Journal of Chromatography, 191 (1980) 9–16

CHROM. 12,222

INFLUENCE OF PARTICLE PARAMETERS ON THE EFFICIENCY OF LIQUID CHROMATOGRAPHIC SYSTEMS

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SUMMARY

The influence on the efficiency of chromatographic systems of the range and distribution of particle diameters was investigated in relation to symmetrical and unsymmetrical distributions. The latter were studied with increasing proportions of very small or very large particles. The efficiency of systems with symmetrical distributions up to the value of $\Delta d_p = 160$ μm was found to be unaffected by changes in fraction width. Significantly increased values of the theoretical plate height were observed for fractions with unsymmetrical distributions only for $\bar{d}_p \neq$ constant.

INTRODUCTION

Maximum separation power of chromatographic columns is attained by using packings with particles as small as possible, and of similar size, shape and microporous structure. Columns packed by the "wet" method with particles in the 5–10-μm diameter range[1–9] have been reported as particularly efficient[4,10–13]. This mainly concerns columns 2–50 mm in diameter, not macropreparative or industrial-scale columns, which cannot be packed with selected particles, since this would be prohibitively expensive and make columns difficult to pack.

In order to choose optimum separation conditions, it is essential to know how the column efficiency is affected by the heterogeneity of the packing material. There are few literature reports on this subject.

The purpose of the present work was to investigate the manner in which the column efficiency is affected by fraction width, Δd_p (d_p = particle diameter), and particle-size distribution within fractions. Although these investigations were conducted with columns of not more than 50 mm in diameter, we believe that the conclusions arrived at can be extended to larger-size columns.

EXPERIMENTAL

Adsorbents

Columns were packed with silica gel fractions prepared by mixing suitable proportions of basic fractions obtained by sieving silica gel Type 60 (Machery, Nagel & Co., Düren, G.F.R.): I, $d_p = 40$–60 μm; II, $d_p = 60$–75 μm; III, $d_p = 75$–102 μm; IV, $d_p = 102$–120 μm; V, $d_p = 120$–150 μm; VI, $d_p = 150$–160 μm and VII, $d_p = 160$–200 μm.

Measurements by microscope have shown all fractions to be characterized by symmetric particle-size distributions in relation to the mean d_p value. The compositions of terminal fractions used in the experiments are listed in Tables I and II. The investigations included both symmetrical and unsymmetrical particle size distributions in relation to the $\bar{d}_p$ value.

TABLE I

COMPOSITION OF FRACTIONS WITH SYMMETRICAL PARTICLE SIZE DISTRIBUTIONS

Symbol	*Percentage by weight of basic fraction*						
	40–60 μm	*60–75 μm*	*75–102 μm*	*102–120 μm*	*120–150 μm*	*150–160 μm*	*160–200 μm*
IV	—	—	—	100	—	—	—
A	—	—	21.6	56.8	21.6	—	—
B	—	6.0	24.1	43.1	21.6	5.2	—
C	4.0	10.7	18.6	28.3	20.3	14.7	3.4

Eluent and other substances

Hexane (Reachim, Moscow, U.S.S.R.) and dioxane (POCH "Xenon", Lodz,

TABLE II

COMPOSITION OF FRACTIONS WITH UNSYMMETRICAL PARTICLE SIZE DISTRIBUTIONS

Symbol	*Percentage by weight of basic fraction*			
	75–102 μm	*102–120 μm*	*120–160 μm*	*160–200 μm*
III	100	—	—	—
D	90.9	9.1	—	—
E	83.3	16.7	—	—
F	71.4	28.6	—	—
G	58.8	41.2	—	—
H	55.6	22.2	22.2	—
L	45.4	18.2	18.2	18.2
M	50.0	50.0	—	—
N	21.0	49.4	29.6	—
P	12.4	29.5	41.0	17.1
VII	—	—	—	100
T	—	—	28.6	71.4
W	—	22.2	22.2	55.6
Z	18.2	18.2	18.2	45.4

Poland) mixture (85:15) was used as mobile phase. Both solvents had previously been distilled. A mixture of benzene and aniline was used as sample.

