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LONGITUDINAL SPREADING IN GAS AND LIQUID CHROMATOGRAPHY AND ITS CONNECTION WITH PACKED BED STRUCTURE AND THE VELOCITY OF THE MOBILE PHASE

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SUMMARY

Mobile phase velocity distributions were measured by laser Doppler anemometry at the outlet of chromatographic columns 46–140 cm in diameter. Large- and small-scale non-uniformities of the velocity field were detected; the influence of column diameter, packing particle size, mobile phase flow-rate and nature of the particle material on these non-uniformities was studied. The effect of velocity field non-uniformities on longitudinal spreading is discussed.

INTRODUCTION

The efficiency of packed bed equipment, notably chromatographic columns, is determined to a large extent by the packed bed structure and the mobile phase flow-rate field.

Granular bed structure has been the subject of many investigations^{1–19}. The existence of a velocity profile in a column cross-section was discovered, but the character of this profile is disputed: the velocity distribution is close to parabolic, but the maximal rate was observed both near the wall^{1,2} and near the axis^{3–5} of the column.

The “wall effect” is also controversial: some workers have discovered areas with accelerated gas flow-rates at a distance of 0.5–1.0 d_p from the wall^{6–8}, whereas others claim that this area is much wider^{9,10}. Most of the above measurements, especially those carried out on chromatographic packings, were obtained using semi-quantitative methods that usually involved trace substances. A number of these trace substances were sorbed under the experimental conditions used. Moreover, diffusion spreading of pulse-injected trace substances can result in errors pertaining to measurements of the velocity profile.

In this work we used laser Doppler anemometry to measure the mobile phase velocity field at the outlet of the packed bed under various conditions. This method is quantitative, its error margin does not exceed 2% and it needs no preliminary calibration; further, it does not distort the measured flow and cannot be influenced by changes in the external conditions. Using the method, we measured not only the velocity profile, *i.e.*, velocity variations whose scale is comparable to the column

diameter, D_k (trans-column effect according to Giddings¹¹), but also smaller-scale variations (short and long inter-channel effects) that also influence longitudinal spreading. Experiments were carried out using gas and liquid mobile phases with identical Re numbers. This study is a continuation of work¹² in which the short and long inter-channel effects were measured for the first time.

EXPERIMENTAL

Experiments were performed on columns 46–140 cm in diameter, made of glass or stainless steel. Sand, silica gel and diatomite chromatographic supports (Spherochrom, Dinochrom and Celite C 22) were used for packing. The particle size range of these packings was 0.25–5 mm. In experiments in which a gas was used as the mobile phase, we resorted to the traditional scheme and a laser Doppler anemometer¹³. When water was used as the mobile phase, it was fed into the column using the device shown in Fig. 1. To create light-dissipating centres in the water, a polystyrene latex of particle size about 1100 Å was added at a volume ratio of 4000:1. The water was then poured into vessel 1, from which pressurized gas bled from tank 2 forced it, by way of valve 4, into the column 5. The liquid flow-rate through the column was measured with a flow meter 6 and regulated by changing the gas pressure. The liquid was poured from the column 5 into tank 1a through valve 4. When tank 1 became empty, tank 1a became the source of mobile phase; this was accompanied by switching valves 3 and 4 in the following way: liquid coming from tank 1 passed through channels a and d, and channels b and c were sealed off; liquid from tank 1a passed through channels b and c, and a and d were sealed off. Use of this scheme with a total liquid volume of 40 l made it possible to carry out experiments without stopping the flow for long periods of time over a wide range of flow-rates and without any latex losses.

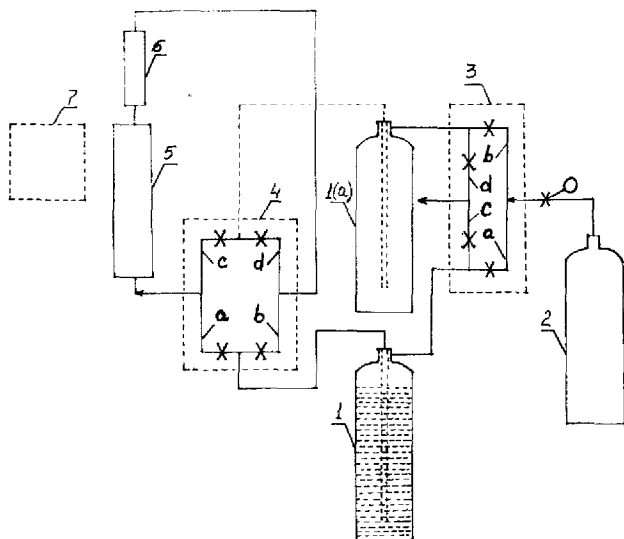


Fig. 1. Arrangement for supply of liquid into column: 1 and 1(a) = tanks; 2 = gas tank; 3 = gas commutation valve; 4 = liquid commutation valve; 5 = column; 6 = flow meter; 7 = laser anemometer.

