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The Effects of the Column Pressure Drop on Retention and Efficiency in Packed and Open Tubular Supercritical Fluid Chromatography

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Summary

The effects of the pressure drop across the column on retention and efficiency in SFC have been studied. Numerical methods are described which enable the prediction of hold-up time and pressure drop in both packed and open tubular columns. Predictions of both hold-up time and pressure drop are in good agreement with experimental data.

The density gradient along the column can be calculated using the numerical methods and a procedure is described which enables the calculation of the overall capacity factors of the solutes from the density profile in the column. Significant variations of the capacity factor are observed along the column.

The effect of the density gradient along the column on local diffusivity and dispersion is studied. The column efficiency in systems with significant pressure drops is affected by changes in: the linear velocity of the mobile phase; the diffusion coefficients; and the capacity factors of the solutes along the column. The overall efficiency of the chromatographic system can be calculated if, as is the case for open tubular columns, adequate plate height equations are available.

1 Introduction

Fluid flow through packed and open tubular chromatography columns requires a pressure difference across the column. In general, pressure drops are low if open tubular columns are used; significantly higher pressure drops are encountered with packed columns. Because in supercritical fluid chromatography (SFC) the mobile phase is both a highly compressible and highly non-ideal fluid the pressure drop across the column has a profound effect on the chromatographic process. The solvating and transport properties of supercritical fluids, and thus the chromatographic retention and efficiency, are a function of the pressure.

The effects of variations in pressure have been studied in both high performance liquid chromatography (HLPC) and gas chromatography (GC). In HPLC, because a virtually incompressible mobile phase is used there is no velocity gradient across the column and, futhermore, the capacity factors are almost independent of the operating pressure [1]. Indeed, HPLC columns can be operated at extremely large pressure drops without any adverse effects on system performance. The effects of the column pressure drop on efficiency in GC were first described by *Giddings* [2]. He presented a theoretical study in which it was shown that even severe pressure drops lead to little loss of resolution in GC. The column pressure drop may also influence capacity factors in GC and a small, but measurable, influence of carrier gas pressure has been observed by several authors [3, 4]. For routine GC, however, this effect is not a major source of concern.

SFC can be regarded as a technique intermediate between GC and LC. The pressure dependence of retention is, however, a notable exception to this rule. Whereas capacity factors are almost independent of the pressure in GC and LC, pressure is the key parameter controlling retention in SFC. The influence of a pressure gradient along packed columns on retention and efficiency in SFC has been studied by a number of authors [5–9]. *Schoenmakers* and *Uunk* [8] studied the effects of the column pressure drop in packed column SFC in order to compare the potential applicability of packed and open tubular columns and showed that the performance of packed columns is limited by the maximum allowable pressure drop. It was concluded that plate numbers in excess of 20,000 are not readily obtainable using packed columns. *Mourier et al.* [9] studied the effect of the density drop on the observed plate height. The considerable peak broadening observed was explained by an increase of the capacity factor along the column and the overall magnitude of this effect was shown to be related to the average density of carbon dioxide, the solute retention, and the pressure drop. Recently, *Poe* and *Martire* [10] published a theoretical description of the effect of the pressure drop on efficiency applicable to all forms of chromatography. The results predicted by the theory agreed with the trends generally observed in experiments. No direct comparison with experimental data was, however, given.

In the present work a systematic study of the effects of the column pressure drop on retention and efficiency in SFC is described. Pressure and density gradients across both open tubular and packed columns are calculated using the Darcy equation for laminar flow. A method is described which enables the calculation of the local and the observed capacity factors of solutes in packed and open tubular columns with considerable pressure gradients. The influence of the pressure drop on efficiency and plate height is quantitatively evaluated for open tubular columns. Experimental data are used to verify the validity of the models derived in the theoretical part of the study.

2 Theory

2.1 Pressure Gradient and Hold-Up Time

The flow of incompressible fluids through packed and open tubular columns in chromatography is described by the well known *Darcy* equation:

$$\Delta P = B_0 \cdot \eta \cdot u \cdot L \tag{1}$$

where ΔP is pressure drop across the column, η the fluid viscosity, L the length of the column, and u the superficial linear velocity calculated from the diameter of the empty column. B_0 is the specific permeability coefficient of the column. For open tubular columns B_0 is given by:

$$B_0 = \frac{32}{d_c^2} \tag{2}$$

while for packed columns

$$B_0 = \frac{\varphi_0}{d_p^2} \tag{3}$$

where φ_0 is the column resistance factor and d_c and d_p are the column diameter and the particle size of open tubular and packed columns, respectively. The superficial linear velocity can be calculated from the following expression:

$$u = \frac{4\, F_m}{\pi \cdot \varrho \cdot d_c^2} \tag{4}$$

where F_m is the mass flow rate through the chromatographic column, d_c the diameter of the empty column, and ϱ the density of the fluid. Substitution of eq. (4) into eq. (1) yields:

$$\Delta P = \frac{4\, B_0 \cdot \eta \cdot F_m \cdot L}{\pi \cdot \varrho \cdot d_c^2} \tag{5}$$

