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Effect of the column length on the characteristics of the packed bed and the column efficiency in a dynamic axial compression column

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Abstract

The axial homogeneity of preparative-scale chromatography columns was studied by measuring the overall properties of similar columns differing only by their lengths. The properties investigated were the packing density, the external porosity, the permeability and the column efficiency. Two different materials were used, one made of large, irregular silica particles compressed under either a high or a low degree of stress; the other of small, spherical and rigid particles. The columns made with the spherical particles were more homogeneous, had a higher external porosity and specific permeability, and a higher efficiency than those made with the irregular ones. For this latter material, the columns prepared with a low level of stress were better than those compressed under high stress. The latter ones experienced extensive particle breakage. These results indicate that the long columns are heterogeneous in their axial direction. © 1998 Elsevier Science B.V.

Keywords: Column length; Column efficiency; Axial compression; Porosity; Packing density; Preparative chromatography

1. Introduction

Packed columns are heterogeneous in both their radial and axial directions [1]. The radial distribution of their local properties at column exit was studied experimentally by Knox and co-workers [2,3], Eon [4], Baur and co-workers [5,6], and Farkas et al. [7–9]. These authors reported that, for slurry-packed columns [5–9], the region close to the wall has a lower permeability and a lower efficiency than the core of the packing. This phenomenon is usually described as the wall effect [1–4]. The region of the packing close to the column wall is known to be less homogeneous than the column core [1–12]. The size of the wall region is not well defined, although it has

been suggested that the wall region reaches about 30 particle diameters from the wall [1–4]. Knox and co-workers [2,3] recommended the use of a wide-diameter column and the injection of the sample in the column center to prevent the bands of the sample components from reaching the region near the column wall before exiting the column. Eon [4] reported that the wall effect influences not only the radial heterogeneity of the column but also the overall axial dispersion. He maintained that the wall effect is minimized in a very short column and that the efficiency of dry-packed columns deteriorates when their length increases. There are many other reports on the properties of columns packed with particles of widely different dimensions and used for a wide variety of applications in the chemical industry, e.g., packed bed absorbers or catalytic reactors [10–12]. Although the sizes of these col-

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umns and the dimensions of the particles of the packing materials are much larger than those encountered in chromatographic columns, the wall effect on the flow velocity and the porosity distributions has been reported [10–12] for relatively large, non-porous particles. Numerous studies of the relationships between the packing parameters and the performance of analytical columns have been published [13–15].

The present study is concerned with the behavior of a preparative-scale column packed successively with different chromatographic packing materials, under dynamic axial compression. Our column is different from the packed towers used in the chemical industry because the particles used here are much smaller and are porous. This study is different from those by Knox and co-workers [2,3] or Eon [4], because (1) the column is prepared from a slurry of the packing material in a suitable solvent, it is not dry-packed as in [2–4]; and (2) the samples are introduced into the column through a distributor, whereas the former authors injected their samples with a syringe, performing a point source injection in their studies. It differs also from the work done on analytical columns which are slurry-packed without mechanical compression [5–8]. By contrast, the packing in a dynamic axial compression column is compressed by a mechanical stress instead of the hydrodynamic stress applied by a high velocity stream to each individual particle. The mechanical nature of the stress applied to the bed in a dynamic compression column makes this packing process similar to the consolidation of pulverulent materials in soil mechanics, to the manufacturing of tablets in the pharmaceutical industry, or to the sintering processes in the ceramic industry. An especially valuable contribution to our knowledge of powder consolidation is the work made by Train [16,17] who was able to illustrate the distribution of the local stress and of the packing density inside a particulate bed, from direct measurements.

The wall effect has been discussed in many past studies in connection with column inhomogeneity for which it could provide a mechanism [1]. This effect could explain the radial distribution of the packing parameters, such as the packing density or the column porosity. It must be emphasized, however, that all the studies of the column heterogeneity

carried out so far have been made by measuring the radial distribution of the column properties at the column exit. There is no information available regarding the dependence of the properties on the column length, although this length is an important design parameter. This study aims at measuring the variations of the column properties, including its efficiency, with its length. Two different commercial chromatographic materials were used for this study. The valuable information gained regarding the axial distribution of the packing parameters can be explained by a combination of the column entrance effect (the conventional ‘extra-column band broadening contributions’) and of the wall effect.

2. Experimental

2.1. Equipment

A dynamic axial compression column (LC-50, Prochrom, Champigneulle, France) and a dual piston pump (Dynamax SD-1, Rainin, Woburn, MA, USA) were used. The column inner diameter is 5.0 cm; its length is adjustable, depending on the nature and the amount of the packing material used to pack it, up to a maximum of 50 cm. The particular feature and the mode of operation of this column skid were described in detail by Sarker and Guiochon [18–20]. The detector was a SpectraFocus (Thermo Separation Products, Riviera Beach, FL, USA), equipped with a preparative-size flow cell. The optical path length of this flow cell was 2.8 mm throughout all the experiments reported here. The UV absorbance of the eluent was monitored at a wavelength of 254 nm. A six-port electropneumatic switching sample valve, actuated with a manual electrical switch, was used for sample injection. The sample volume injected was 0.5 ml, unless specified otherwise.

A pressure transducer (Omega, Stamford, CT, USA) was used to measure the column back pressure. A position sensor allows the accurate determination of the variation of the column length during packing consolidation, as described previously [21]. Electrical signals from the pressure transducer, the position sensor and the UV detector were collected with a data acquisition module (Waters, Milford, MA, USA) and analyzed on a microcomputer.

Table 1
Physical properties of the packing materials used

	Baker I-130 C ₁₈	Nova Pak C ₁₈
Average particle diameter (μm)	130	6
Particle shape	Irregular	Spherical
Specific surface area (m ² /g)	312	120
Average pore size (Å)	141	60
Specific density (g/ml)	0.48	2.2
Specific pore volume (ml/g)	1.1	0.3

2.2. Packing material

Two different packing materials, both chemically bonded octadecyl silica, were used in this study. Baker I-130 (J.T. Baker, Phillipsburg, NJ, USA) has irregularly shaped, large particles, with an average particle size of 130 μm (100–200 mesh). Nova Pak C₁₈ (Waters) has fine, nearly spherical, particles (average particle size, 6 μm). The physical properties of these two packing materials are listed in Table 1.

2.3. Procedures

The packing procedure used was the same for all columns. Isopropanol was used as the slurry solvent. The frits at both ends of the column were cleaned carefully before packing each new column. These frits are fine mesh grids which keep the particles inside the column and contribute to the homogeneous distribution of the solvent flow velocity inside the column. Some particles are trapped inside these grids, causing partial obstruction and an uneven flow distribution. Their accumulation must be avoided

carefully to maintain the even distribution of the solvent flow and of the incoming bands into and out of the column. To clean them, the frits were soaked first in distilled water, then in methanol, for 20 min each, inside an ultrasonic bath. This mechanical cleaning was chosen because it is fast, usually most effective to remove the fine particles trapped on the surface of the frits, and it is pretty gentle.