Column 5 was a glass or glass-metal tube (metal bottom, glass top). The glass top was fitted into grooves and secured by a coupling flange in experiments with gas, or with a threaded bandage seal at the top of the metal tube in experiments with liquids.

Flow-rates were measured with a laser anemometer 7, whose beams passed at a distance of not more than 5 mm from the top of the packed bed. The velocity was measured along diameter lines with a 1 mm pitch. The total number of measurements in each mode was 150–300. Changes in the refractive index on transition from a gas to a liquid medium were accounted for in the process of scanning and calculations. The overall error did not exceed 2%.

RESULTS AND DISCUSSION

We obtained a velocity distribution that enabled us to distinguish two major kinds of non-uniformities (Fig. 2):

(1) Large-scale non-uniformities (trans-column effect) that can in principle be described by a velocity profile $U(r)$ (where r is the column radius). These non-uniformities reflect the existence of a hydraulic resistance distribution along column diameter, for instance, reduced resistance of wall-adjacent areas.

(2) Small-scale non-uniformities, which are probably caused by regions of higher packing density (aggregates), interspaced with comparatively looser packing. These non-uniformities are random in nature and may be described by statistical moments. In turn, small-scale non-uniformities take two forms: variations over the small section characterized by high "frequency" (micro-variations), which probably correspond to what Giddings¹¹ called short-range inter-channel effects, and variations with a low "frequency" (macro-variations), which correspond to the term long-range inter-channel effect. The existence of micro- and macro-variations is probably due to the fact that the larger macroaggregates consist of smaller microaggregates.

To establish the quantitative characteristics of these non-uniformities, experimental data were subjected to statistical analysis using to a special computer program¹³. The main statistical characteristics of velocity variations were calculated: following calculation of mean velocity U , the mean positive and mean negative deviation from U were determined together with the difference between these two values, ΔU ; moreover, the mean square deviation σ and the ratio σ/U were determined. These values describe the intensity of both large- and small-scale variations. To distinguish micro-variations, we resorted to smoothing¹⁵, which made it possible to determine a velocity distribution that reflected large-scale non-uniformities and macro-variations. The next step was the calculation of the above statistical values using a smoothed profile at each point as a mean value, *i.e.*, calculating, for instance, the mean square deviation from the smoothed profile of σ' and σ'/U .

Microaggregate sizes were determined as the distance between adjacent velocity maxima (Fig. 2a), following which the average microaggregate diameter d_a was determined along with the mean square deviation σ_{d_a} and relative mean square deviation σ_{d_a}/d_a . The same operation was performed for the smoothed profile, taking the distance between maxima in this profile to be the microaggregate size (Fig. 2b). The results obtained are discussed below.