Throughout this paper we shall assume isothermal conditions and neglect radial and axial variations in temperature across the column [11]. For compressible media, such as gases or supercritical fluids, the density is a function of the pressure: for a supercritical fluid, moreover, the viscosity may also be affected by pressure changes. For all compressible fluids eq. (5) can be applied only over short segments of the column. If the column is divided into n segments of (equal) length dL, the pressure drop over the ith segment is given by:

$$dP_i = \frac{4\, B_0 \cdot \eta_i \cdot F_m \cdot dL}{\pi \cdot \varrho_i \cdot d_c^2} \tag{6}$$

The subcript i indicates that the values of these parameters pertain to the conditions in the segment i. The appropriate densities must be calculated for every segment from an equation of state and the viscosities from equations describing this property as a function of either pressure and temperature or density and temperature. The total pressure drop over the column can be calculated by integration of eq. (6). Because accurate equations describing the density and the viscosity of carbon dioxide are complex, this integral can only be solved numerically. If the segments are chosen sufficiently small, the total pressure drop over the column can be approximated by:

$$\Delta P_{total} = \sum_{i=1}^{n} \frac{4\, B_0 \cdot \eta_i \cdot F_m \cdot \Delta L}{\pi \cdot \varrho_i \cdot d_c^2} \tag{7}$$

The procedure for solving eq. (7) starts with the numerical calculation of the density of the mobile phase in the first segment,

where the pressure equals the inlet pressure of the column: the density at this pressure is calculated from the IUPAC equation of state [12]. Next the viscosity is taken from tabulated data published by *Stephan* and *Lucas* [13]. The pressure drop across the first segment, ΔP_1, can be calculated from eq. (6). The pressure in the second segment is then calculated by subtracting ΔP_1 from the inlet pressure. Repeating this procedure for all n segments gives the pressure profile over the column and, ultimately, the column outlet pressure (*i.e.* the pressure just prior to the restrictor).

The approach described above enables the calculation of the pressure and density in every segment of the column. From the mass flow rate through the column in combination with the density in a segment, the residence time in that segment can be calculated. The residence time $t_{0,i}$ of an unretained component in segment i is given by:

$$t_{0,i} = \frac{\pi \cdot \Delta L \cdot \varrho_i \cdot d_c^2 \cdot \varepsilon}{4\, F_m} \tag{8}$$

Here ε is the void fraction (porosity) of the column. For open tubular columns ε equals unity. The total hold-up time of the column is given by the summation of the hold-up times in the individual segments:

$$t_{0,i} = \sum_{i=1}^{n} \frac{\pi \cdot \Delta L \cdot \varrho_i \cdot d_c^2 \cdot \varepsilon}{4\, F_m} \tag{9}$$

2.2 Capacity Factors

The residence time of a retained solute in the ith segment is given by:

$$t_{r,i} = t_0\,(1 + k_i) \tag{10}$$

Here k_i is the local capacity factor of the solute in segment i. Summation of the residence times in the n segments yields the elution time of the solute. The observed overall capacity factor can be calculated from:

$$k_{obs} = \frac{\displaystyle\sum_{i=1}^{n} t_{r,i} - \sum_{i=1}^{n} t_{0,i}}{\displaystyle\sum_{i=1}^{n} t_{0,i}} = \frac{\displaystyle\sum_{i=1}^{n} (t_{0,i} \cdot k_i)}{\displaystyle\sum_{i=1}^{n} t_{0,i}} \tag{11}$$

This approach to calculating the observed capacity factor for systems with a significant pressure drop requires knowledge of the capacity factor of a solute as a function of the mobile phase density. Such a function can be established by measuring capacity factors at very low flow rates where the effect of the pressure drop on the capacity factor is negligible. At constant temperature the capacity factors thus obtained can be described accurately by an equation of the form:

$$\ln(k) = a + b \cdot \varrho + c \cdot \varrho^2 \tag{12}$$

Martire has presented a theoretical basis for this expression for adsorption chromatography [14].

2.3 Plate Height and Efficiency

If the length of the segments is chosen sufficiently small, a local plate height can be defined which can be considered constant within a segment. Plate height expressions derived for incompressible fluids can then be used to calculate the band broadening

in every segment. The chromatographic band broadening in segment i, σ_i, is given by:

$$\sigma_i^2 = \frac{H_i \cdot t_{r,i}^2}{\Delta L} \qquad (13)$$

Here H_i is the local plate height. The total observed bandwidth can be obtained by applying the rule of the additivity of variances:

$$\sigma_t^2 = \sum_{i=1}^{n} \sigma_i^2 \qquad (14)$$

where σ_t^2 is the total variance of the peak observed at the column outlet. Evaluation of eqs. (13) and (14) requires knowledge of the individual plate heights and the residence times in each of the segments. Methods for obtaining the residence time of both retained and unretained components have been described above.