The ratio of dry weight of packing material to total slurry volume was kept constant for all columns packed with the same material. At first, an excess of isopropanol was poured in a large glass beaker to achieve a slurry volume approximately 1.5 times larger than the volumes given in Table 2. The slurry was left to settle for a few hours, and the volume of supernatant liquid necessary to obtain the slurry volume required was removed. Then, the slurry was stirred for 2 min in an ultrasonic bath and immediately poured into the column to maintain uniform suspension of the particles. The column was closed and compressed as quickly as possible, up to the desired level of stress, and left to equilibrate for a few hours. In previous reports dealing with consoli-

Table 2
Characteristics of each column prepared

Column	Material	Dry mass/slurry volume	Compression (kg/cm ²)
A1	Baker I-130	15 g/50 ml	65
A2	Baker I-130	60 g/200 ml	65
A3	Baker I-130	150 g/500 ml	65
A4	Baker I-130	240 g/800 ml	65
A5	Baker I-130	15 g/50 ml	23
A6	Baker I-130	60 g/200 ml	23
A7	Baker I-130	150 g/500 ml	23
A8	Baker I-130	240 g/800 ml	23
B1	Nova Pak	30 g/75 ml	55
B2	Nova Pak	120 g/300 ml	55
B3	Nova Pak	240 g/600 ml	55
B4	Nova Pak	360 g/900 ml	55

dition issues [18,19,21,22], the compression stress was raised by incremental steps, small ones in the low stress range and increasingly larger steps at high compression stress. By contrast, in this work, the compression pressure was raised immediately to its maximum, approximately 65 and 23 kg/cm² in the two series of measurements made with Baker I-130 and 55 kg/cm² for Nova Pak. This procedure allows the preparation of more efficient columns, as reported previously [18]. Four different columns were successively packed with each of the two materials, using increasingly large amounts (see column characteristics in Table 2), at the compression stress indicated above. The amount of column material used to pack each column was determined in such a way that the final length of each column would be in a range from 1 to 25 cm. For each material and compression stress, four columns of different lengths were packed.

A compression stress around 60 kg/cm² is typical of those achieved for good performance with strong packing materials in axial compression columns. For irregular-particle materials or when the particles have a large pore size or a large internal pore volume, however, a lower compression stress is recommended by the manufacturer. The suggested stress corresponds to a piston pressure less than 40 kg/cm² in general for irregular-shaped particles and less than 30 kg/cm² when the average pore size is larger than 150 Å. The Baker I-130 material belongs to both categories of materials requiring a low compression stress. For this reason, two series of columns were studied at the specifically recommended pressure (below 30 kg/cm²) as well as at the typical compression pressure (65 kg/cm²).

Three different types of measurements were carried out on each column: (1) the determination of the kinetics of consolidation of the bed [18,19]; (2) the measurement of the column permeability; and (3) the determination of the column efficiency. The kinetics of consolidation was followed by monitoring, with the displacement sensor, the variation of the column length under constant compression stress, until the column length reached a plateau. The column permeability was determined by measuring, with the pressure transducer, the back pressure as a function of the flow-rate, up to 500 ml/min. The solvent used for this determination was a 40% solution of metha-

nol in water. The column efficiency was determined from the width of the peak obtained following the injection of a 0.5-ml sample of a 0.8-g/l solution of uracil in the same solution, at the following flow-rates: 2, 5, 10, 30, 50, and 100 ml/min. The experiment was repeated twice at each flow-rate. The extracolumn contribution to peak broadening was measured at the same flow-rates before the packing of each column. This correction is negligible when the column is long but it is not so with the short column. The main contribution is due to the volume of the detector cell.

3. Results and discussion

3.1. Compression kinetics

The variation of the column length during the compression of the slurry is shown in Fig. 1, for Baker I-130 (Fig. 1a and 1b) and for Nova Pak (Fig. 1c). In each figure, four different graphs are reported, corresponding to columns having approximate lengths of 1, 5, 15, and 25 cm, respectively. Note that the scales of the ordinate axes are different for the four graphs in Fig. 1a and 1b. The ranges are 1, 4, 10, and 16 mm, respectively, approximately proportional to the amount of packing material in each one of the four columns. In Fig. 1c, by contrast, the scales of the y-axes are the same for the four graphs, 1.0 mm, because no significant change in the column length was observed during the consolidation of either of the four Nova Pak columns, regardless of the amounts of packing material used, i.e., of the column length. The entire consolidation takes place during the first few seconds following the application of the compression stress, too quickly to allow any meaningful record. This result is similar to those previously reported regarding the consolidation of packing materials made with spherical particles [21].

In the case of the Baker I-130 material, the consolidation under high compression stress takes place through a series of successive collapses, at randomly spaced times, often followed by a progressive shifting (Fig. 1a). This result is in agreement with observations made previously with another packing material having irregular-shaped particles [21]. The shorter columns tend to stabilize more

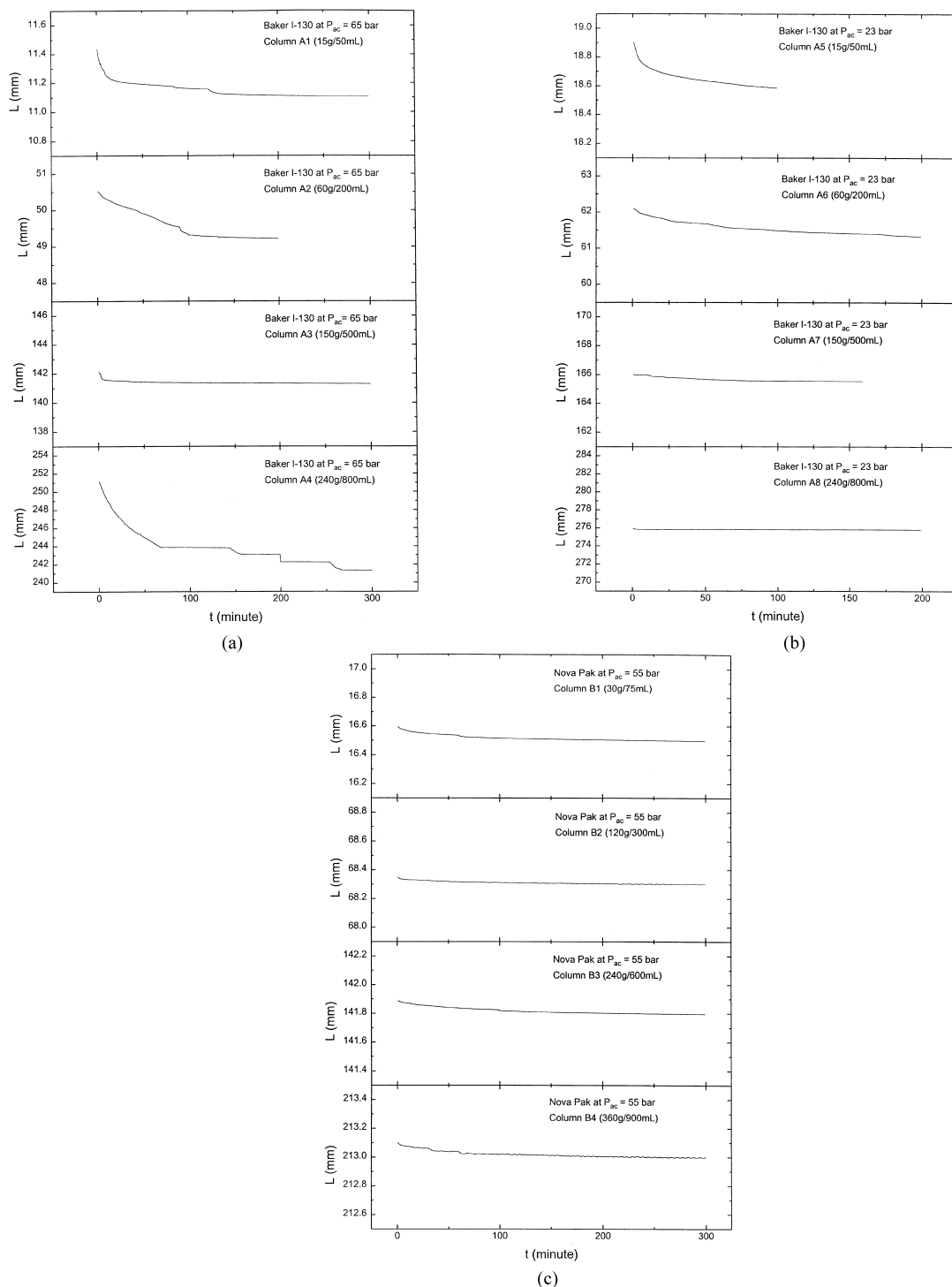


Fig. 1. Plots of the dynamic variations of the length of the columns packed under axial compression. (a) Baker I-130 material compressed under 65 kg/cm². (b) Baker I-130 material compressed under 23 kg/cm². (c) Nova Pak material compressed under 55 kg/cm².