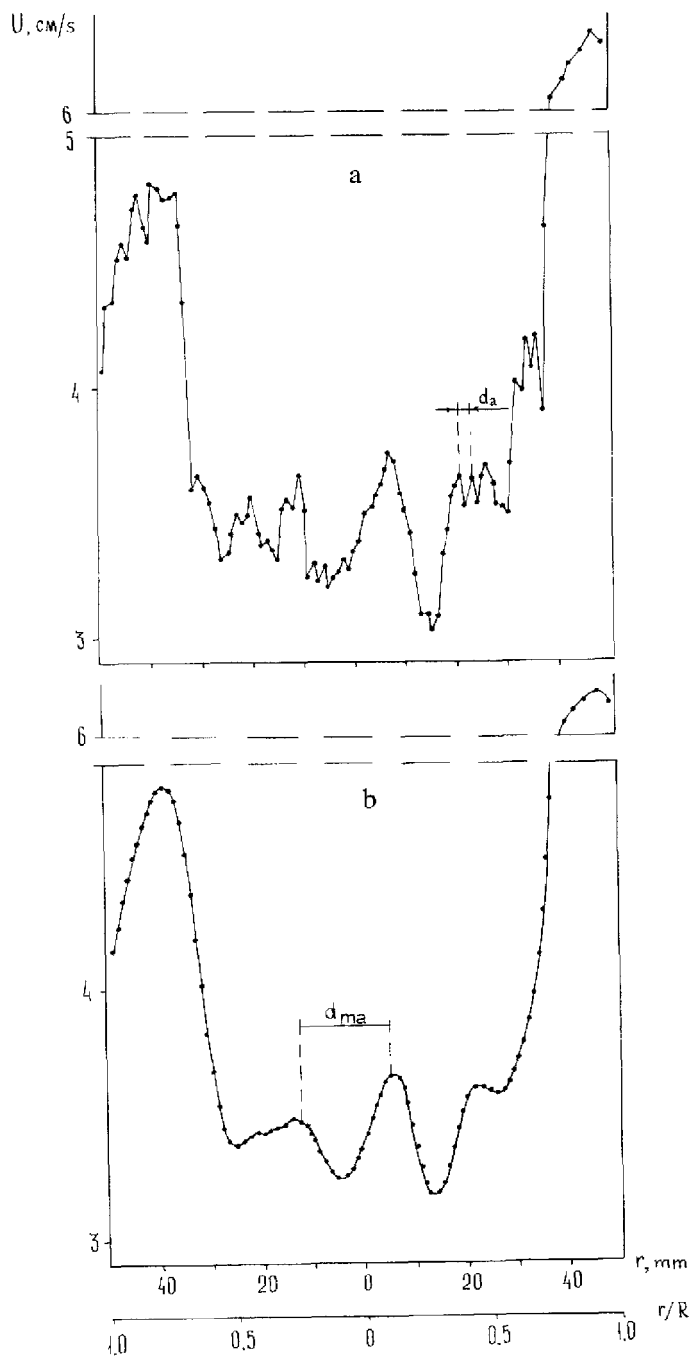


Fig. 2. (a) Initial and (b) smoothed distribution of carrier gas velocity at column outlet (diameter 100 mm). Spherochrom-1 packing, granule size 0.5–1.0 mm.

Large-scale velocity non-uniformities

The character of large-scale velocity non-uniformities depends greatly on the mean particle size, their size distribution and the packing method. It is therefore difficult to speak of one profile being formed in the packed bed. This also explains the differences in reference data that were discussed above. However, it is possible to point out typical velocity distributions. In most of our experiments, the sorbent particles were packed into the column portion by portion and compacted with a plunger; simultaneously, the column was evacuated from below by a vacuum pump. This yielded, with gas flows, a velocity profile that could be approximated by a parabola with the velocity minimum located close to the axis of the column. However, the maximum was often observed at some distance from the wall rather than close to it. Such a nearly parabolic distribution was clearly revealed in a 46 mm column packed with Spherochrom of particle size 0.5–1.0 mm (Fig. 3a). On increasing the column diameter to 100 mm, the general character of the profile remained unchanged, although local maxima did appear near the axis of the column, caused, in our opinion, by macroaggregates superimposed on the large-scale velocity variation (Fig. 3b). Finally, in 140 mm diameter columns, the velocity profile is comparatively weak: there are areas close to the wall with a greater velocity (in a few instances, the maximum was observed at some distance from the wall); in the remaining part of the column the velocity is roughly constant, although with considerable macro-variations (Fig. 3c). Hence a parabolic distribution is observed with several instances of velocity deceleration close to the wall. Further, packing the column with smaller sized par-