Appropriate plate height equations are required to calculate the local plate height in every segment. For capillary columns the well known Golay equation can be used:

$$H_i = \frac{2 \, D_{m,i}}{u_i} + \frac{f(k_i) \cdot d_c^2 \cdot u_i}{96 \, D_{m,i}} \qquad (15)$$

Here $D_{m,i}$ and u_i are the binary diffusion coefficient and the linear velocity in the ith segment, respectively. The function $f(k_i)$ is given by:

$$f(k_i) = \frac{1 + 6 \, k_i + 11 \, k_i^2}{(1 + k_i)^2} \qquad (16)$$

The value for u_i can be calculated from eq. (4). The diffusion coefficient can be estimated from the Wilke and Chang equation [15], which has previously been shown to yield accurate estimates for diffusion coefficients in supercritical carbon dioxide [16]. The equation reads:

$$D_m = 7.4 \times 10^{-8} \, \frac{\sqrt{M_b} \cdot T}{\eta \cdot V_a^{0.6}} \qquad (17)$$

where M_b is the molecular mass of the solvent, T the absolute temperature, η the dynamic viscosity, and V_a the molar volume of the solute at its boiling point. Of these parameters only the viscosity changes along the column. Substitution of η_i in the Wilke and Chang equation yields the diffusion coefficient in segment i. From eqs (4), (12), (16) and (17) the input data for eq. (15) can be calculated. Applying eq. (13) yields the chromatographic band broadening in the individual segments. Summation of these individual contributions according to eq. (14) finally yields the total band width upon elution. The apparent plate number of the column, N_{obs}, is given by:

$$N_{obs} = \frac{\left[\sum_{i=1}^{n} t_{r,i} \right]^2}{\sum_{i=1}^{n} \sigma_i^2} \qquad (18)$$

The overall observed plate height, H_{obs}, is

$$H_{obs} = \frac{L \cdot \sum_{i=1}^{n} \sigma_i^2}{\left[\sum_{i=1}^{n} t_{r,i} \right]^2} \qquad (19)$$

For packed columns there is no exact analytical plate height equation comparable to the Golay equation for open tubular columns. For liquid chromatography several plate height expressions for packed columns have been reported. Schwartz et al. [17] selected the Horvath and Lin equation [18] for use in SFC. Schoenmakers [19] used the Knox equation in a comparative study of the speed of analysis in packed and open tubular SFC. More recently, Poe and Martire [10] discussed the influence of density on the various terms of the Knox and the Horvath and Lin plate height equations. In any case, some empirical coefficients which appear in the plate height equation need to be established in order to use the present procedure for calculating the observed plate height. In the present work we have limited our efficiency studies to open tubular columns.

3 Experimental

All experiments using packed columns were carried out on a home made SFC system which has already been described in detail [6, 20]. The system consisted of a PU 4011 HPLC pump, a PU 4030 controller, a PU 4020 variable wavelength UV detector, and a series 304 GC oven, all from Philips Analytical (Cambridge, UK). The electronics of the pump and controller were modified to enable constant pressure operation. Digital pressure sensors (Model PDCR 610, Druck, Barendrecht, The Netherlands) were installed between the injector and the column and just downstream of the detector: the accuracy of the absolute pressure measurements was better than 0.15 %. Flow was controlled using a standard reducing valve for carbon dioxide (Hoekloos, Amsterdam, The Netherlands). The mass flow rate through the column was measured using a soap bubble flow meter. The signal from the detector was processed on a Philips P3202 personal computer using the PU6000 software package for data processing (Philips Analytical). The column used in the experiments was a RoSil octadecyl-modified reversed phase HPLC column (150 × 4.6 mm, 5 μm particles) obtained from Alltech (Eke, Belgium). Pure carbon dioxide was used as the mobile phase in all experiments (99.8 %, Air Liquide, Eindhoven, The Netherlands). The solutes were ethylbenzene, naphthalene, and biphenyl. Dichloromethane was used as solvent. UV detection was performed at $\lambda = 220$ nm.

Experiments with the open tubular column were performed on a Carlo Erba SFC 3000 instrument (Carlo Erba, Milan, Italy). The column was a 10 m, 50 μm nominal i.d. CP-Sil 5 CB column (Chrompack, Middelburg, The Netherlands). The film thickness was 0.2 μm. The measured inner diameter of the column was 55.2 μm. The coil diameter of the column was 15 cm, which was sufficiently large to neglect disturbances of the laminar flow profile as a result of coiling-induced secondary flow [21]. Samples were injected in the combined timed split–flow split injection mode. The injector was equipped with a 100 nL internal injection loop and was used at room temperature. The injection time was 50 ms. The flow split ratio was approximately 1:40. The test solutes were the normal alkanes docosane, tetracosane, and octacosane dissolved in cyclohexane. Flame ionization detection was used in all experiments. Methane was used as the hold-up time marker. Observed capacity factors ($k = (t_i - t_0) / t_0$) were calculated from the peak maxima. Plate heights were calculated from the second moments of the peaks. Statistical evaluation of the peaks was performed using the peak summary software of the Nelson Analytical (Cupertino, CA, USA) integration system.