Columns

Columns of length 50 cm and 2, 6, 17 and 50 mm I.D. were used. These of 17 and 50 mm I.D. were equipped with home-made heads ensuring uniform distribution of the mobile phase over the whole surface of the packing section. Identical heads were placed on the column outlets.

Packing procedure

Columns were dry-packed by the impact method, using home-made impacting devices. The columns were raised by 2.5 cm at a rate of 120 times per minute and descended by their own weight. Adsorbents were poured uniformly over the whole surface of the column section. Optimum tapping time was 30 min.

Apparatus

The efficiency of the packed columns was tested with an apparatus ensuring linear mobile phase flow-rates within the 0.3–2.0 cm/sec range which is the most frequently encountered in practice.

Measurements for columns with 2 and 6 mm I.D. were made using a KB 5101 liquid chromatograph equipped with micropreparative KABID-Warszawa accessories. Larger-size columns were investigated with a home-made preparative liquid chromatograph. The same UV-254 KABID-Warszawa detector was used for all measurements.

RESULTS AND DISCUSSION

To investigate the influence of particle-size range on the plate height, $H =$

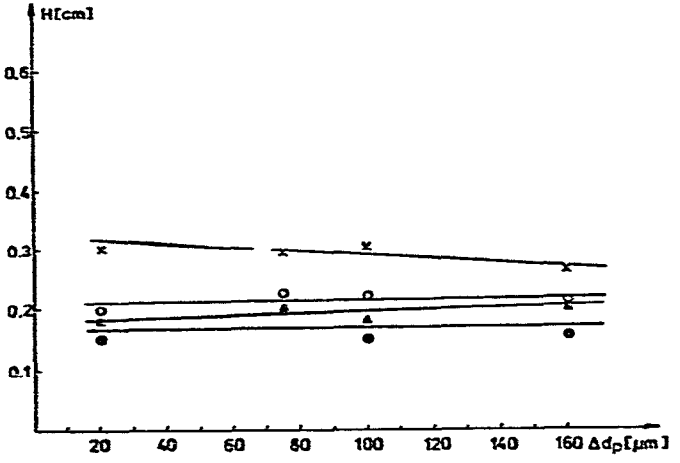

Fig. 1. Dependence of plate height on the width of silica gel fractions with symmetrical particle distribution. Eluent, hexane–dioxane (85:15). Sample, aniline. Velocity of mobile phase, 0.4 cm/sec. Columns: ○, 2 mm I.D.; ×, 6 mm I.D.; △, 17 mm I.D.; ●, 50 mm I.D.

f(Δd_p), we used the gel fractions listed in Table I. The mean weighted values calculated from the particle diameters were *ca.* 110 μm. These fractions were characterized by symmetrical particle-size distributions around the mean value, $\bar{d}_p$.

The plotted dependences $H = f(u)$ were linear and approximately parallel within the range of the most frequently encountered mobile phase velocities, $u = 0.3$–2.0 cm/sec. This allowed us to compare the efficiencies of various columns on the basis of plate height values determined for selected mobile phase velocities.

The results of investigations of $H = f(\Delta d_p)$ for the silica gel fractions described above are shown in Fig. 1. They lead to the conclusion that the efficiency of the chromatographic systems discussed is not affected by changes in the Δd_p values, within the particle diameter ranges investigated, up to $\Delta d_p = 160$ μm. These results deviate from those for analytical columns[14] where *ca.* 50% drop in the efficiency of the systems was observed for $\Delta d_p = 125$ μm.

Our result may be evidence of a lower eddy diffusion value. This may occur when, owing to an improved loading technique, column packings become more compact, and interparticle spaces are smaller and homogeneous in size and shape.