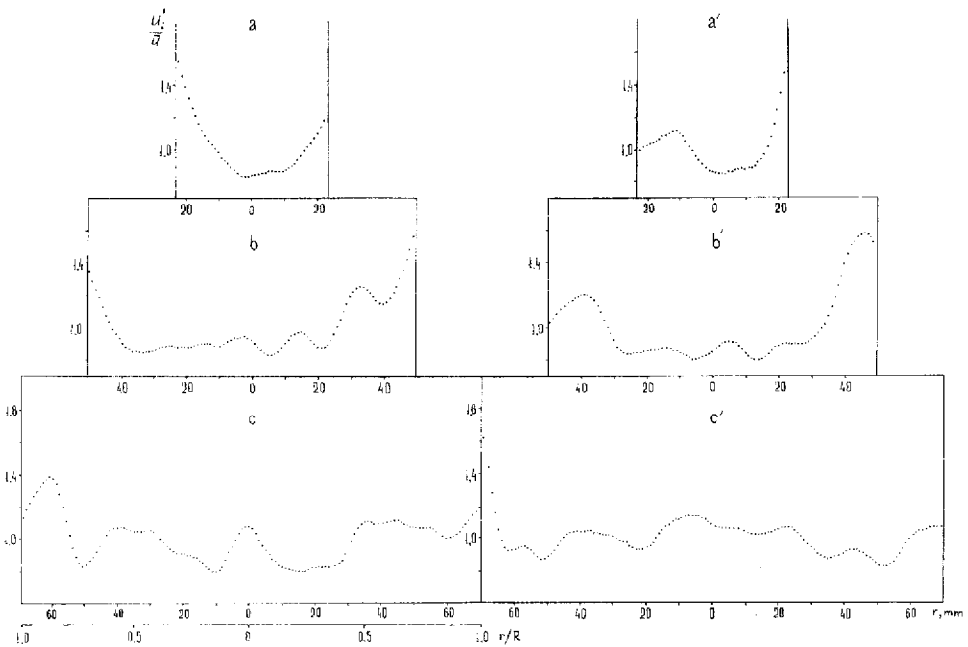


Fig. 3. Smoothed gas velocity distributions for columns of varying diameter along two mutually normal diameter lines. a,a', Diameter 46 mm; b,b', 100 mm; c,c', 140 mm. Spherochrom, granule size 0.5–1.0 mm; bed thickness, 400 mm.

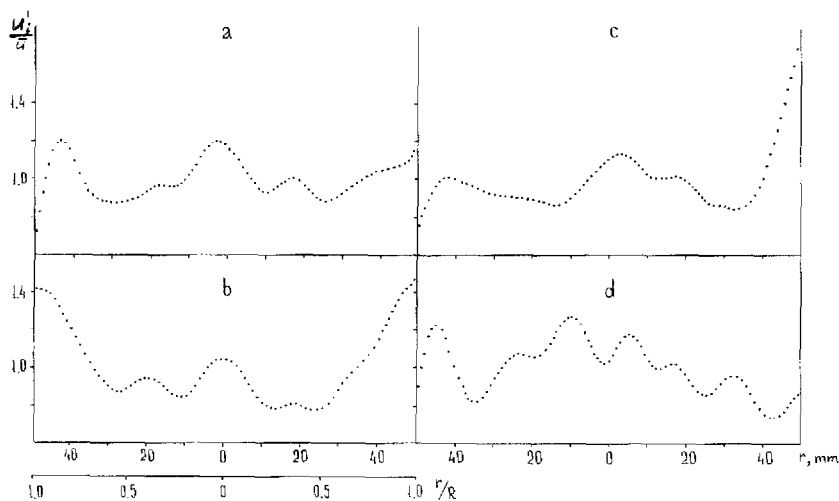


Fig. 4. Smoothed gas velocity distributions for different supports of granule size 0.315–0.5 mm. (a) Dinocrom H; (b) Celite C 22; (c) sand; (d) Spherochrom. Column diameter, 100 mm.

ticles (0.315–0.5 mm) generally led to certain increases in velocity close to the column axis, with the maximum of this increase sometimes surpassing the average velocity (Fig. 4). It is difficult, however, to determine whether this increase is part of a regular profile or an accumulation of macroaggregates. The fact that it is reproduced on particles of different natures indicates that this velocity increase probably belongs to large-scale variations.

In our experiments with liquid flows we did not study columns of 100 and 140 mm diameter, restricting our investigations to a 44 mm column. The packing particle size in this column was varied. The most typical profiles are presented in Fig. 5. They are generally of a parabolic nature. However, in most instances the greatest velocity is observed at some distance from the wall of the column, and the maxima themselves are clearer. As with gas flows, another maximum in some instances is observed close to the axis of the column.

The velocity profiles obtained cannot be explained by particle separation according to size during packing, as claimed by Giddings and Fuller²⁰; particles were evenly distributed over the entire column cross-section during packing. The appearance of large-scale velocity variations is probably due to the dependence of packing density (the number of inter-particle contacts) on the distance from the wall of the column. The loosening influence of the wall spreads a considerable distance into the packed bed. It is difficult to explain the origin of the velocity maximum that is sometimes observed close to the axis of the column. It is possible that a similar maximum was observed in experiments with a parabolic distribution and maximum velocity close to the axis of the column^{3–5}. It is more feasible, however, that the reason for the appearance of such a profile lies in the existence of a lateral temperature gradient in the column due to heating of the carrier gas in the vaporizer²¹.