3.1 Packed Column Characteristics

Accurate calculations of pressure gradients in packed columns require accurate values for both the column porosity, ε, and the

column resistance factor, φ_0. The porosity was determined by means of the gravimetric method described by Berendsen et al. [22]. In this method the column is separately filled with two fluids of different density and weighed on each occasion. The porosity of the column can then be calculated from the weight difference:

$$\varepsilon = \frac{4 \ (m_1 - m_2)}{\pi(\varrho_1 - \varrho_2) \ d_c^2 L} \qquad (20)$$

where m_1 and m_2 are the total masses of the column filled with the fluids 1 and 2, respectively, and ϱ_1 and ϱ_2 the corresponding fluid densities. From the gravimetric experiments a column porosity of 0.583 was obtained. The porosity determined in this way reflects both the inter- and intraparticle volumes. It was assumed that the pores accessible to the fluids which were used to determine the porosity (methanol and gaseous carbon dioxide) were equally accessible to supercritical carbon dioxide, regardless of the operating pressure.

The column resistance factor φ_0 was calculated from the inlet pressure required to pump a given flow of liquid methanol through the column. The expression for φ_0 reads:

$$\varphi_0 = \frac{\Delta P \ \pi \ d_c^2 \ d_p^2}{4 \cdot \eta \cdot L \cdot F_v} \qquad (21)$$

Here F_v is the volumetric flow rate of liquid through the column. Column permeabilities were calculated at 5 different flow rates resulting in an average permeability of 1088 ($\sigma = 0.9$ %).

4 Results and Discussion

4.1 Fluid Flow Through Packed and Open Tubular Columns

The methods described in Section 2 enable the calculation of the pressure and velocity gradients across both packed and open tubular columns in SFC. Only the outlet pressure and the observed hold-up time are accessible for experimental verification. To verify the calculated hold-up times, a truly unretained solute is needed. Considerable care must be taken to select a solute which is neither retained by the stationary phase nor excluded from the pores of the particles. Several authors reported problems in the determination of the hold-up time in packed-column SFC. Van Wasen [23] could determine the hold-up time for columns packed with particles of large surface area only by extrapolation from data obtained on columns packed with materials of low surface area. Perrut et al. [24] examined several different t_0 markers: hexane, benzene, and carbon tetrachloride were shown to exhibit some degree of retention even at pressures exceeding 200 bar. Following the proposition of Paulaitis, a fluorohydrocarbon (bromotri-fluoromethane) was used as the t_0 marker. This yielded values in good agreement with results calculated via a method similar to that described in Section 2. In recent work we measured the capacity factors of dichloromethane on a number of different columns used for packed column SFC [25]. Only at inlet pressures above approximately 150 bar was dichloromethane approximately unretained (at 45 °C on an ODS column). At lower pressures it was found to be significantly retained. Capacity factors as high as 4 to 5 were observed at pressures around 80 bar.

For determining the hold-up time on the packed column we adopted the method proposed by Springston and Novotny [26]. According to these authors the elution time of a plug of helium can be used as an accurate measure for the hold-up time in SFC.

Figure 1A shows the experimental hold-up times for the packed column measured using the helium plug method plotted against the calculated hold-up times under various experimental conditions. In **Figure 1B** the calculated pressure drops are compared with experimentally observed data. Very good agreement is observed between the calculated and the measured hold-up times under all circumstances. The deviations for the calculated pressure drops are somewhat larger but the data are still fairly accurate.
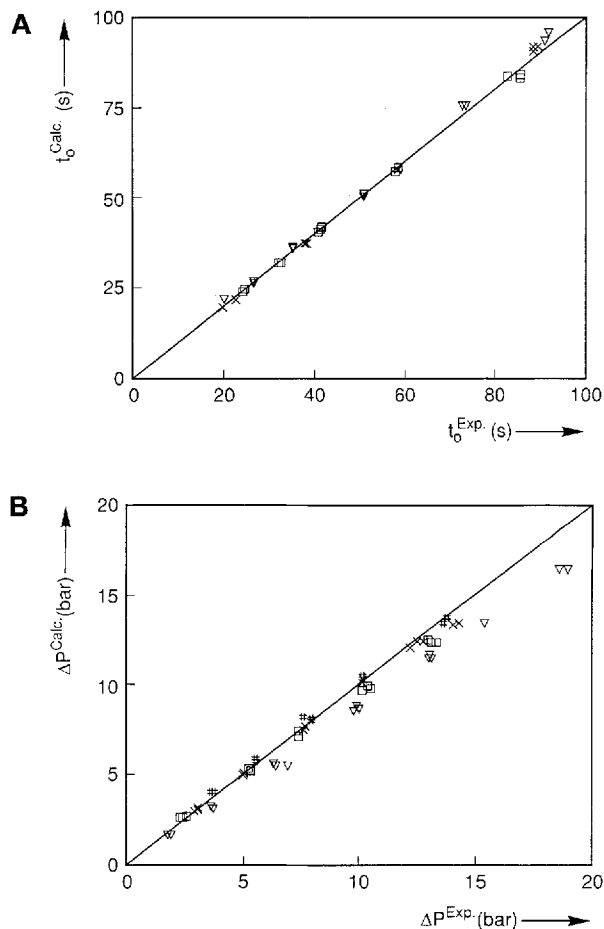