rapidly than the longer ones, after an initial abrupt drop in length. The longest column (bottom graph) required multiple steps of partial collapse before reaching an apparent plateau. This behavior is in agreement with independent reports that the consolidation of packing materials having irregular particles is unpredictable, especially when these particles are large. This phenomenon is probably related to the nonuniform stress distribution inside compressed beds [16,17] and to the formation of metastable arcs, leading to the eventual breakage of those particles on which the stress is conveyed by the arcs. Obviously, with this type of consolidation behavior, one can never be sure whether the column has finally become stable or is still in a metastable state. In the latter case, vibrations or mechanical shocks can cause further collapses.

The consolidation of Baker I-130 under low compression stress proceeds differently (Fig. 1b). It is continuous, without collapses. Obviously, there was much particle breakage under 65 kg/cm^2 while we may assume that few particles are broken under 23 kg/cm^2 . Still, the particles move slowly to their final place. It is interesting that the longest column (A8) appears to be the most stable under low compression stress while it was the most unstable and unpredictable column (A4) during consolidation under high stress (Fig. 1a). Its consolidation curve is flat, probably a reflection of the distribution of the mechanical stress over a larger volume of packing [16,17]. We know that the consolidation of irregular particles is influenced by the compression stress. From Fig. 1a,b we derive that longer columns react in a more complex fashion to the application of the compression stress than shorter columns.

The second material used in this study behaves in a most different way than the first, because of the major differences in its particle sizes and shapes. The consolidation behavior of Nova Pak is similar to that of other spherical materials studied previously [21]. It is rapid and smooth. Note that Baker I-130 is probably the material with the coarsest particles used in preparative HPLC while Nova-Pak has small, smooth, spherical particles and is rarely used for preparative purposes, for economic reasons. These two materials are at the opposite ends of the spectrum of the packing materials of practical interest, slightly outside the typical range used in industry

(10–50 μm). This gives additional relevance to a comparative study of their packing properties, independently of their chromatographic characteristics.

3.2. Packing density

We observed for Nova Pak a nearly linear dependence of the final column length on the weight of dry packing material used. For Baker I-130, the column length increased more rapidly than the weight of packing. The lengths of the columns measured after consolidation were used to calculate the column volumes. From these volumes and the amounts of material used to pack the column (Table 2), the packing densities were derived. They are plotted against the amount of packing material used in Fig. 2. In all three cases, the packing density decreases with increasing column length. Shorter columns are denser than longer ones. This result was expected, considering the nature of consolidation in dynamic axial compression columns, the stress distribution determined by Train in a particulate bed and the distributions of packing densities reported by this author [16,17]. The piston applies the set compression stress to one end of the column bed while the other end of the bed is merely pushed against the corresponding frit and flange, without experiencing any direct stress. Compression stress in packed beds

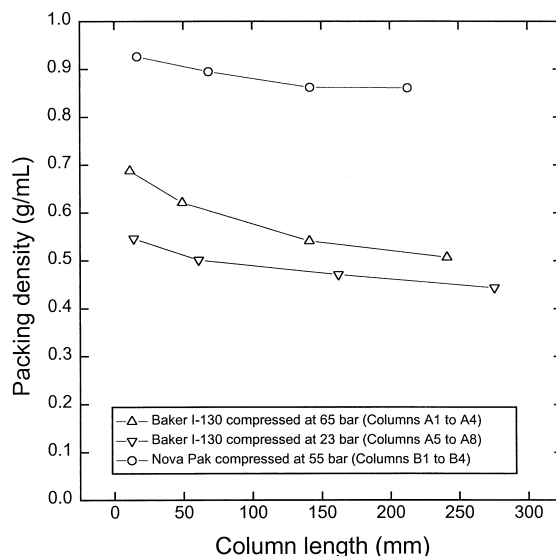


Fig. 2. Packing density of the material versus the column length.

do not convey as pressure in liquids [16,17]. The data obtained by Train for the consolidation of a bed of heavy magnesium carbonate powder, in a 13.5×5 cm I.D., cylinder, compressed by a mobile piston show a much higher stress against the piston than against the opposite, fixed end, even at the lowest stress for which data are reported, 28, 45, 62, and 90 kg/cm², values which are relevant to the behavior of chromatographic beds. The only significant difference between the experimental conditions used by Train and ours is that his beds were dry-packed while our chromatographic columns were impregnated with isopropanol.

The decrease in the compression stress from the piston face to the opposite end of the column was explained by friction between the particles and between the particles and the wall. This phenomenon causes a distribution of the compression stress in the axial direction as well as in the radial direction. The range of the stress distribution is expected to increase with increasing column length, the stress at the end opposite to the piston decreasing with increasing bed length. Since the packing density increases with increasing stress, this explains the decrease in the apparent column packing density under constant applied stress. The packing density reported in Fig. 2 is the average packing density measured over the entire column volume. In short columns which have a length smaller than the column diameter (first data point, columns A1, A5, and B1) or even a length nearly equal to the diameter (second data point, columns A2, A6, and B2), the local compression stress is less heterogeneous than in longer columns, more typical of those used in HPLC. Accordingly, the packing of these short columns should be more homogeneous than that of the long columns. Thus, there is a gradient of compression stress and of packing density along the axis of the column. There is a possibility that the shortest column be relatively homogeneous [23].

The difference in the ranges of values of the packing densities of Nova Pak and Baker I-130 in Fig. 2 is due to their different internal porosities. The differences in the variation of the packing density with increasing column length arises from their different shape. The small, spherical particles of the former material pack more tightly than the large, irregular particles of the latter and are less compress-

ible [22]. The friction between the particles in the bed and between the consolidated bed and the column wall is less intense with these spherical particles than with the irregular-shaped particles of the latter material. This is one of the reasons why the packing density of the Baker I-130 material decreases more rapidly with increasing bed length than that of the Nova Pak material. The other reason is that particle breakage of the irregularly shaped particles takes place at high compression stress. Particle breakage explains also the difference between the curves obtained with the two different compression stress. The packing density is always lower under 23 than under 65 kg/cm², especially for the short columns (Fig. 2). This interpretation is supported by the similarity of the length–density plots obtained for Baker I-130 under 23 kg/cm² and Nova Pak under 55 kg/cm². This last observation suggests that the pattern of axial heterogeneity of the stress is consistent if similar particles are consolidated into a mechanically stable state, without breakage. This would assume similar friction coefficients for the two beds against the column wall.

