. Results on the relative delay of the peak in the peripheral portion of the section At are given in Table II, where At is the difference of retention times measured with detectors connected to the central and peripheral capillaries.

It can be seen from these values that a decrease in the relative delay occurs when the helium content in the carrier gas is greater than 20%. As the diffusion coefficient in helium is significantly higher than in nitrogen, the slight variations

TABLE I

THE FRACTION COMPOSITION OF THE PACKING WITH TWO METHODS OF COLUMN FILLING

Weight	Fraction of packing (mm)					
	Vibration			Striking		
	1.0-0.65	0.65-0.5	0.5-0.35	1.0-0.65	0.65-0.5	0.5-0.35
Central zone weight (%)	64.8	30.0	5.2	60.4	27.1	3.5
Periphery zone weight (%)	69.6	20.4	4.0	68.4	27.7	3.0

TABLE II

RELATIVE DELAY OF PEAK DURING ELUTION OF *n*-PENTANE IN NITROGEN-HELIUM MIXTURES

Parameter	Helium content (%)			
	0	20	50	100
Δt (sec)	39	42	28	23
$\Delta t/t \cdot 10^2$	8.9	8.9	0.2	5.4

in radial diffusion due to the compactness of the packing should not exert any significant influence upon the concentration profile.

Fig. 4d shows the profiles of the zone for *n*-pentane and a non-sorbing gas (helium) obtained after compaction of the column packing by tapping it 200 times. The two profiles coincide although the *n*-pentane profile is sharper.

In conclusion, it should be noted that the zone profiles constructed from the readings of the detectors and thermocouples virtually coincide. The divergence in Δt of 5-6 sec, with absolute values of Δt generally in excess of 30 sec, does not affect the results obtained.

DISCUSSION

From the results presented above, the inference can be made that the rate profile of the component is to a considerable extent determined by the rate profile of the carrier gas.

The profile of the carrier gas flow-rates originates from a difference in the hydraulic resistance of portions of the column located at different distances from its walls. These differences in the hydraulic resistance may arise from two sources: a non-uniform distribution of the packing particles of different sizes across the column section, and a non-uniform packing of these particles. From published results it is known that the coarser particles accumulate mainly along the column walls. In our experiments, we have found either no distribution of particles or a similar distribution that cannot account for the rate profile of the carrier gas and the component observed, with a maximum flow-rate along the column axis.

The following scheme for the formation of the rate profile of the component seems to be the most justifiable. When the packing is compacted, its layers located within different distances from the column axis are non-uniformly compacted, the peripheral layer being more and the central layer less intensely compacted. Because

of the non-uniform packing of particles, a rate profile of the carrier gas that is convex to the path of flow is produced, and as a consequence a similar rate profile of the component movement is formed. A certain fractionation of the packing particles according to size, which is especially marked after vibration, makes the rate profile flatter. It is not improbable that the rate profile is affected not only by the distribution of the carrier gas flow-rates but also by a number of effects related to sorption and mass exchange.

Indirect evidence in favour of the assumption that the rate profile of the component arises not because of the distribution of particles according to size but for some other reason, is offered by experiments with an artificially produced distribution of particles. In these experiments, a thin-walled tube of wall thickness 0.2 mm and 20 mm in diameter was inserted into a column 46 mm in diameter. The inner space of the thin-walled tube and the annular clearance were packed by three procedures, *viz.*: (i) both spaces were filled with particles of the same size, 0.25–1.0 mm; (ii) 0.25–0.5 mm fraction in the centre, 0.5–1.0 mm grain size in the annular clearance; (iii) 0.5–1.0 mm fraction in the centre, 0.25–0.5 mm grain size in the annular clearance (Fig. 5). The packing was compacted by striking the column, after which the inner tube was carefully removed, and the packing was subjected to additional compaction. After this, the HETP was measured for *n*-pentane. The values obtained were as follows: packing without tube, 4.6 mm; equal grain size in the centre and at the periphery, 4.8 mm; coarse fraction in the centre, fine fraction at the periphery, 30.0 mm; and fine fraction in the centre, coarse fraction at the periphery, 9.4 mm.

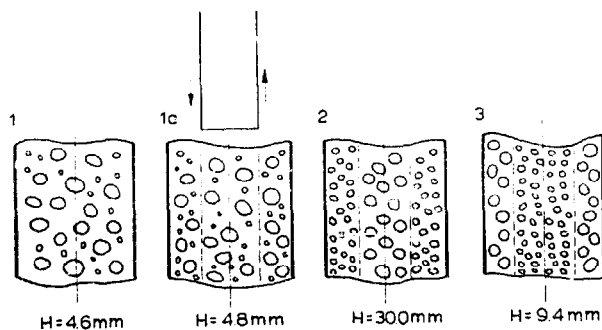


Fig. 5. An artificially produced distribution of particles.

It can be seen from these figures that the insertion of the tube and its removal did not affect the HETP. When an artificial distribution of particles is produced, the HETP should not depend on the location of the coarser particles, whether in the centre or at the periphery.

Actual experience, however, revealed a different situation. The location of coarse particles in the centre caused a considerably sharper increase in HETP than the location there of fine particles. In the former case, a decrease in the hydraulic resistance in the centre of the column caused by the location there of coarse particles of the packing is intensified by the loose arrangement of these particles, which results in a very convex rate profile. On the contrary, however, when fine particles are located in the centre, the increase in the hydraulic resistance is partly decreased by their looser arrangement. It can be expected that with a less sharp difference in the fraction

composition of particles, a virtually flat profile of the zone may be obtained when the finer particles are placed in the centre and the coarser particles at the periphery of the column.