Figure 1

Comparison of the calculated and the experimental hold-up times (A) and pressure drops (B) for the packed (150 × 4.6 mm) column: A ($\triangledown$) **T, 40 °C; P_{in}, 120 bar ($\square$) T, 45 °C; P_{in}, 147 bar; (×) T, 60 °C; P_{in}, 201 bar; B (#) T, 45 °C; P_{in}, 147 bar ($\square$) T, 60 °C; P_{in}, 148 bar; (×) T, 60 °C; P_{in}, 122 bar; ($\triangledown$) T, 60 °C; P_{in}, 215 bar.**

In **Figure 2** the calculated pressure (A) and density profiles (B) across the column at an inlet pressure of 110 bar and a temperature of 50 °C are plotted for three different mass flow rates. As already noted by Schoenmakers [11], the pressure gradients are almost linear whereas the density gradients are slightly convex. Good pressure linearity is preserved even at high flow rates, where considerable expansion takes place along the column. The explanation of this observation is that the ratio of the dynamic viscosity over the density (i.e. the kinematic viscosity) is roughly independent of the column pressure [7]. Only in the direct vicinity of the critical point, or at extremely high pressure drops, can

distinct curvature of the pressure profile be observed. Operating conditions close to the critical point are, however, not attractive for practical operation, so that essentially linear pressure profiles will usually be encountered.
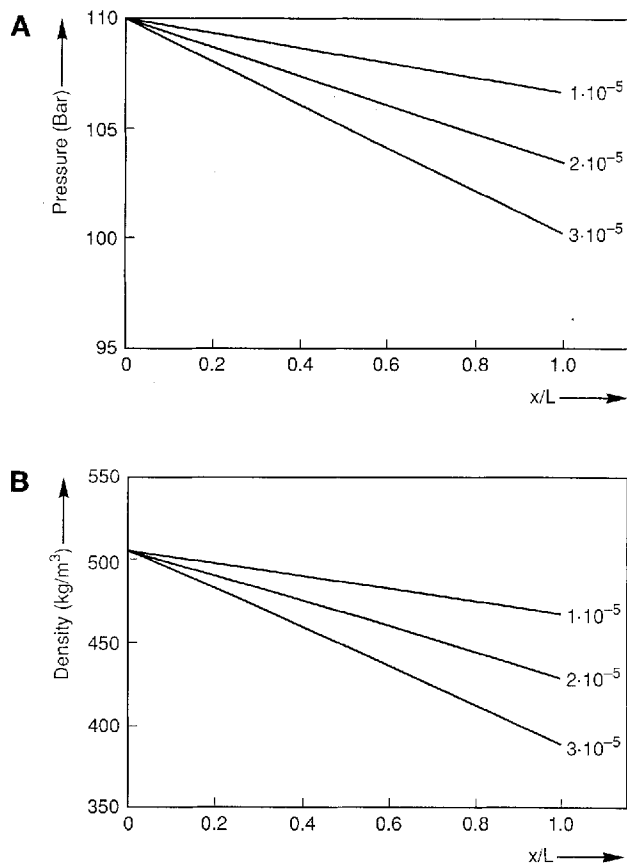
A

B

Figure 2

Pressure (A) and density profiles (B) for packed columns (150 × 4.6 mm) in SFC for various mass flow rates: P_{in}, 110 bar; T, 50 °C; mass flow rates [kg/s] are indicated in the figures; calculated hold-up times were 64, 31, and 20 s, respectively.

4.2 Capacity Factors

Once the density profile along the column is known, the local capacity factors of the solutes can be calculated at every position in the column from an appropriate relationship between the density and capacity factor. Here an expression of the type $\ln k = a + b\varrho + c\varrho^2$ was used to relate the capacity factor to the density. The values of the coefficients a, b and c for the solutes studied on the packed column (at 50 °C) and the open tubular column (70 °C) are given in **Table 1**. The coefficients were determined by measuring the capacity factors of the solutes at various densities. These experiments were performed at very low linear velocities where the effect of the pressure drop on k is negligible. The hold-up times needed for calculating the capacity factors were determined using either helium (packed column) or methane (open tubular column) as the t_0 marker.