The stability of the slurry and the nature of the slurry solvent used are important factors in the preparation of chromatographic columns, whatever the method of consolidation used [24]. Isopropanol was used for both column materials. It usually gives good results for the packing of chemically bonded octadecyl silica [24]. However, the suspensions of Nova Pak were more stable than those of Baker I-130, an obvious consequence of the difference in the average particle sizes. Sedimentation of the large particles was quicker than that of the small ones. It is possible that, because of the quicker sedimentation, the beds of Baker I-130 experienced more friction resistance during the compression process. With a significantly higher friction coefficient, the distribution of the local compression stress would be wider and the volume occupied by the regions of relatively loose packing in the corresponding columns more important, especially in the longer columns. Because of the similarity of the length–density plots, this is unlikely.

3.3. Total and external porosities

The total column porosities or fraction of the

column volume accessible to the solvent were obtained from the retention volumes of the peak of uracil, a compound which is assumed to be unretained on chemically bonded C_{18} silica. The retention volumes were derived from the product of the flow-rate and the retention time of the peak maximum. Fig. 3 shows plots of the mean retention volumes (i.e., mean value of two or several data points) measured at different flow-rates, for the 12 different columns. Since these volumes are nearly constant, as shown in Fig. 3, the retention volumes obtained for each column were averaged over the whole flow-rate range. The total porosity was obtained by subtracting the mean extracolumn volume from the mean column retention volume. This volume was determined in the same way, using an entirely empty column, with the two frits in contact. The external bed porosity was calculated from the total porosity and the internal porosity of the packing material.

The internal porosity was obtained independently,

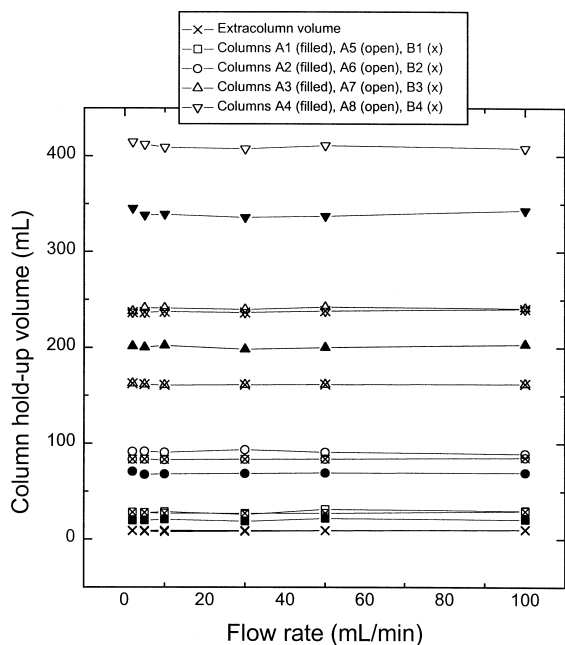


Fig. 3. Plot of the average retention volumes of uracil (i.e., hold-up volume) versus the flow-rate. The retention volumes were measured from the peak maximum. Symbols: \times , extracolumn volume; Column A1, \blacksquare ; A5, \square ; A2, \bullet ; A6, \circ ; A3, \blacktriangle ; A7, \triangle ; A4, \blacktriangledown ; A8, \triangledown ; B1, \times ; B2, \times ; B3, \times ; B4, \times .

from experiments of inverse size-exclusion chromatography (ISEC), carried out with authentic samples of polymers of known molecular mass and narrow molecular mass distribution, under experimental conditions in which these molecules are not retained [25,26]. The retention volumes of samples of increasing molecular masses of dextran in methanol-water mixtures (Nova Pak) or of polystyrene in methylene chloride (Baker I-130) were measured and plotted versus the logarithm of the molar volume of the probe. In both cases, these plots are made of two straight lines which intersect at a volume corresponding to the internal porosity [25]. From these results, internal porosities of 0.469 for Baker I-130 and 0.266 for Nova Pak were determined. The internal porosity has been shown to be independent of the consolidation process [22].

The total and external porosities of the three column sets are shown in Fig. 4, in which they are plotted versus the column length. The two lines corresponding to the total and the external porosities are parallel because the distance between these two curves reflects the contribution of the internal porosity, which is constant. Thus, only the external porosity, which is widely used to characterize packed beds, needs to be discussed. For Nova Pak, the external porosity depends little on the column length.

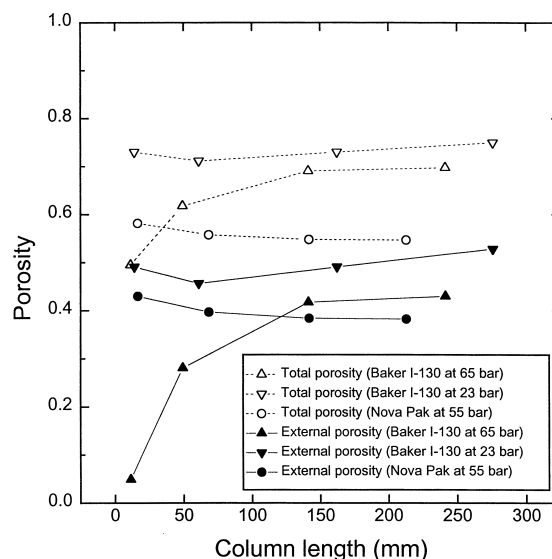


Fig. 4. Total and external porosity of the columns as a function of their length.

It is slightly larger than 0.4 for the shortest columns, slightly less for the two longest columns. The total variation is less than 5%. A value of 0.40 is typical of the void fraction of packed beds.

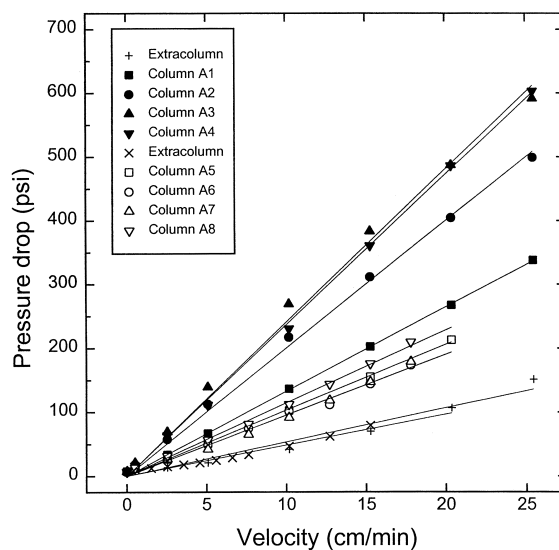
For Baker I-130, the results are quite different depending on the compression stress applied. With a compression stress of 23 kg/cm², the external porosity increases with increasing column length, except for the shortest column (column A5). With a high compression stress, the result is entirely different. The porosity of the shortest column (A1) is extremely low (approximately 0.05). This value cannot be explained otherwise than by assuming extensive particle breakage, although part of the low value could be explained by an underestimate of the retention volume due to the strong peak asymmetry which will be discussed later (see Fig. 9a,b). Theoretically, the lowest possible porosity of a packing made with spheres of uniform diameter is between 0.2 and 0.3 [27]. However, such low values are never encountered with columns packed with irregular-shaped particles and this is not an explanation for the porosity of the 5-cm long column which certainly did experience particle breakage too. The order of increasing external porosities of the long columns (Nova Pak < Baker I-130 under 55 kg/cm² < Baker I-130 under 23 kg/cm²) as well as the influence of the compression stress on the external porosity are consistent with the packing density data (Fig. 2).