Small-scale non-uniformities

Together with large-scale variations, the packed bed also contains small-scale

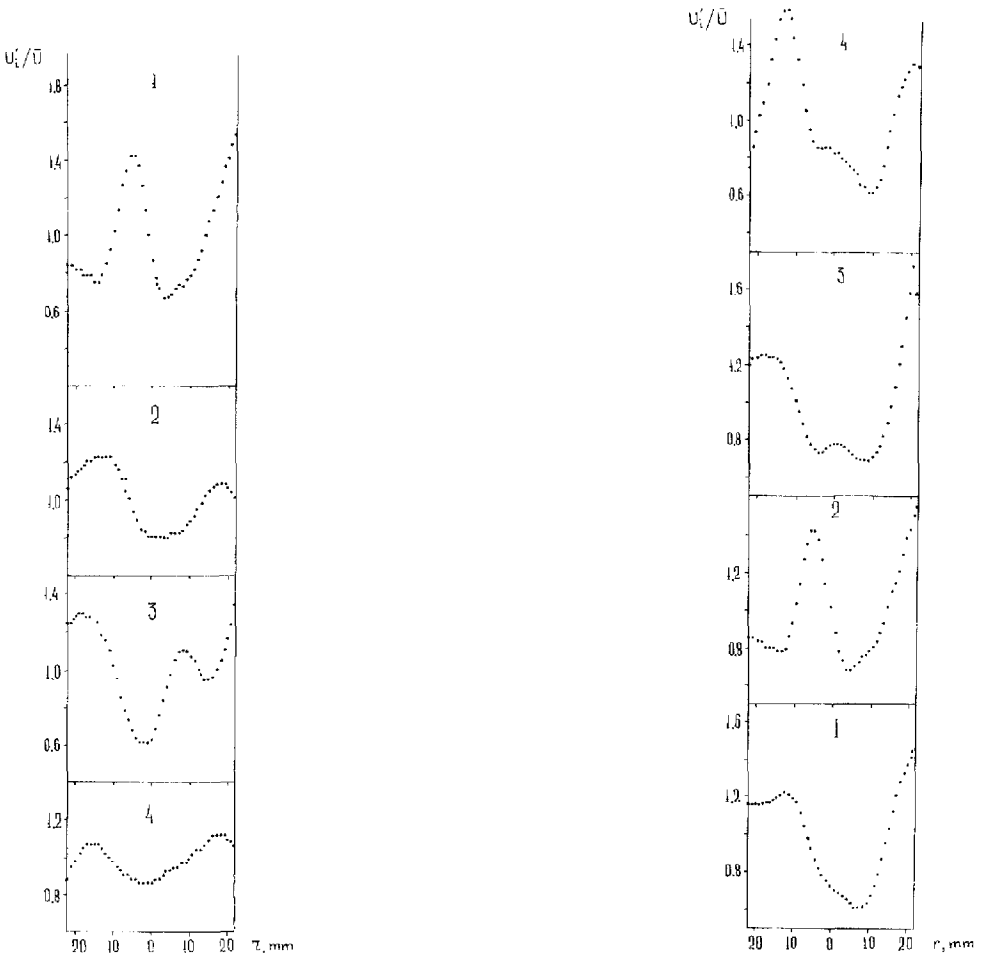


Fig. 5. Smoothed profiles of liquid velocity distributions (column diameter 44 mm). Particle size: (1) 0.5–1.0 mm; (2) 0.5–0.8 mm; (3) 0.315–0.5 mm; (4) 0.15–0.315 mm.

Fig. 6 Smoothed gas and liquid (1,3 and 2,4) distributions at $Re \approx 2.8$. Spherochrom, granule size 0.5–1.0 mm.

variations. We studied the dependence of the above statistical characteristics of non-uniformities on particle size and form, column diameter and mobile phase flow-rate. To evaluate the effect of packing particle size with gas flows, we used the diatomite support Spherochrom-1 with granule sizes of 0.8–0.65, 0.65–0.5, 0.5–0.4 and 0.4–0.315 mm.

Non-uniformity characteristics and the mean particle size d were in the following proportions when using gas flows: $y = a + bd$, where a and b had the following values:

y :	d_a/d	d_{ma}/d	σ_{a_0}/d_a	$\Delta U/U$	σ/U	$\Delta U'/U$	σ'/U
a :	9.9	61.7	0.44	-0.1	-0.05	-0.05	-0.02
b :	-8	-46.9	-0.05	0.4	0.25	0.19	0.11

TABLE I

PARAMETERS OF LIQUID FLOW NON-UNIFORMITY WITH PARTICLES OF DIFFERENT SIZE

44 mm column, Spherochrom-1.