In **Figure 3** the local capacity factor is plotted as a function of the dimensionless distance along the packed column at an average velocity of 4 mm/s. The lines in the figure clearly illustrate the increase of the local capacity factor in going from the column inlet

Table 1

Coefficients of the quadratic relationship ($\ln k = a + b\varrho + c\varrho^2$) describing the variation of k with ϱ [g/ml]: Packed column, T = 50 °C; open tubular column, T = 70 °C.

Solute Packed column	a	b	c
Ethylbenzene	5.23	−13.6	7.86
Naphthalene	7.52	−18.0	11.3
Biphenyl	8.81	−21.3	13.7
Open tubular column			
n-docosane	7.87	−22.5	11.2
n-tetracosane	8.90	−24.5	12.3
n-octacosane	12.5	−34.1	19.5

to outlet. For the first eluted component the capacity factor at the column outlet is about 50 % higher than at the inlet. For the last eluted component the capacity factor increases by about 75 %. The increase of the capacity factor along the column is a fundamental problem in SFC which complicates physico-chemical measurements; it also adversely affects the detection characteristics of the chromatographic system. The higher the capacity factor of a solute while eluting, the larger is its elution bandwidth. Hence concentrations in the solute band are lowered, thereby reducing the signal-to-noise ratio.
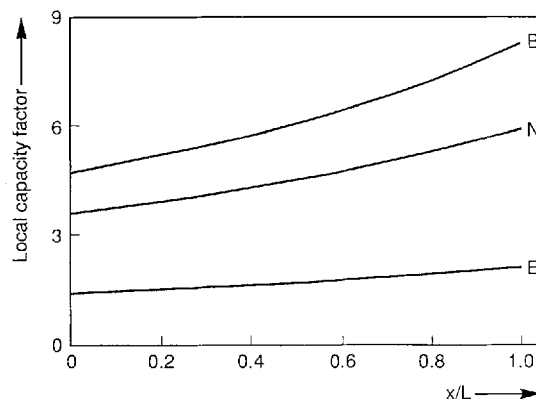

Figure 3

Local capacity factors calculated for the packed column: T, 50 °C; P_{in}, 110 bar; mass flow rate 2 × 10^{-5} kg/s; E, ethylbenzene, N, naphthalene; B, biphenyl.

If the local capacity factors of the solutes and the local linear velocities are known, the elution time of a solute can be calculated. In combination with the calculated hold-up time, it is then possible to predict the observed capacity factor of a solute as a function of the pressure drop. This is illustrated in **Figure 4** for the open tubular column. Under practical operating conditions the pressure drops over open tubular columns with an inner diameter of about 50 μm are very small. In this work we used extremely high flow rates, far beyond practical values, to generate significant pressure drops to test our calculation procedure. Figure 4 shows the calculated and experimental capacity factors of n-octacosane as a function of the average linear velocity in the column. The practical operating range is indicated in the figure. The linear velocities were determined from the elution time of methane. As
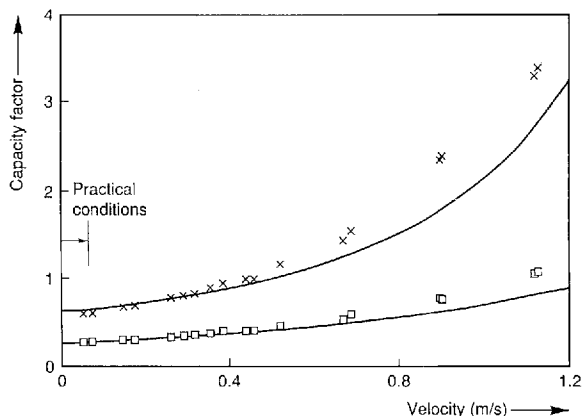
Figure 4

Comparison of calculated and experimental capacity factors as a function of the linear velocity for the open tubular column: T, 70 °C; P_{in}, 165 bar. Experimental data: □, docosane, ×, octacosane. Calculated data: drawn line.

can be seen in the figure, the capacity factor is virtually independent of the linear velocity at low velocities (<5 cm/s). At higher values, the capacity factor increases with the velocity owing to the increasing pressure drop across the column. The agreement between the calculated and the observed capacity factors is fairly good. Slight deviations, however, occur at very high velocities.

Figure 5 shows a representative chromatogram of the separation of docosane, tetracosane, and octacosane normal alkanes at a very high linear velocity (in this chromatogram > 1 m/s). The calculated pressure drop was about 50 bar. As is evident from the figure, good peak shapes are observed even at extremely high velocities.
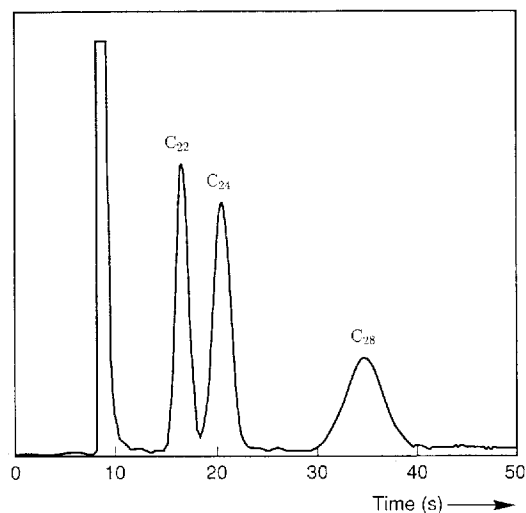

Figure 5

Representative chromatogram obtained at an extremely high linear velocity with the open tubular column: T, 70 °C; P_{in}, 165 bar.

