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HYDRODYNAMIC STUDIES IN LARGE-DIAMETER COLUMNS*

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SUMMARY

Axial dispersion resulting from the flow pattern alone has been investigated in two columns with internal diameters of 8 and 60 mm. To eliminate interactions between the solute and the support, a bed of non-porous glass beads was used, with sulphuric acid as a tracer. The solute concentration was measured at various points inside the column by conductivity probes. On the smaller column, the mean values of the concentration over the column cross-section were observed, in addition to local values at the centre of the packing, at two locations along the central line. On the larger column, local values were determined at two locations along the central line and at different points on a diameter; external cells were also located at the column inlet and outlet. The axial dispersion was evaluated with the dispersed plug-flow model, by comparing the conductivity signals at the two positions in the column. Various results are presented and compared with existing models: the dispersion in the two columns is compared; on the larger column, the local dispersion in the packing is explored and the contributions to dispersion caused by the packing and the column heads are evaluated.

INTRODUCTION

In order to use liquid chromatography as an industrial separation technique, it is necessary to increase the internal diameter of the columns. To maintain an high efficiency with large columns, the flow regime must remain as close as possible to plug-flow. Thus it seems important to study the different sources of axial dispersion in a chromatography column.

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DISPERSION IN POROUS MEDIA

Dispersion associated with flow through a porous medium has been widely studied in such diverse fields as chemical engineering, hydrology, petroleum engineering and chromatography, as reviewed by De Ligny and Hammers[1]. Two models are often used to describe such a flow: (a) the dispersed plug-flow model, where the amount of dispersion is characterized by the Peclet number, $Pe = uL/D$, where u = interstitial velocity (cm/s), L = column length (cm) and D = dispersion coefficient (cm^2/s); this parameter indicates the importance of diffusion relative to convection; (b) the cascade of perfectly mixed cells, commonly used in chromatography, where dispersion is taken into account through the number of cells, N, or the reduced plate height, $h = L/Nd_p$, where d_p is the particle diameter (μm). For the high Peclet numbers encountered in chromatography, these two models are practically identical, with $Pe = 2N$.

Influence of fluid velocity

Much theoretical and experimental work has been carried out on the dependence of the dispersion upon the fluid velocity and the parameters of the porous medium. For comparative purposes, it is convenient to express the fluid velocity in dimensionless terms: the Reynolds number, $Re_0 = \rho \varepsilon u d_p/\mu$, used in chemical engineering, is a measure of the degree of turbulence, where ρ is the fluid density, ε the bed porosity and μ the fluid viscosity; the reduced velocity, $\nu = ud_p/D_m$, is preferred by chromatographers when comparing gaseous and liquid systems, where D_m is the molecular diffusivity (cm^2/s).

Giddings[2], De Ligny[3] and Edwards and Richardson[4] suggested the same type of equation, based on semi-theoretical studies

$$h = \frac{2\gamma}{\nu} + \frac{2\lambda}{1 + \omega\nu^{-1}} \qquad (1)$$

where the parameters γ, λ, ω depend on the shape and size of the particles, and on the physical state of the fluid (gas or liquid). In this equation, the first term arises from axial molecular diffusion and the second one from velocity variations within the mobile phase, generally termed "eddy dispersion". Sie and Rijnders[5] expressed the coefficients λ and ω as functions of the ratio of column to particle diameters.

Gunn[6], applying probability theory to the study of dispersion, obtained a rather complicated equation containing two parameters. Miyauchi and Kikuchi[7] suggested a mass-transfer effect between rapidly and slowly moving parts of the streaming fluid and obtained an equation of the same form as that of Gunn. Following the same approach, several authors have established that the flow contribution of h may be expressed as

$$h = \frac{1}{A + B\nu^{-m}} \qquad (2)$$

where m = 0.33 according to Horváth and Lin[8], 0.48 or 0.5 according to Miller and

King[9] and Chung and Wen[10]. However, for practical purposes, the most commonly used form of the flow contribution is

$$h = Av^m \tag{3}$$

with $m = 0.20$ according to Perkins and Johnston[11], Pfannkuch[12], Knox *et al.*[13], 0.33 according to Knox[14]. From the numerous experimental works collected by Cluff and Hawkes[15], it is seen that these data present a wide scatter and that no rigorous theoretical equation can fit them all precisely.