3.4. Column back pressure and permeability

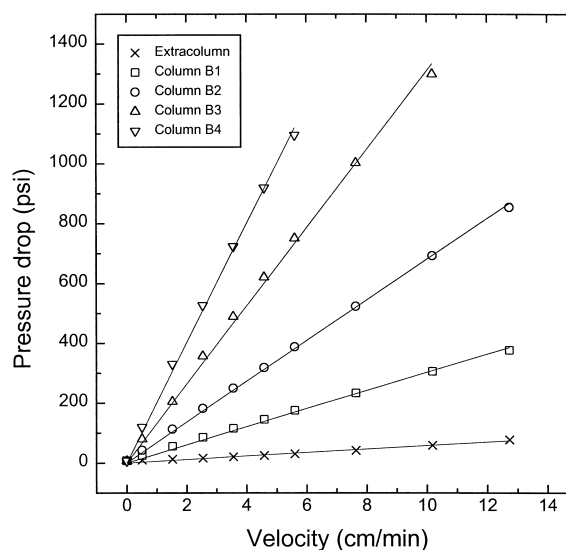
The column back pressure was measured in the flow-rate range of 10–500 ml/min for Baker I-130 and 10–250 ml/min for Nova Pak. The data obtained are shown in Fig. 5a and 5b, respectively, as plots of the pressure drop versus the linear velocity of the mobile phase. These plots are straight lines, as expected because Darcy's law is usually valid under the experimental conditions of liquid chromatography [18–20,28]

$$\frac{\Delta P}{u_o} = \mu \frac{L}{k} \quad (\text{Darcy's law}) \quad (1)$$

Note that the contribution of the equipment (mainly the connecting tubes) to the hydraulic resistance is



(a)



(b)

Fig. 5. Column back pressure as a function of the superficial velocity of the solvent, methanol–water (40:60). (a) Baker I-130 material. (b) Nova Pak material.

not negligible. The appropriate correction was made to all data.

The plot of $\Delta P/u_o$ vs. the column length (L) should also be linear with an ordinate equal to $\Delta P/u_o$ for the extracolumn volumes if the permeability is independent of the column length, which is true for

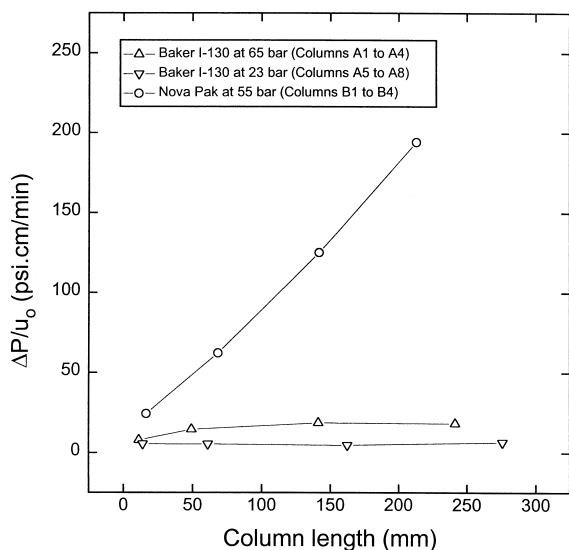


Fig. 6. Plot of the slopes of the straight lines in Fig. 5a and 5b versus the column length.

homogeneous columns. As shown in Fig. 6, $\Delta P/u_0$ is nearly constant, almost independent of the column length, for Baker I-130, under both values of the compression stress used. Note, however, that the value of $\Delta P/u_0$ is very small, which hides its actual variations (the slopes of the straight lines in Fig. 5a are obviously different). $\Delta P/u_0$ increases almost linearly (but slightly faster) with L for Nova Pak. This suggests that the permeability of the Nova Pak columns is nearly constant, which is confirmed in Fig. 7 (permeabilities on a logarithmic scale). The permeability measured for the shortest Nova Pak column is 5% lower than for the other columns, which is barely significant. A constant permeability for the Nova Pak columns is the conventional, expected result for packed columns. It is in agreement with the constant porosity reported in Fig. 4. Conversely, for Baker I-130, the permeability increases rapidly with increasing column length (Fig. 7). This result is in agreement with the similar variation of the column external porosity (Fig. 4). It is explained by the same phenomena, higher degree of consolidation of the packing material and particle breakage.

As expected, the permeability measured for the columns packed with the larger, irregular-shaped particles of Baker I-130 is much higher than the

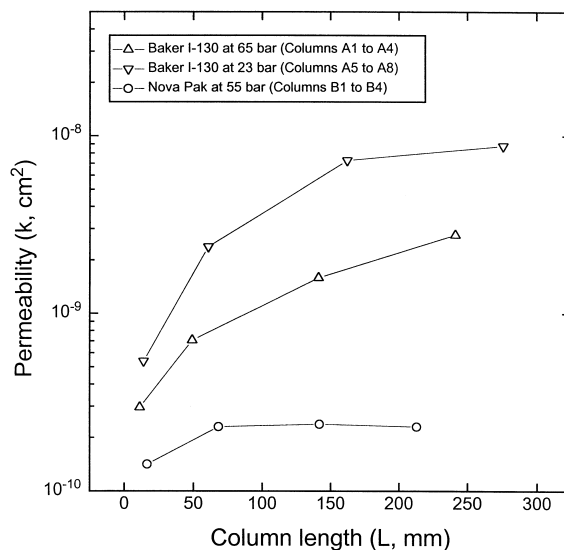


Fig. 7. Semi-logarithmic plot of the column permeability versus its length.

permeability of the columns packed with the smaller, spherical particles of Nova Pak. The ratio of these permeabilities is approximately one order of magnitude, which is less than expected from the ratio of the average particle sizes, 22. By combining Darcy's law and the Blake–Kozeny (or Kozeny–Carman) equation [28], the permeability can be related to the particle diameter, d_p , and the external porosity, ϵ_e , as follows:

$$K_0 = \frac{\epsilon_e^3 d_p^2}{(1 - \epsilon_e)^2 k} \quad (2)$$

where K_0 is the constant of Kozeny–Carman. For spherical particles, its value is usually assumed to be 150 or 180, depending on the reference [28,29]. Since we know or have determined independently the average particle size, the external porosity and the permeability, we can evaluate the Kozeny–Carman constant from the above equation. The values obtained are reported in Table 3 for the different columns. The values obtained for Nova Pak are rather high (ca. 25% higher than commonly accepted) but consistent and still reasonable, except for the shortest column (B1), for which it is much too high. These high values are explained by the high degree of consolidation, under an important me-

Table 3
Kozeny–Carman constants for the columns

	$L \approx 1$ cm (A1, A5, B1)	$L \approx 5$ cm (A2, A6, B2)	$L \approx 15$ cm (A3, A7, B3)	$L \approx 25$ cm (A4, A8, B4)
Baker I-130 at 65 kg/cm ²	73	10 179	22 709	14 886
Baker I-130 at 23 kg/cm ²	143 083	22 912	10 582	12 693
Nova Pak at 55 kg/cm ²	619	268	226	229

chanical compression stress and possibly a certain degree of particle breakage, already observed in Ref. [21]. By contrast, the values of the Kozeny–Carman constant for Baker I-130 are enormous and vary systematically. Although it is expected to find a value larger for irregular-shaped particles than for spherical ones, the values in Table 3 are unacceptable. They demonstrate an important degree of particle breakage, even at the low compression stress.