Experiments similar to those described above were also performed on the packed column. In these experiments the capacity factors of ethylbenzene, naphthalene, and biphenyl were measured at 50 °C and an inlet pressure of 110 bar. The capacity factors show a steady increase with increasing pressure drop

across the column. Good agreement was again obtained between the calculated and experimental capacity factors. At pressure drops exceeding 10 bar, however, the peaks became distorted and the experimental capacity factors were much lower than the calculated values. In this pressure range the experimental capacity factors were found to be only slightly affected by a further increase in the pressure drop.

Figure 6 shows a chromatogram obtained at an inlet pressure of 110 bar and an outlet pressure of 93.5 bar. Tailing peaks are observed for all three components and the tailing appears to increase with increasing retention. In **Figure 7** the asymmetry factor (defined as the width of the descending part of the peak divided by the width of ascending part at 10 % of the peak height) is plotted against the pressure drop. A sharp increase in the asymmetry is observed at pressure drops above 10 bar.
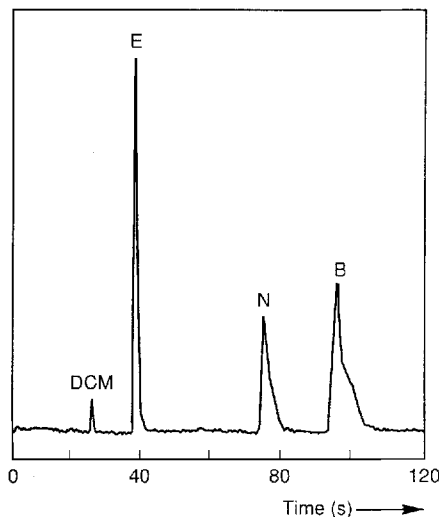

Figure 6

Chromatogram obtained at a high flow rate and low density on the packed column: T, 50 °C; P_{in}, 110 bar; P_{out}, 93.5 bar; DCM, dichloromethane (solvent); E, ethylbenzene; N, naphthalene; B, biphenyl.
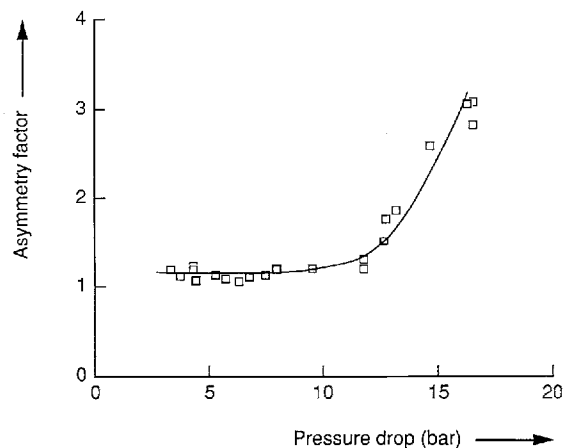

Figure 7

Experimental peak asymmetry on the packed column as a function of the pressure drop: T, 50 °C; P_{in}, 110 bar; solute, biphenyl.

The occurrence of peak tailing when working with large density gradients and, hence, low outlet densities in packed column SFC has been reported by several authors [e.g. 9, 27]. The poor peak shapes are usually attributed to lack of solubility of the sample components in the low density mobile phase at the column exit. This explanation is, however, doubtful in the light of the results presented here. When the separation given in Figure 6 was repeated at an approximately constant, low density throughout the column (inlet pressure: 90.5 bar, outlet pressure: 88.7 bar), symmetrical peaks were obtained. This appears to indicate that the poor shape of the peaks results from a combination of low outlet densities and high linear velocities. Furthermore, if lack of solubility of the components is to blame for the poorly shaped peaks, this means that zones of high concentration would be expected to migrate at a slower migration rate than zones of low concentration. The peak shapes suggest, however, that zones of high concentration travel through the column most rapidly. Also the observation that the capacity factor depends only slightly on the pressure drop cannot be explained by assuming solubility problems in the final part of the column. Finally, we failed to observe asymmetric peaks on the open column, not even at velocities of about 2 m/s with a concomitant pressure drop of over 60 bar. This suggests that the occurrence of poorly shaped peaks when working at large pressure drops is limited to work with packed columns.