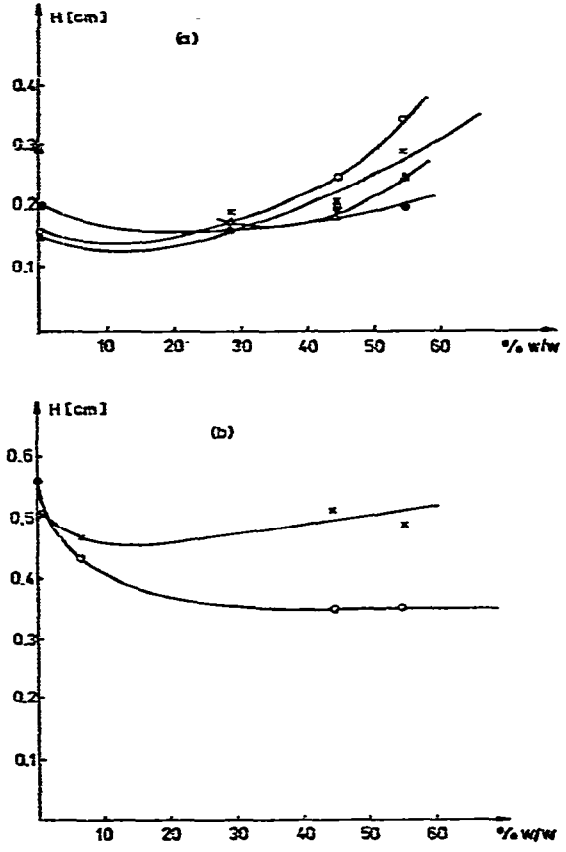

Fig. 2. (a) Dependence of plate height upon the contents of the fraction causing tailing of the curves for particle size distribution, $\Delta d_p \neq$ constant, $d_{p(max.)}$ = constant. Conditions as in Fig. 1. (b) As in (a) but Δd_p = constant.

On this basis it can be concluded that our impact loading technique has proved more effective than the vibratory technique employed by Halász and Naefe[14]. Another advantage of the present method is the greater efficiency of columns with 50 mm I.D. compared with columns of smaller diameter. Our observations concerning the significance of column diameter are similar to those made by other authors[9,15], despite the fact that we used much larger particles and wider fractions.

We conclude that our loading technique prevents heterogeneity of packings caused, *e.g.*, by agglomeration of particles of the same size.