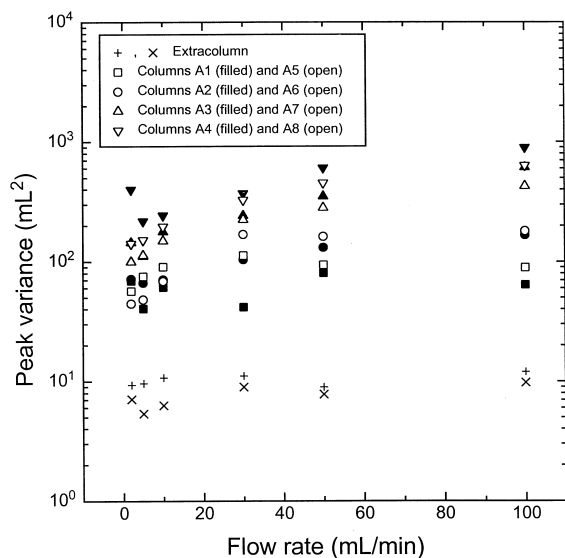
3.5. Extracolumn volume effects

Both the extracolumn contribution to the band variance (i.e., the band variance with no column) and the column band variances were determined using the same sample (uracil), in the same flow-rate range (2–100 ml/min). The sample was injected twice and the two data points obtained were averaged. A new series of sample injections and determinations of the extracolumn contributions to the volume variance of the bands was obtained whenever a new column was packed or unpacked. The total number of data points in the band profiles collected for each peak was 500–800 points, with a volume increment (ΔV , column effluent) of 0.05–0.5 ml, depending on the actual volume of the column. The band variances were calculated from the band width at half-height, using a program which determines successively the position of the peak maximum, its height and its width at half-height.

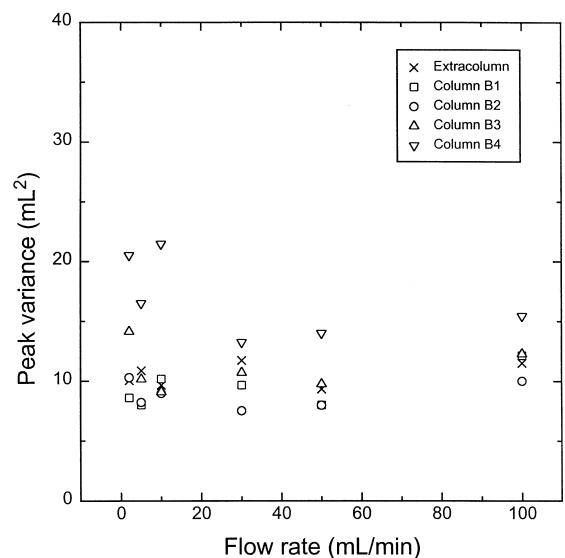
The band variances are plotted in Fig. 8 versus the mobile phase flow-rate. The variances of the bands obtained with Baker I-130 (Fig. 8a) are much larger than the contributions of the extracolumn sources of band broadening which, therefore, are negligible in this case. By contrast, the band variances obtained with the much more efficient Nova Pak columns (Fig. 8b) are barely larger than the extracolumn

contributions to their volume variance. In some instances, an extracolumn variance contribution larger than the variance of the bands recorded for an actual column was measured. This was attributed to the strong degree of asymmetry of the bands recorded with an empty column. The band asymmetry, derived from the ratio of the rear and the front half-widths of the bands, is plotted in Fig. 9 for the bands recorded with a zero-length column (determination of the extracolumn contributions) and in Fig. 10 for the bands recorded with the different columns.

Fig. 9 illustrates some of the difficulties encountered when operating the axial compression column with packing materials made of small particles. All the measurements of the contributions of extra-column sources of band broadening were carried out with the empty column, after unpacking it and prior to its repacking. The frits were carefully cleaned following the procedure described in Section 2 (mechanical cleaning in an ultrasonic bath) before recording the band profiles on the empty column. The results obtained should be practically identical. As illustrated in Fig. 9, they are not. The values obtained for the mean extracolumn volume are an average of 9.39 ml for the measurements made during the study of Baker I-130 and 8.96 ml for those made with Nova Pak. This is not a significant difference (ca. 5%). There are quite significant differences between the degrees of asymmetry measured, however, as illustrated in Fig. 10. The only experimental difference between the two sets of results was the use of a different packing material in the two series of measurements. This suggests that the size of the particles used in prior experiments may have a significant influence on the distribution of the flow velocities in the frits, which are designed to allow uniform flow but are most sensitive to clogging by small particles or fragments thereof. A more intensive cleaning method, such as a chemical



(a)



(b)

Fig. 8. Variance of the uracil peaks versus the mobile phase flow-rate. The variances were calculated from the peak width at half-height. Sample: 0.8 g/l uracil. Solvent: methanol–water (40:60). (a) Baker I-130 material and extracolumn volume. (b) Nova Pak material and extracolumn volume.

cleaning [18], may help in reducing the asymmetry of the bands observed with columns packed with fine particles.

In principle, the influence of the extracolumn

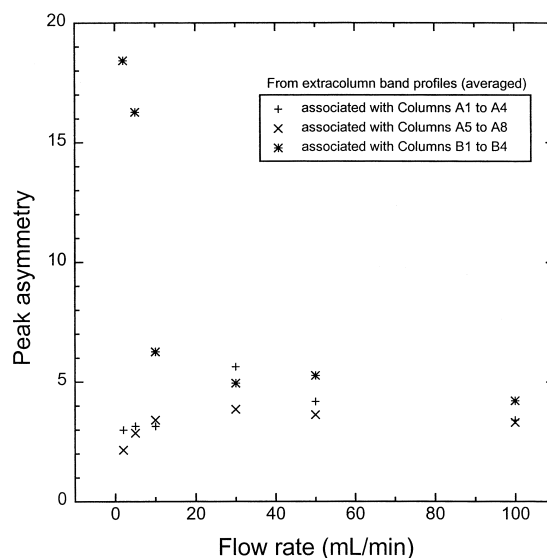


Fig. 9. Plot of the peak asymmetry measured for the extracolumn volumes versus the flow-rate. The peak asymmetry is measured as the ratio of the rear half-width to the front half-width, from the peak maximum position and at the 10% of the peak maximum height. Each measurement reported was carried out after unpacking the column indicated and cleaning up the frit.

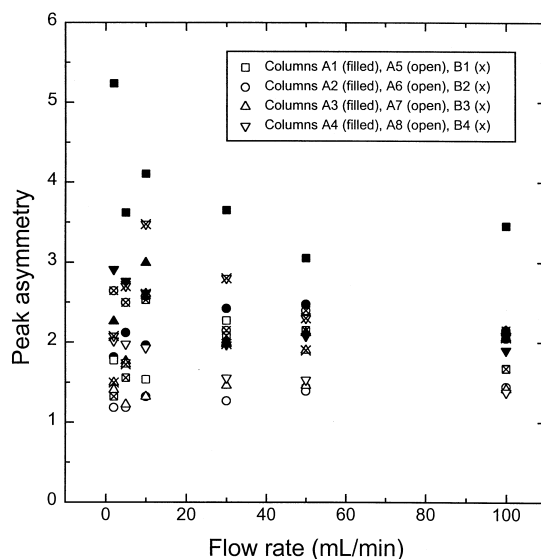


Fig. 10. Plot of the peak asymmetry measured for the different columns.

sources of band broadening on the apparent column efficiency can be eliminated by subtracting the extracolumn variance contribution from the measured band variances. However, this procedure is not much useful in the present study. The columns packed with Baker I-130 have a much larger variance than the extracolumn contribution and the correction is negligible. On the other hand, when applied to the Nova Pak columns, the correction is inaccurate because it fluctuates markedly from one series of experiments to the next, which indicates that it probably does not remain constant during a series of determinations of the column efficiency as a function of the flow-rate. The progressive clogging of the frits is an ongoing phenomenon which cannot be avoided nor prevented with fine particles.