No.	Support fraction	$\Delta U/U$	$\Delta U'/U$	σ/U	σ'/U	$d_a(\text{mm})$	d_a/d	σ_{a_a}/d	d_{ma}	d_{ma}/d
1	0.8–0.5	0.28	0.13	0.16	0.08	2.7	4.2	0.31	32	48
2	0.5–0.4	0.28	0.14	0.17	0.1	2.8	6.2	0.39	22	49
3	0.4–0.315	0.3	0.15	0.18	0.11	3.1	8.6	0.37	21	58
4	0.5–0.315	0.43	0.20	0.25	0.12	3.3	8.0	0.42	18.2	44
5	0.315–0.15	0.21	0.12	0.13	0.07	2.9	12.5	0.30	32	141
6	0.5–1.0	0.46	0.24	0.28	0.16	3.27	4.4	0.53	22	29

Microaggregate sizes and local velocity distributions are represented by asymmetric curves with a maximum. The "tails" observed in local velocity distributions that reach high positive values are probably due to the higher gas velocity near the wall. Calculating local velocity deviations from the smoothed profile rather than from the average value visibly improves the symmetry of the distribution curves, to the point when they begin to resemble Gaussian curves.

The data obtained show that particle size has little effect on the absolute size of microaggregates and their dispersion, although it does have a considerable influence on velocity variations; these variations decrease with diminishing d . Widening of particle size distribution leads both to larger aggregate sizes and to larger velocity variations. For the particles of the sizes studied, d_a changes from 2.5 to 3.0 mm, and d_{ma} constitutes 15–17 mm. A decrease in particle size increases their number in aggregates.

A more sophisticated dependence was observed when water was used as the mobile phase (Table I). The first three rows in Table I illustrate the influence of particle size on the non-uniformity characteristics. A decrease in mean particle size produced almost no changes in this characteristics; a certain increase in non-uniformity of the flow was even observed with decreasing particle diameter. However, a further decrease in particle size (0.315–0.15 mm) led to a decrease in non-uniformity parameters (row 5), leaving only the microaggregate size unaffected. Use of a wider particle size distribution, 0.5–0.315 mm (row 4), instead of the narrower 0.5–0.4 and 0.4–0.315 mm, resulted in an increase in all parameters, except for microaggregate size. The greatest flow non-uniformity was observed for the widest distribution of large 0.5–1.0 mm particles; however, this produced minimal microaggregate sizes, particularly the relative parameter d_{ma}/d . All these data correspond in general to the known reduction in column efficiency with increasing particle size and widening size range.

To study the effect of particle shape on packed bed non-uniformity, we carried out measurements with spherical particles (Spherochrom), rounded particles (sand) and irregular particles (Dinochrom and Celite C 22). In all instances a particle size of 0.5–0.315 mm was used. The sizes of micro- and macroaggregates consisting of Spherochrom are smaller by about 30–40% than the sizes of the aggregates consisting

TABLE II
INFLUENCE OF CARRIER GAS FLOW-RATE ON CHARACTERISTICS OF FLOW NON-UNIFORMITY

Parameter	Gas flow-rate (l/min)			
	15	25	30	40
$\Delta U/U$	0.288	0.285	0.325	0.299
$\Delta U'/U$	0.048	0.044	0.044	0.053
σ/U	0.180	0.193	0.187	0.183
σ'/U	0.038	0.036	0.031	0.037

of irregular particles, although the mean square deviations, σ_{d_s}/d and $\sigma_{d_{msd}}/d$, are roughly the same in all instances. The velocity variations for different particles also differ by 30–40%; however, no apparent dependence on particle shape of material could be established. Thus, the above relationships obtained for Spherochrom particles can also be used for other types of packing; the error margin will be about 30–40%, and aggregate size calculated according to these equations must be increased by 30–40%.

In fact, all characteristics are strongly dependent on the packing method. A number of results pertaining to the influence of this method have already been obtained¹³. The mobile phase flow-rate has no apparent effect on flow non-uniformity, as shown by the results in Tables II and III.

Non-uniformity characteristics are subject to a complex influence of the column diameter. We investigated columns with diameters of 46, 100 and 140 mm using gas as the mobile phase and the results are given in Table IV. Increasing the column diameter generally reduces the velocity field non-uniformity, although this dependence is unclear. It seems that for the 46 mm column the influence of the wall is stronger, which accounts for the greater non-uniformity of the packed bed.