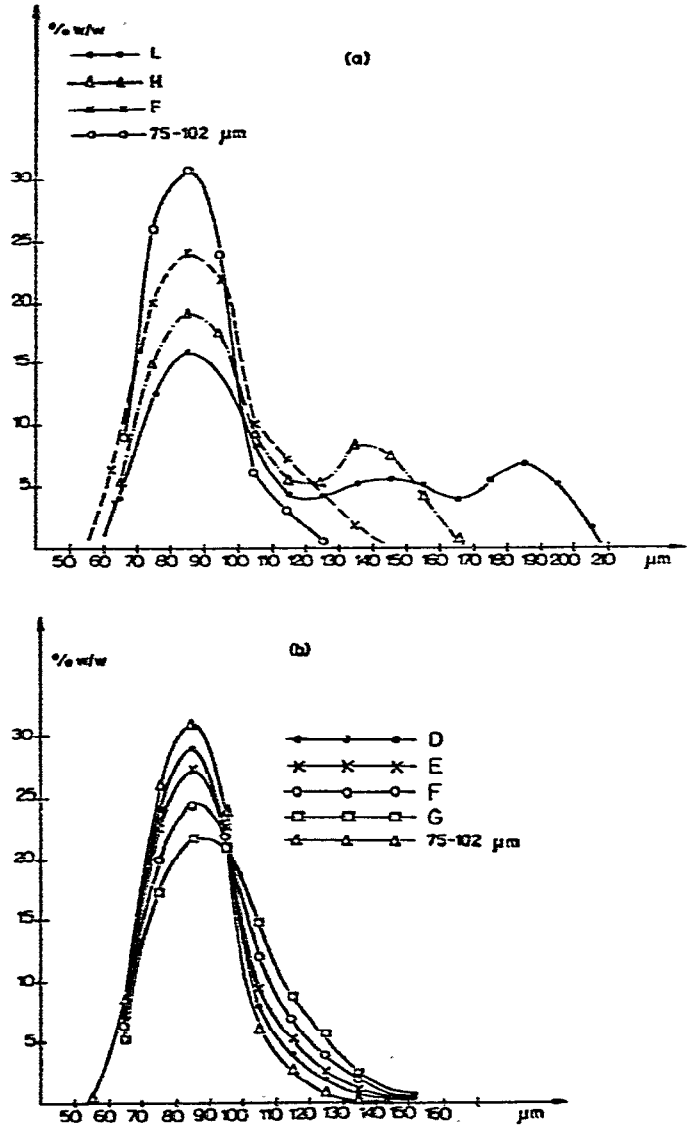

Fig. 3. Particle size distribution of silica gel fractions: (a) fractions 75–102 μm and L, F, H from Table II; (b) fractions 75–102 μm and D, E, F, G from Table II.

Next, we investigated the effects on the efficiency of asymmetry of the particle-size distribution in gel fractions. Fig. 2 presents the dependence of the theoretical plate height on the percentage by weight of basic fractions which comprise the tailing part of mixtures. Particle size distributions in these mixtures are presented in Fig. 3b (fractions $d_p = 75$–102 μm; D, E, F, G from Table II) and in Fig. 3a (fractions $d_p = 75$–102 μm; F, H and L from Table II). As can be seen, the distribution of the d_p value on the descending part of the curve is asymmetrical.

Our measurements have shown that column efficiency decreases only if the percentage by weight of particles in the tailing part exceeds 45% (Fig. 2a). It is interesting that the greatest changes, *i.e.*, decreases with increase in diameter, were observed for analytical columns. This supports our earlier observations, according to which radial particle segregation is prevented if the packing methods developed by us and the previously described technique of pouring packings are employed. The diminished efficiency of analytical columns under the circumstances described above points to unfavourable structural changes occurring in the layer near the walls, a fact of particular significance for analytical columns.

Even in analytical columns, increased percentage by weight of the tailing part at Δd_p = constant does not affect the value of the plate height (see Fig. 2b).

Results of investigations aiming at finding out the effect on theoretical plate height of increasing a symmetry of particle size distribution on the ascending side of the curve are presented in Fig. 4. The measurements were made on silica gel fractions

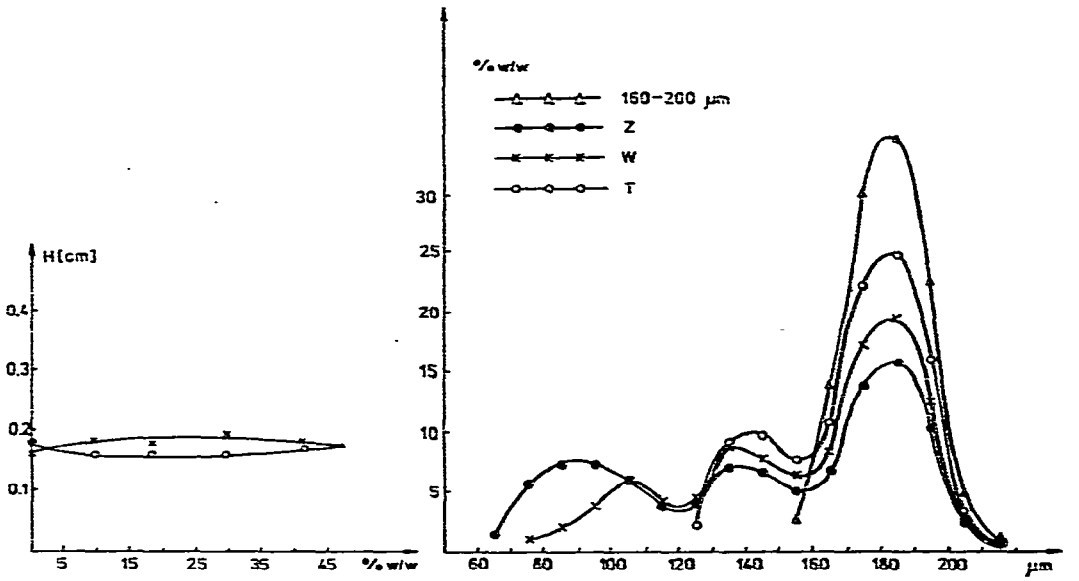

Fig. 4. Dependence of plate height on the contents of the fraction causing asymmetry on the ascending side of the distribution curve at $d_{p(max.)}$ = constant and $\Delta d_p \neq$ constant. Conditions as in Fig. 1.