3.6. Column efficiency

The column efficiency was calculated from the peak half-width. The extracolumn sources of band broadening were not taken into account, for the reasons explained above. The molecular diffusivity of uracil in the methanol–water solution (40:60) used as the mobile phase was calculated from the Wilke–Chang correlation (and found equal to $1.2 \times 10^{-5} \text{ cm}^2/\text{s}$). The reduced plate height is plotted as a function of the reduced velocity in Fig. 11a for Baker I-130 and in Fig. 11b for Nova Pak. Obviously, because of the large difference in the average sizes of the particles of the two packing materials, the range of reduced velocities investigated is quite different in the two plots since the data were acquired in similar ranges of actual flow-rates.

Except for the shortest columns (A1 and A5), the plots reported in Fig. 11a (Baker I-130) are mostly typical van Deemter plots, exhibiting a minimum plate height at a reduced velocity of 5 or lower. The minimum reduced plate height is approximately 3 for columns compressed under $65 \text{ kg}/\text{cm}^2$ and 2 for columns compressed under $23 \text{ kg}/\text{cm}^2$. Those are good values. They demonstrate that particle breakage is not adverse to good column efficiency, at least as long as the broken pieces remain in place. Obviously, unpacking of the column and attempts at reusing the material would not be so successful. Under both compression stresses, the shortest columns have a significantly lower efficiency than the other three

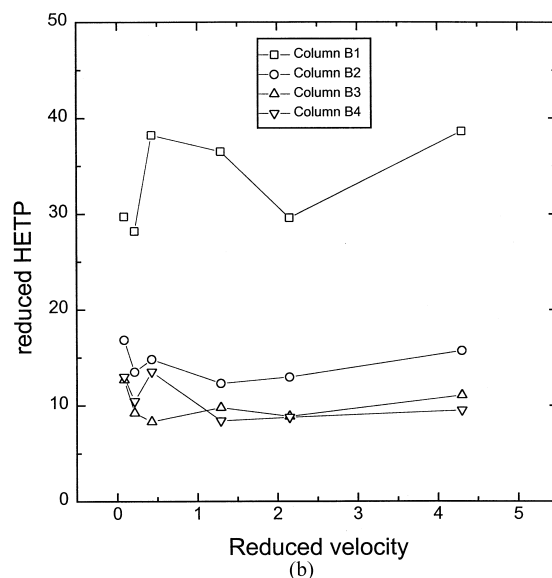
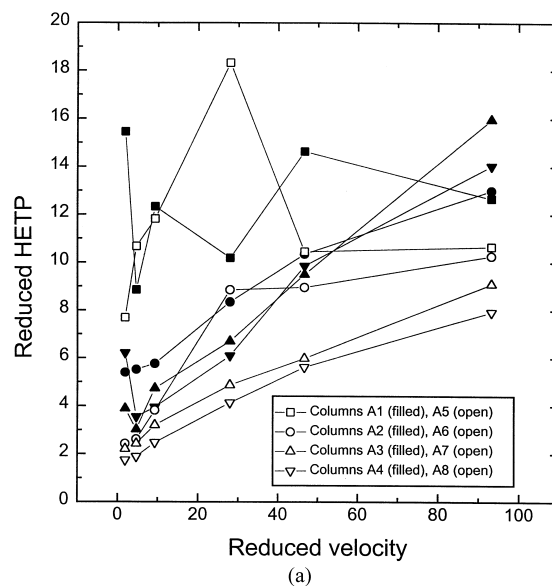


Fig. 11. Plot of the reduced plate height as a function of the reduced velocity. Average of two data points measured under the same condition. Sample: 0.8 g/l uracil. Solvent: methanol–water (40:60). Sample volume: 0.5 ml. (a) Baker I-130 material. (b) Nova Pak material.

columns, with reduced plate heights ranging between 8 and 18. These values are quite imprecise, because of the low efficiency. A reduced efficiency of 10 for a 11.2-mm long column (A1), packed with 130- μm particles corresponds to an efficiency of fewer than

nine theoretical plates, which causes significant asymmetry and errors (see Fig. 10 for the asymmetry). Still, the data available suggest a plot similar to those corresponding to the other columns, but with a lower efficiency.

Our result is the opposite of Eon's [4], who reported a significant increase of the reduced plate height with increasing column length, which he attributed to the wall effect. However, the experimental conditions of these two studies are profoundly different. First, Eon's result was based on the use of a point source for the sample injection, which was carried out with a centrally located needle. In this case, the band of the injected solute cannot reach the wall region if the column length is short enough. The sample injected in the axial compression column was distributed over the entire cross-section area, at the column entrance. In this case, the band has access to the whole packed bed. Second, the wall effect is of a different nature in the dry-packed columns used by Eon [4] and in slurry-packed columns. In the former case, the larger particles segregate along the wall. It is more probable that the poor efficiency of the shortest column made with Baker I-130 is due to column disturbance near the entrance zone, i.e., near the piston. This would include the consequences of an uneven flow distribution and of axial and radial dispersion at or near the column entrance, as well as tailing originating in the sample loop. Because the length of the shortest column (ca. 1 cm) is small compared to its diameter (5 cm), the entrance effect cannot be ignored if there is any. The column entrance will directly affect the fluid flow pattern and the sample mass transfer. Fig. 10 shows that the peak asymmetry decreases markedly with increasing column length. If the injection is tailing, the column efficiency is reduced. This explanation is in agreement with the decrease in the plate height observed when the column length increases (Fig. 11a). The influences of the column entrance disturbances and of the wall effect on the efficiency are independent.

Although quite different from those in Fig. 11a, the plots in Fig. 11b for Nova Pak are also typical of the Van Deemter curves, taking into account the narrow range of reduced velocity sampled. This range is only 5% of the one in Fig. 11a, and is insufficient to illustrate the features of the van

Deemter plot at high reduced velocities. Measurements could not be carried out at higher flow-rates with our pumping system which has a safety device disconnecting it when the pressure rises beyond a limit equal to 1500 p.s.i. (ca. 105 atm (1 p.s.i. = 6894.76 Pa)). As in the previous case, the shortest column has a much poorer efficiency than the other three columns and exhibits the widest fluctuations of the experimental data. The entrance effects should affect this column at least as much as it does the corresponding Baker I-130 column, since the band variance originating from dispersion inside the column is less important in this case (Fig. 8b). However, we observe that, with the Nova Pak material, the peak asymmetry is less (Fig. 10) and the efficiency higher than with the Baker I-130, although the reduced height equivalent to a theoretical plate (HETP) does not go much below 8 (Fig. 11b), i.e., is nearly three times higher than with Baker I-130. The longest two columns (B3, B4) are more efficient than the shortest one, with the 4 cm long column (B2) slightly less efficient than those long columns. Compared to the data for Baker I-130, the minimum reduced plate height for Nova Pak is much higher and the corresponding reduced velocity lower (around 2). This lower efficiency can be explained by the extracolumn effects. Fig. 8b shows that the band variances measured on the Nova Pak columns are close to those obtained for the contribution of the extracolumn volume. Accordingly, the correction would be important. Unfortunately, it is inaccurate because of the strong asymmetry of the bands recorded without a column. For this reason, it was not made. This important result illustrates well one of the practical limitations encountered with the use of fine particle materials in preparative chromatography. Because of the large extra-column band broadening which often takes place, the actual performance achieved in terms of efficiency and resolution is mediocre and is rarely worth the cost in terms of the high pressure head required.