Some procedures for diminishing the HETP of large diameter columns

The most radical method for obtaining a flat profile of the component flow-rates would be to ensure a uniform compactness of the packing of sorbent particles over all portions of the column section. At present, however, no procedure for filling the column is known that would ensure such a uniformity of packing. A flat rate profile can also be obtained by placing the finer particles of the column packing in the centre of the column; however, it is very difficult to do so in practice. Such a distribution of the sorbent particles over the section of the column seems to be partly produced when some methods for compacting the packing are used, e.g.,

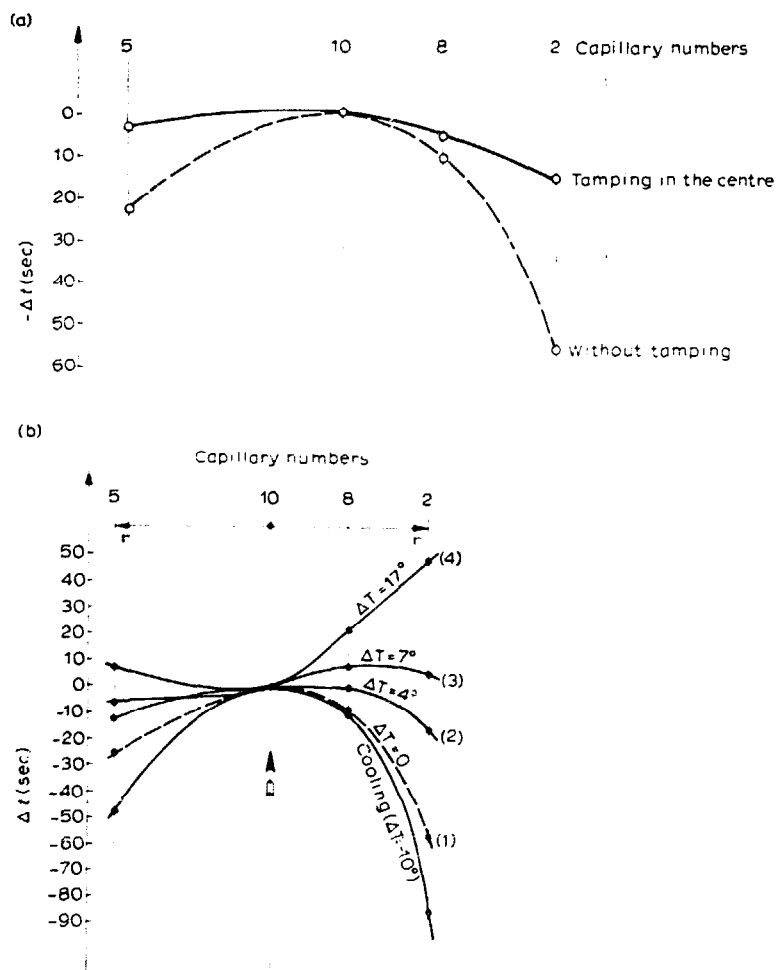


Fig. 6. Flattening of the zone shape by (a) additional tamping of the packing in the centre; (b) heating the column wall: $\Delta T = 0^\circ$ (1), $\Delta T = 4^\circ$ (2), $\Delta T = 7^\circ$ (3), $\Delta T = 17^\circ$ (4).

vibration of the column; in our experiments, this procedure has given the highest efficiency of resolution.

One may also attempt to obtain further compaction of the packing in the centre of the column. For this purpose we poured the packing into the column in several portions. After pouring and compacting each portion by tapping, the packing was subjected to additional tamping in the centre with the aid of a plunger 50 mm in diameter. Then a control run was made in which the column was packed in a similar manner but without tamping. It can be seen from Fig. 6a that the tamping of the packing flattens the rate profile and increases efficiency.

Finally, a flat rate profile of the component can be obtained with a convex profile of the carrier gas flow-rates by changing the sorption capacity of the packing in a definite way over the section of the column. This can be achieved by placing in the centre of the column the packing containing a high proportion of the stationary phase; this procedure, however, meets with the same practical difficulties as does an artificial distribution of particles by their sizes. It would be simpler to produce a certain temperature difference between the wall and the centre of the column, e.g., by raising the wall temperature at a slow rate. After some time, a stationary difference in temperature between the wall and the centre of the column would be established. Fig. 6b shows the zone profiles obtained at different rates of heating the column wall and with different temperature gradients between the wall and the centre of the column. As this gradient is increased, the profile at first becomes flatter and afterwards concave. With a definite difference in temperature between the wall and the centre of the column, the zone profile can be entirely flattened.

When large diameter columns are used, the cones at the ends of sections must be packed with a non-sorptive material.

In almost all of our experiments we have found a direct relationship between the zone profile and HETP: the more convex the profile obtained, the higher is the HETP value. However, the rise of HETP with increased column diameter can result not only from a regular profile of the component rates but also from accidental variations in the packing density over different portions of the column section. Such occasional changes in the compactness of the packing have not been observed in similar experiments. To ascertain their effect upon the HETP value in large diameter columns, special studies are required.

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