Influence of geometrical factors

During the past few years, new aspects of dispersion in the field of preparative liquid chromatography have been investigated: the use of large diameter columns has demonstrated the need for a flat velocity profile over a cross-section of the column, and also along the entire length of the eluent flow.

Coq[16] observed more precisely the external sources of dispersion (injection, detection and end effects). The main source of dispersion is the flow through the column itself; it then becomes necessary to explore the structure of the packing in order to compare the efficiency of two columns.

Thus Mehta *et al.*[17] introduced two sets of conductivity probes inside a column to isolate the dispersive effect of the column itself. More recently, Knox *et al.*[13] suggested the use of a polarographic detector, one electrode being fixed at the centre of the bed and the other one movable radially across the column exit frit. This technique enabled the authors to confirm the existence of two regions in the packing: the core of the column with a rather perfect plug-flow, and a volume in the vicinity of the wall where a less dense packing structure might be responsible for flow irregularities. Better column performances were obtained by De Stefano and Beachell[18] when they injected the sample in the centre of the bed, so that it never made contact with the walls before reaching the end of the column. This technique, introduced by Knox and Parcher[19], is known as the "infinite diameter effect" technique.

Using the same detection system, Eon[20] pointed out the favourable effect of radially compressing large diameter columns, so that the wall region is of less importance. Kamiński and co-workers[21,22] proposed another detection technique: they observed the concentration on concentric rings on the outlet frit. It was thus possible to investigate the local structure of the packing and to deduce the influence of the packing technique (tamping or slurry method) upon the quality of the eluent flow.

We can conclude that a direct and accurate measurement of the axial dispersion in the column (packing and heads) appears to be necessary to assess the quality of the column and to estimate the efficiency of a chromatographic process. Our purpose has been to develop a technique to evaluate directly the axial dispersion in the column itself. In order to suppress mass-transfer phenomena, we used a packing of nonporous beads and in order to eliminate external sources of dispersion we detected the solute concentration at two points inside the column. A comparison of these two signals yields the dispersion caused by the packing alone.

APPARATUS

A schematic diagram of the apparatus is shown in Fig. 1. The columns used had the following dimensions: 1, 30 cm × 8 mm I.D., acrylic plastic; 2, 60 cm × 60 mm I.D., stainless steel. The packing consisted of non-porous glass beads with diameters in the ranges 60–80 and 140–160 μm. Prior to packing, the glass beads were washed with sulphochromic acid, rinsed with water and dried. Finally, the column was carefully dry-packed. The eluent was water, at room temperature. 0.01 *N* Sulphuric acid was injected through a loop of volume: 250 μl for column 1 and 40 cm^3 for column 2. To obtain concentration pulses, only a fraction of the loop volume was injected. Electrical conductivity detection was employed in order to give a local or an integrated measurement of the tracer concentration.