We compared the non-uniformity characteristics when using gas and liquid mobile phases. Gas was passed through a 46 mm column dry-packed with Spherochrom, granule size 0.5–1.0 mm, and the velocity field was measured. The same diameter lines were used for measurements with a liquid mobile phase. Finally, gas was

TABLE III
INFLUENCE OF LIQUID FLOW-RATE ON CHARACTERISTICS OF FLOW NON-UNIFORMITY

Parameter	Flow-rate (l/min)			
	0.3	0.35	0.45	0.55
$\Delta U/U$	0.2	0.26	0.23	0.19
$\Delta U'/U$	0.14	0.22	0.15	0.14
σ/U	0.13	0.16	0.15	0.12
σ'/U	0.09	0.14	0.1	0.09
d_a	3.1	3.1	3.4	3.0

TABLE IV

INFLUENCE OF COLUMN DIAMETER ON CHARACTERISTICS OF PACKED BED NON-UNIFORMITY

Parameter	Column diameter (mm)		
	46	100	140
d_n/d	5.57	6.51	5.37
d_{na}/d	35.20	27.60	25.40
σ_{d_n}/d	0.60	0.70	0.48
$\Delta U/U$	0.32	0.39	0.21
σ/U	0.21	0.22	0.15
$\Delta U'/U$	0.078	0.045	0.079
σ'/U	0.06	0.035	0.077

used again and the measurements were repeated after the column had been dried. Fig. 6 presents smoothed profiles and Table V gives the non-uniformity characteristics. Two packing methods were studied: free packing without compaction and packing with compaction by a plunger and evacuation with a vacuum pump. In both instances the bed was pressed down with a metal screen. The gas flow-rate was 5 l/min and the liquid flow-rate 0.36 l/min, which corresponded to identical Re values of 2.8. Non-uniformity of the liquid flow exceeded that of the gas flow with regard to most parameters, especially on first measurement. Apparently, the introduction of a liquid into the column led to a particle shift, which increased the non-uniformity of the bed structure. This is especially visible with free packing, when the bed is looser and the particles have more freedom of movement. The bed uniformity is decreased after drying, although it does not attain the original level. With a gas the velocity profile has the form of a parabola (Fig. 6), which is greatly distorted in the case of liquid, with a zone of acceleration also appearing close to the axis of the column. This zone is preserved after drying, although the relative velocity therein experiences a decrease.

Influence of packed bed non-uniformity on longitudinal spreading

Packing non-uniformity may affect longitudinal spreading. The latter is usually

TABLE V

VELOCITY VARIATIONS OF GAS AND LIQUID MOBILE PHASES

Packing method	Mobile phase	$\Delta U/U$	$\Delta U'/U$	σ/U	σ'/U
Free packing	Gas	0.11	0.10	0.07	0.06
	Liquid	0.52	0.26	0.35	0.19
	Gas	0.41	0.16	0.24	0.11
Plunger compaction	Gas	0.49	0.14	0.29	0.09
	Liquid	0.46	0.24	0.29	0.16
	Gas	0.56	0.18	0.33	0.12

determined by the spreading of the concentration profile of an unadsorbed substance and is characterized by the HETP value (H), which can be described as follows:

$$H = \frac{2\gamma D}{U} + \frac{2d^2 U (\lambda_1 + \lambda_2 \rho^2)}{\lambda_R d U + \gamma D} \quad (1)$$

where D is the diffusion coefficient of the substance in the carrier gas, $\rho = d_k/d$, d_k is the column diameter, γ is the tortuosity factor and λ_1 , λ_2 and λ_R are constants whose empirical formulae were obtained²².

The first term on the right-hand side ($2\gamma D/U$) accounts for molecular diffusion, the first term in the numerator of the second term ($2d^2 U \lambda_1$) for eddy diffusion and the second term ($2d^2 U \lambda_2 \rho^2$) for the velocity profile $U(r)$. The first term in the numerator of eqn. 1 characterizes particle-size non-uniformities and the second column diameter-size non-uniformities.

To take account of non-uniformities of a size greater than the particle diameter but smaller than the column diameter, additional terms may be included in the numerator of the second term, $2\lambda_3 \rho_a^2 d^2 U$ and $2\lambda_4 \rho_{ma}^2 d^2 U$, where $\rho_a^2 = (d_a/d)^2$, $\rho_{ma}^2 = (d_{ma}/d)^2$ and λ_3 and λ_4 are constants.

Eqn. 1 contains mean values of d_a and d_{ma} , which are believed to exert the main effect on H . The aggregate size distribution and its variance as the main distribution characteristic cannot be included in this equation in its actual form; it is believed that its influence is weaker than that of mean values, and it is exhibited through λ_3 and λ_4 . This is in complete accordance with the meaning of eqn. 1, where mean particle size d is used as a main parameter, and particle size distribution is not taken into account.