Although the reduced plate heights of the Baker I-130 columns are lower than those of the Nova Pak columns, their actual efficiencies are much lower, the average particle diameters of the first packing material being 22 times larger than that of the second. Generally, column efficiency increases as particle size decreases. The large values of the band vari-

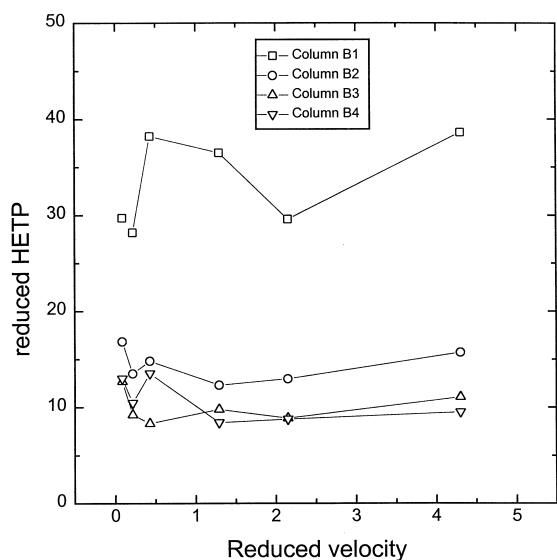


Fig. 12. Plot of the number of plates per unit column length versus the actual column length. Average of six data points in the flow-rate range of 2–100 ml/min.

ances obtained with Baker I-130 indicates that the peaks are not sharp. To compare the efficiency achieved with all these columns, Fig. 12 shows the total number of theoretical plates, averaged in the flow range considered (2–100 ml/min), reported to the column length. This graph illustrates the much higher (ca. one order of magnitude) efficiency of the columns packed with Nova Pak, as compared to the same data for Baker I-130. The most salient feature of the graph, however, is that the shortest columns always have lower efficiency than the others and the increase of efficiency at increasing column length levels off somewhere between 10 and 15 cm. This column length seems to be the optimum beyond which the column efficiency per unit length would tend to remain same. Accordingly, the use of columns shorter than that should be avoided.

Fig. 12 supports the idea of column entrance effect discussed previously. Column end effects are a general phenomenon, described in hydrodynamics: an entrance length, a function of the column diameter and the Reynolds number, is required for the build-up to the parabolic profiles in an empty cylindrical tube [28]. Similarly, there is a thermal entrance region in heat transfer problems [28]. By analogy, there must be a column entrance region in

mass transfer problems, albeit this is ignored in most cases. The entrance effect should obviously be a function of the specific experimental conditions. To explain the data obtained in our study, several possible contributions to a column entrance effect in the dynamically compressed packed columns should be discussed.

First, we can consider a nonuniform flow distribution through the inlet of the column, specifically in the piston frit. During the column operation, some fine particles may be trapped inside the frit, as explained earlier in this paper, and lead to uneven flow paths at the column entrance. A recent study of the column radial homogeneity showed that there was no significant radial disturbance at the column inlet of the same system as used for this study [9]. Although coarser particles (10- μ m Zorbax PRO-10/150 C₁₈ bonded spherical silica from BTR Separations, Wilmington, DE, USA) and a lower compression stress (45 kg/cm²) were used in this last work, this result weakens the possibility of a strong effect of the piston frit. Still some questions remain about the effect of the particle size. Large, rigid particles can maintain a stable contact with the piston frit but fine particles could be moved and trapped inside the frit. These fine particles may originate from the packing material itself (Nova Pak) or from their breakage products (Baker I-130).

Second, the local homogeneity of the column near the piston may be poorer than in the bulk of the column. This is possible because the stress distribution inside the column is not uniform. Intense stress near the piston is expected from the density data (Fig. 2) as well as from independent results [16,17]. This stress causes strong disturbance of the local column homogeneity, both axially and radially. Particles break in the region of high stress, not in the regions where the mechanical compression stress is low [19]. Finally, the low efficiency of very short columns may be related to the total surface area of contact between the particles and the column wall. This ratio is a measure of the perturbation caused by the walls to a packing which would, otherwise, be homogeneous. Fig. 13 shows the total wall area per column volume as a function of the column length. The figure compares also the cases in which either both ends or only one end of the column (its inlet) are taken into account and shows that the result is

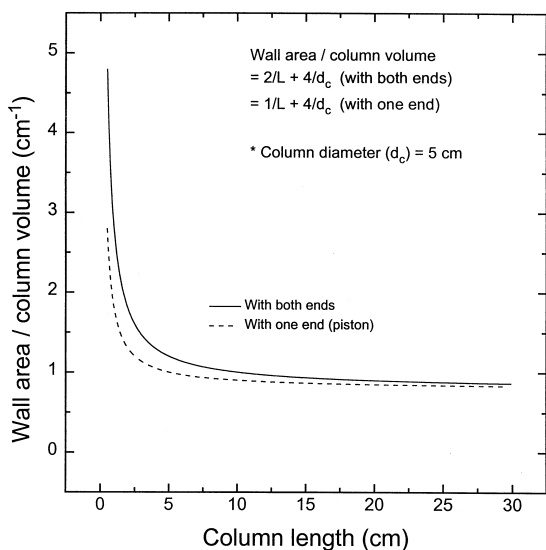


Fig. 13. Plot of the total contact area between the packed bed and the column wall or ends versus the column length.

practically the same. In either case, the ratio of the total wall area to the column volume decreases rapidly in the first few centimeters and becomes nearly constant for column lengths exceeding approximately 5 cm, a result which correlates well with the plot of the column efficiency versus the column length in Fig. 12.

4. Conclusions

Our results show that the properties of a dynamic axial compression column depend on its length in an unexpected, nonlinear fashion. This is because the packed bed is not homogeneous axially. The region close to the piston experiences a higher degree of compression stress. Accordingly, the average column packing density (Fig. 2) decreases with increasing column length while the average column external porosity (Fig. 4) and permeability (Fig. 7) increase. The average column packing density increases with increasing compression stress while the average column external porosity and permeability decrease. The amplitude of these changes is much larger with

the material having large, irregularly shaped particles than with the one made of small, spherical ones.

As a first approximation, these results could be explained by assuming that the column packing density and the other properties controlled by this density vary regularly along the axial coordinate. The amplitude of the variation of this property and its gradient depend on the column length. When the length is short compared to the diameter, the whole bed is under a high level of stress and is relatively homogeneous, both radially and axially. The packing density is high and the permeability low. When the length increases, friction of the bed along the wall causes a progressive decay of the stress, which decreases more and more rapidly along the column axis, away from the piston. In the same time, the stress remains larger close to the column wall than in its center. It seems that the volume of packing in which a high level of stress is reached decreases with increasing column length. The phenomenon is made more complex and specific of the particular material used. Depending on the crushing resistance of the particles, a more or less intense breakage can be achieved. Depending on their coefficient of mutual friction and on the friction coefficient of the bed against the wall, a different fraction of the stress can be transferred to the wall.

The results of this work suggest that the two-dimensional picture of the radial heterogeneity of the column [9] is incomplete. It must be completed by considering that the column is also heterogeneous along its axis, as strongly suggested by the data of Train [16,17]. On a more practical side, we conclude that moderation should be exercised in the selection of the axial compression pressure. The mechanical stress applied by the piston to the packing is not homogeneously distributed but is higher in some regions where particle breakage takes place first and most intensely. Lower values of the stress should be applied to large particle size materials than to those made of fine particles which are stronger for the same chemical composition and internal porosity. Lower stress should also be applied to the more porous materials. The stress selected should decrease with decreasing column length. A compression stress of the order of 20–25 bar is a maximum for the Baker material and should not be exceeded for

columns of any length. For Nova Pak, a compression stress of 40–45 bar would be reasonable.

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