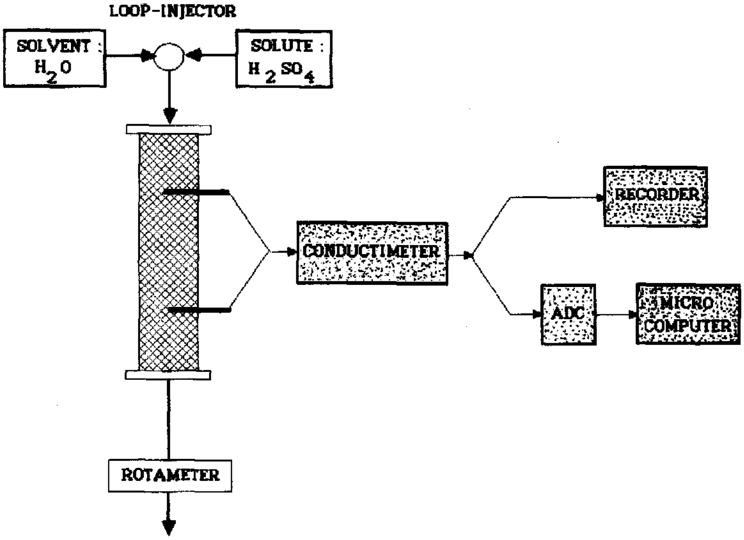

Fig. 1. Apparatus. ADC = Analogical digital converter.

Two series of probes were used in column 1. The AA′ probes consisted of two 1-mm diameter platinum wires sealed in the column wall; they were positioned radially, perpendicular to the eluent flow, with the electrode faces parallel and tangential to the inner wall of the column so that they did not disturb the flow (see Fig. 2). They measure the mean concentration over a volume encompassing the entire width of the column. The probes BB′ were coated with an insulating film so that their only active part was their tip, located 1.5 mm from the axis of the column. The measurement is restricted to a small volume in the central part of the column. These probes were located at two different levels along the column (as shown in Fig. 2) in order to observe the concentration (mol/l) response curves, $C(t,x_1)$ and $C(t,x_2)$, at the axial positions x_1 = 5 cm and x_2 = 25 cm; *t* is the time in seconds.

In order to achieve local measurement of the concentration in column 2, five sets of probes (a, b, c, d, e) were located along a diameter (Fig. 3): each set consisted of two parallel small pieces of 1-mm platinum wire, 2 mm apart. They were sealed

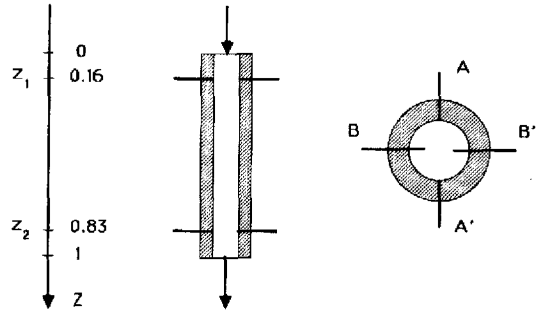

Fig. 2. Column 1 and the conductivity probes.

in a 1/8-in. plastic tube, so that their only active part was their tip. Two series of probes were positioned at $x_1 = 10$ cm and $x_2 = 50$ cm.

In preliminary experiments, the conductimeter response to various acid concentrations was examined. In the concentration range used, the response was found to be proportional to concentration.

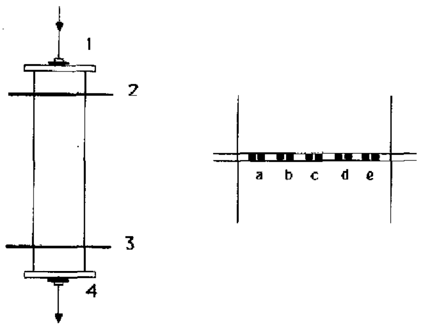

Fig. 3. Column 2 and the conductivity probes.

FLOW MODEL

The dispersed plug-flow model[23] was used for data analysis. This model assumes a uniform value of the concentration over the column cross-section, and a dispersive action superimposed over a plug-flow. Thus the following partial derivative equation holds

$$\frac{1}{\mathrm{Pe}} \cdot \frac{\partial^2 C}{\partial z^2} - \frac{\partial C}{\partial z} - \tau \cdot \frac{\partial C}{\partial t} = 0 \qquad (4)$$

where z = a dimensionless length ($= x/L$) and τ = mean residence time of the solute ($= L/u$). Using the transfer-function notation, we may write

$$\bar{C}(s,z) = H(s,z)\,\bar{C}(s,0) \qquad (5)$$

where $\bar{C}(s,z)$ is the Laplace transform of $C(t,z)$ and $H(s,z)$ is the transfer function associated with the flow between levels 0 and z; s is the Laplace variable (s^{-1}). The following expression can then be derived

$$H(s,z) = [Pe \cdot \exp(zV)]/U \tag{6}$$

with $U = Pe(1 + \sqrt{1 + 4\tau s/Pe})/2$ and $V = Pe(1 - \sqrt{1 + 4\tau s/Pe})/2$.