4.3 Plate Height and Efficiency

The efficiency observed for packed or open tubular columns is affected by the diffusion coefficient of the solute in the mobile phase and by its capacity factor; the linear velocity, moreover, has a strong influence on the plate height and the efficiency. For open tubular columns the effect of these three parameters on the plate height can be described quantitatively. For packed columns no exact analytical plate-height equation exists, but a number of density-dependent factors are likely to affect the plate height. If a considerable density drop occurs across the column, the three above-mentioned parameters are liable to vary along the column. In **Figure 8** the calculated changes in the linear velocity, the diffusivity, and the capacity factor along an open-tubular column are plotted for the case of a considerable density gradient. In this figure the local plate height is also indicated. All parameters were normalized to a value of unity at the column inlet. As can be seen in the figure, all parameters increase across the column. It is noteworthy that the changes in the velocity and the diffusion coefficient are almost identical. The linear velocity at constant mass flow is inversely proportional to the fluid density, which is apparently also (almost) the case for the diffusion coefficients. This implies that the ratio of the velocity to the diffusivity is almost constant along the column. As can be seen in the plate height equation for open tubular columns (eq. (15)) only the ratio of u over D_m (or D_m over u) is important. This means that the variations of the local plate height along an open column arise mainly from variations in the capacity factors. The effects of increases in the linear velocity and diffusion coefficient on the local plate height effectively cancel.

The observed band width at the column exit can be calculated from the local plate heights in the column, as is demonstrated in Section 2. **Figure 9** shows a comparison of the calculated and the experimental plate heights for the open tubular column as a function of the linear velocity. The agreement between calculated and experimental data is excellent at low velocities, but deviations are observed in the high velocity range. The plate height
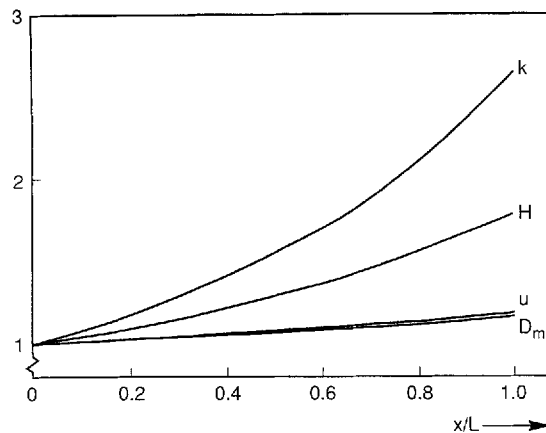

Figure 8

Variation of the local parameters u, D_m k, and H as a function of the dimensionless distance along the column: open tubular column; T, 70 °C; P_{in}, 165 bar; mass flow rate, 6.5 × 10^{-7} kg/s; calculated outlet pressure, 145 bar; calculated (average) linear velocity, 51 cm/s; solute, n-octacosane.
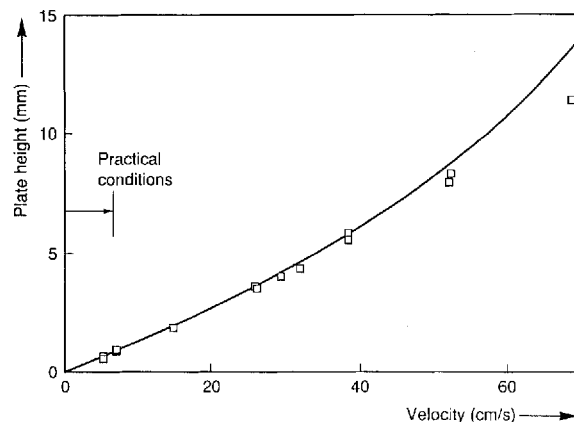

Figure 9

Comparison of the experimental and calculated plate heights as a function of the linear velocity in the open tubular column: T, 70 °C; P_{in}, 165 bar; solute, n-octacosane.

curve is clearly concave, which reflects the increase of the capacity factor at high linear velocities. Although these experiments were carried out in a velocity region which is not of practical interest, the general conclusions obtained here are also applicable to columns with much smaller inner diameters, where significant pressure drops might occur even at practical velocities.

5 Conclusions

1 Retention and efficiency in SFC are affected by the pressure drop across the column. Both effects are accessible to theoretical and experimental investigation.

2 Fluid flow through packed and open tubular columns in SFC can be described accurately by numerical expressions derived from the Darcy equation for laminar flow; pressure or density profiles in SFC columns can be calculated from these expressions.

3 The variation of the capacity factors along both packed and open tubular columns can be modelled accurately by combining density profile data with the appropriate relationships between the capacity factor and the density established at negligible pressure drop. Significant variations of the capacity factor do occur along the column.

4 Packed columns operated with large pressure gradients frequently generate poorly shaped peaks. While the exact cause of this remains to be established, it appears that the poor peak shapes cannot simply be related to a lack of solubility in the low density mobile phase at the column outlet.

5 The local plate height along SFC columns varies as a result of changes in the linear velocity, diffusion coefficients, and local capacity factors. The effect of the increased linear velocity is effectively compensated by an increase in diffusion coefficients. Changes in the local plate height are, therefore, mainly caused by variations in capacity factors.

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