The constants λ_3 and λ_4 should depend primarily on the mean relative difference in the velocities of gas flows through the aggregates and through the space between the aggregates, $\Delta U/U$: if this difference is zero, the aggregates vanish and the spreading for which they are responsible also vanishes. In other words, longitudinal spreading caused by aggregates should be affected both by aggregate size and by the relative packing density of the aggregates, characterized by $\Delta U/U$. This value should have a decisive effect on λ_3 and λ_4 , whereas the velocity distribution should have a comparatively smaller effect (it is characterized by σ/U).

Of course, the introduction of additional terms into the equation for H has little effect on calculations of longitudinal spreading: as already proved²², it is almost impossible to determine λ_1 and λ_2 separately from experimental data; only the complex term $\lambda_1 + \lambda_2 \rho^2$ is available. Nevertheless, the introduction of additional terms widens the physical meaning of the equation and will make it possible to use it as a basis for more accurate calculations.

The considerable discrepancy between the calculated and experimental H versus U curves can be cited as an indirect corroboration of the existence of an additional source of spreading besides those accounted for in eqn. 1. Calculations with eqn. 1 for $d_k = 100$ mm and mean particle sizes of 0.36, 0.52 and 0.75 mm have shown that in the velocity range from 1 to 70 cm/s this dependence decreases monotonously (Fig. 7); a slow increase in H with the formation of a minimum on the plot starts only at rates of about 500 cm/s. The calculations were performed for the elution of hydrogen by nitrogen.

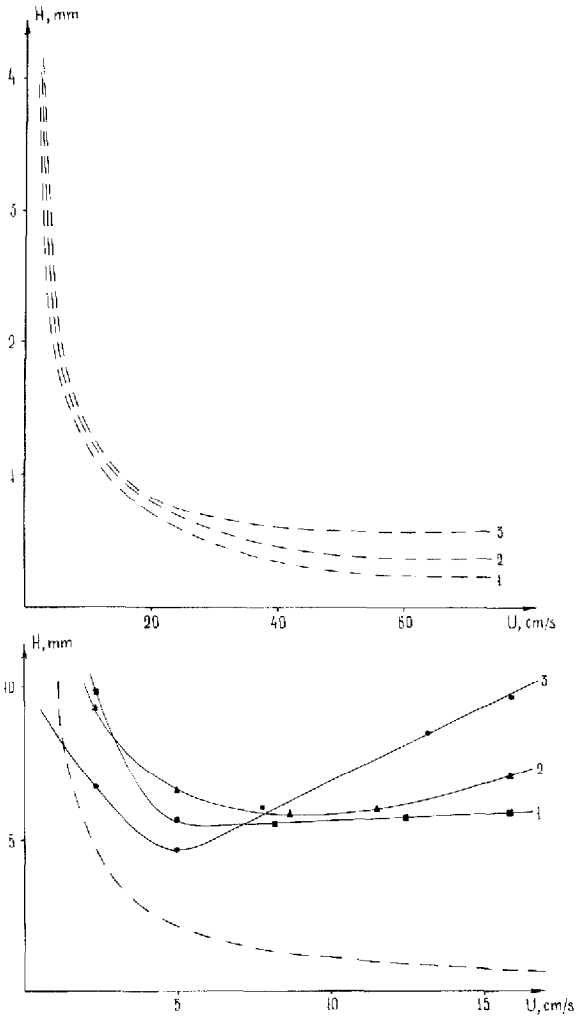


Fig. 7. HETP for hydrogen *versus* velocity of carrier gas (nitrogen), calculated according to eqn. 1. (---), experimental: (—), for Spherochrom particles of mean granule size (1) 0.358, (2) 0.515 and (3) 0.75 mm.

However, our experiments have shown that at similar d_k and d values in the velocity range 1–16 cm/s, the H *versus* U curve has a well defined minimum (Fig. 7). The calculated points are located above the theoretical curve. Other workers have also observed analogous variations in H with increase in U . These differences between theoretical and experimental data can be explained by the fact that eqn. 1 does not account for all the factors responsible for spreading.

CONCLUSION

The above experimental data indicate considerable small-scale variations of the packing density that are random in nature, and are superimposed on the regular

velocity profile which is approximately described by a parabola. These variations are likely to affect the processes taking place in chromatographic columns, notably longitudinal spreading.

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