Fig. 5. Size distribution of silica gel particles (fractions T, W, Z and VII from Table II).

within the 160–200 μm range and T, W and Z from Table II. The particle size distributions for these fractions are presented in Fig. 5. Fig. 4 shows the results for plate height under conditions of the greatest "sensitivity" of analytical columns to changes in Δd_p for columns with 2 and 6 mm I.D. The efficiency of these columns was not changed in the investigated range of the content of the fraction causing asymmetry.

Analysis of the diagrams in Figs. 2a, b and 4 suggests that the change in the plate height value was mainly due to changes in the particle diameter in the mixtures investigated.

To check the validity of these statements, all results have been listed in Fig. 6 in the form of the dependence $\log h = f(\log \bar{d}_p)$. Fig. 6 shows that the mean particle size has a greater influence on the plate height value than has the particle size range Δd_p and the nature of the particle size distribution. The linearity of the plotted dependence demonstrates that the empirical equation $h \approx d_p\beta$ for analytical columns has been satisfied. As can be seen from Fig. 6, the value of the coefficient β is *ca.* 1.55 for analytical and micropreparative columns of 2 and 6 mm I.D. and 1.2 for preparative columns of 17 and 50 mm I.D. Such values have to date been

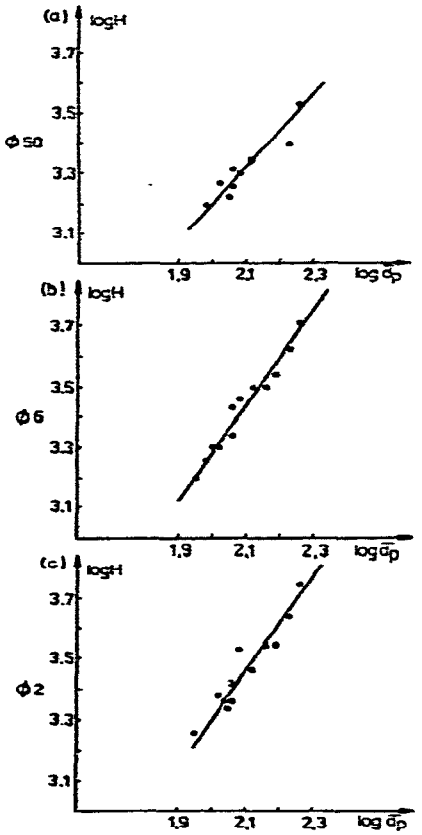

Fig. 6. Dependence of log H on log $\bar{d}_p$. Columns: (a) 50 mm I.D.; (b) 6 mm I.D.; (c) 2 mm I.D. Other conditions as in Fig. 1.

determined under similar conditions only for analytical columns[14,15]. The fact that Halász and Naefe[14] had obtained $\beta = 1.8$ for similar mobile phase velocities shows that the packing technique employed by them had been less effective than the one employed by us. The value of 1.34 obtained by Endele *et al.*[16] approximates ours, but these authors used particles with $d_p = 5$–25 μm and had loaded columns by the balance density method. The value $\beta = 1.2$ found by us for preparative columns shows that the role of particle size is less important in preparative than it is in analytical columns.

The values of the plate height in our studies are of the order of 20 d_p for a sample with capacity factor, $k' = 2.6$ and mobile phase velocities several times greater than the so-called optimum velocity. It is difficult to compare these values with the theoretical plate heights obtained by other authors for smaller particles and narrower fractions, because the columns have usually been packed and separation processes conducted by special techniques[17,18], and sample dosing had been unconventional[19,20]. The most comparable data reported are by Beck and Halász[9] who had also obtained theoretical plate height values of 20 d_p for silica gel with $d_p = 36$–50 μm and substances with $k' = 1.1$.

ACKNOWLEDGEMENT

These investigations were supported by a grant from the Polish Academy of Sciences (MR I-14).

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