With this model, the flow of solute through the column can be characterized by two parameters, Pe and τ.

DATA ANALYSIS

From two experimental responses, $C(t,z_1)$ and $C(t,z_2)$, it is possible to obtain values of Pe and τ, characteristics of the flow between z_1 and z_2. The effects of external factors, such as the injection system and end effects, are thus eliminated.

The two parameters can be obtained directly from an evaluation of the first and second moments of the response curves[4,17,24]. In our case, this method was not satisfactory. For similar operating conditions, the results were highly dispersed and this could not be explained by experimental errors. We thus preferred a method based on the comparison between the experimental and calculated response curves. For a pair of concentration functions at two positions z_1 and z_2, we can consider that $C(t,z_2)$ is the response of the test section z_1z_2 to the input $C(t,z_1)$.

Using the Laplace transforms of these functions and eqn. 6 we obtain:

$$\bar{C}(s,z_2) = [H(s,z_2)/H(s,z_1)] \cdot \bar{C}(s,z_1) \tag{7}$$

$$= \exp[(z_2 - z_1)V] \cdot \bar{C}(s,z_1) \tag{8}$$

In these equations the values of Pe and τ are always related to the overall length of the column as defined in eqn. 6. If $C_{\text{exp}}(t,z_1)$ and $C_{\text{exp}}(t,z_2)$ are the measured concentration curves and $C_{\text{theo}}(t,z_2)$ is the theoretical response:

$$\bar{C}_{\text{theo}}(s,z_2) = [H(s,z_2)/H(s,z_1)] \cdot \bar{C}_{\text{exp}}(s,z_1) \tag{9}$$

Parameters Pe and τ can be evaluated by fitting the calculated concentration curve, $\bar{C}_{\text{theo}}(s,z_2)$, to the experimental one, $\bar{C}_{\text{exp}}(s,z_2)$.

This involves the following steps: calculation of the Fourier transform (using FFT algorithm)[25,26] of the conductivity signals, to obtain $\bar{C}_{\text{exp}}(j2\pi f,z_i)$, where j is a complex number ($j^2 = -1$) and f is the frequency (s^{-1}); calculation by means of eqn. 9, of the theoretical response curve, $\bar{C}_{\text{theo}}(j2\pi f,z_2)$, as a function of Pe and τ; minimization of a criterion of the form

$$E = \sum_{i=0}^{N-1} [\bar{C}_{\text{theo}}(j2\pi f_i,z_2) - \bar{C}_{\text{exp}}(j2\pi f_i,z_2)]^2 \tag{10}$$

by a Gauss–Newton method.

By this method, we obtained a very good agreement between the experimental and calculated curves, indicating that the model accurately describes the behaviour of the column.

RESULTS AND DISCUSSION

Influence of the eluent flow-rate

Fig. 4 shows the dependence of the Peclet number based on particle diameter, Pe_p ($= ud_p/D$), upon Re_0. This can be more simply expressed as a function of h ($Pe = 2/h$). Three sets of data points were obtained with: column 1, probes AA′, two ranges of particle diameter, 60–80 and 140–160 μm; column 2, probes c, d_p = 140–160 μm. These results may be described by an equation similar to eqn. 3:

$$Pe_p = k \cdot Re_0^m \tag{11}$$

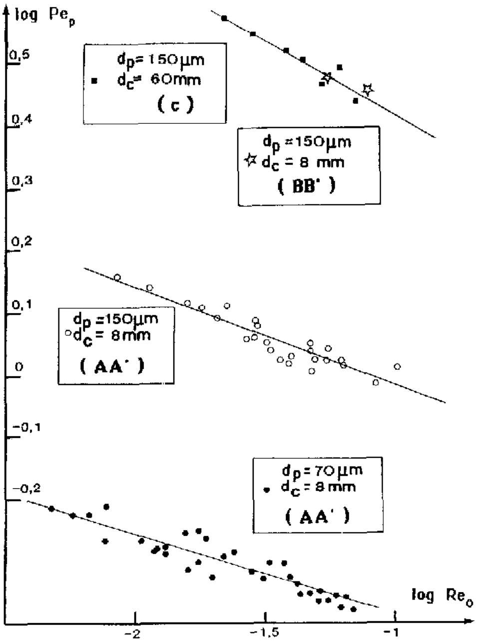

Fig. 4. Variations of the Peclet number with the Reynolds number.

The values found for m (Table I) are similar for the two ranges of particle diameter and the two column diameters, and are in agreement with those found by Pfannkuch[12] and Knox *et al.*[13] ($m = -0.20$). The k values are dependent on the particle diameter and column diameter. Pfannkuch showed that this parameter depends on particle size and packing structure.

The uppermost graph in Fig. 4 compares Pe_p measured with column 1, probes BB′, and with column 2, probes c. The data obtained at the centre of the bed with both columns are superimposable. The interest of this graph lies in the similarity of the core region for the two columns.

We can also compare the dispersion values for column 1, d_p = 150 μm, using the two sets of probes AA′ and BB′. The Peclet values obtained with probes BB′ are

TABLE I

EXPERIMENTAL VALUES OF PARAMETERS m AND k FOR COLUMNS 1 AND 2

	Column 1 (AA')		*Column 2 (c)* $d_p = 150\ \mu m$
	$d_p = 70\ \mu m$	$d_p = 150\ \mu m$	
m	−0.13	−0.16	−0.23
k	0.30	0.67	1.52

approximately five times higher than those observed with probes AA′. Considering that only the central part of the column is observed by probes BB′ and that the entire cross-section is seen by probes AA′, we attribute this difference to wall effects.

Influence of radial position

With column 2 it is possible to achieve a local detection of the concentration: keeping a reference point at the centre of the bed (2 c), we can observe the different signals at probe 3 (a, b, c, d, e) or keeping (3 c) as reference, we can observe the different signals detected by probe 2 (a, b, c, d, e). Fig. 5 shows residence times, τ, and peak variances, σ^2 (s^2), so obtained with probe 2 and a mean flow-rate of 0.72 cm^3/s and with probe 3 and a flow-rate of 0.64 cm^3/s. This 12% variation in the flow-rate is responsible for the difference between the τ (or σ^2) values at 2c and 3c which should coincide.

The residence times suggest a rather flat velocity profile; the region very close to the wall cannot be explored since the nearest probes are 1 cm from the wall. As for the variances, probes 2 provide the variances just after the column inlet: there is a wide scatter of these values which reveals the poor distribution of the eluent at the column inlet. Probes 3 provide the variances at the end of the packing, just before the column outlet: this profile is more in agreement with the findings of Eon[20], Knox *et al.*[13] and Klawiter *et al.*[21], *i.e.*, a minimum of dispersion in the core of the column and an important rise from the centre to the wall. Surprisingly, the core region (having low σ^2 values) seems to be of little importance since no flat profile can be observed. This could be due to a poor quality of packing; in fact, the column was dry-packed with no special care.

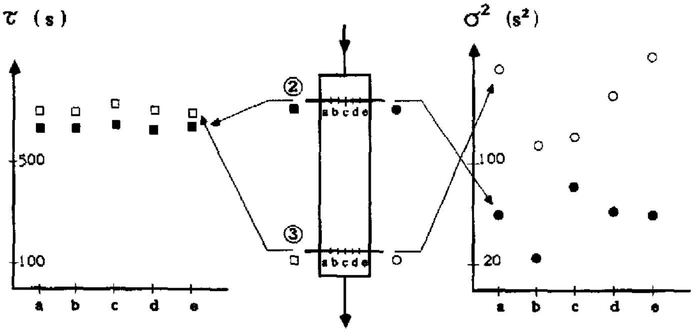

Fig. 5. Variations of the residence times and variances with the radial position.

This local measurement seems to be a good way to assess the quality of a packing.

Influence of column heads

With column 2 we can compare the *Pe* and τ values obtained by detection of signals 2 and 3 (inside the packing) or signals 1 and 4 (in the inlet and outlet fittings). The results are reported in Table II.

TABLE II

PECLET NUMBERS AND RESIDENCE TIMES MEASURED ON COLUMN 2

Flow-rate (cm^3/s)	*Probes*	*Peclet number*	*Residence times (s)*
0.53	2, 3	13 091	1238
	1, 4	6318	1268
0.85	2, 3	12 128	784
	1, 4	6392	803
1.02	2, 3	11 591	658
	1, 4	5731	673
1.19	2, 3	12 299	560
	1, 4	5000	572
1.35	2, 3	10 928	485
	1, 4	5719	496

The residence times do not differ greatly from one system to the other, but the Peclet numbers measured inside the column are approximately twice those measured outside the column. This reveals an important dispersive effect due to the column heads. In order to take account of this phenomenon, we chose to represent the column as a set of three elements (Fig. 6): the packing itself, described by the dispersed plug-flow model (with *Pe* and τ as parameters), and two perfectly mixed cells (with a time constant of τ_0) simulating the dispersion due to the column ends.

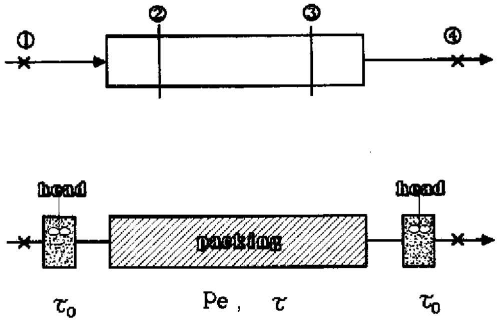

Fig. 6. Representation of column 2.

The residence time and the variance of this new system can be written as

$$\tau_t = \tau + 2\,\tau_0 \tag{12}$$

$$\sigma_t^2 = 2\,\tau^2/Pe + 2\,\tau_0^2 = 2\,\tau_t^2/Pe_t \tag{13}$$

where Pe and τ are evaluated from probes 2 and 3 and Pe_t and τ_t are evaluated from probes 1 and 4. The resulting values of τ_0 are reported in Table III. In order to assess the validity of our model, we verified that τ_0 is proportional to $1/Q$ where Q = eluent flow-rate (cm/s).

TABLE III

VARIATIONS OF τ_0 WITH FLOW-RATE

Flow-rate *(cm³/s)*	τ_0 *(s)*
0.53	13
0.75	12
0.85	8
1.02	7
1.19	7
1.35	5

We evaluated the relative contributions of the different parts of the column to the residence time and variance: τ_0/τ_t = 1%; σ_0^2/σ_t^2 = 32%. For our experimental system, the contribution of the column heads is more important than that of the packing. This result is rather surprising, but we should bear in mind that in a separation process, mass-transfer terms will add to the dispersive effect of the packing without changing the effect due to the column heads.

CONCLUSION

Using different sets of concentration detectors located inside a chromatography column, it has been possible to estimate the amount of local dispersion associated with the flow through the packing and to correlate it with the eluent velocity. It has been shown that the flow in the core region is optimal, with a reduced plate height, *h*, below 1, and it does not depend on the size of the column. When the flow through the entire cross-section of the column is considered the *h* values are approximately five times higher, indicating a strong wall effect.

On a wide column (diameter 60 mm), measurements were made at the column ends, and also inside the packing at different points on the diameter. It appeared that the residence time did not depend on the radial position, but the variance at a distance of 10 mm from the wall was considerably larger than in the centre of the bed (measured with the detectors in the packing). The contribution of the column ends to the variance is considerable.

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