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# Compressibility Effects in Packed and Open Tubular Gas and Supercritical Fluid Chromatography

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## Key Words:

SFC Pressure drop

Efficiency

Compressibility effects

Analysis time

## Summary

**The influence of the pressure drop on the efficiency and speed of analysis in packed and open tubular supercritical fluid chromatography (SFC) is described: methods previously developed to describe the effects of mobile phase compressibility on the performance of open tubular columns in SFC have been extended to packed columns.**

**The Horvath and Lin equation has been used to elucidate the influence of variations in velocity, diffusivity, and capacity factor along the column on the overall efficiency of packed column SFC. In packed columns, in contrast with the situation in open tubular columns, because the increase in velocity is no longer compensated by an increase in diffusion coefficients, the increase in both linear velocity and capacity factor which result from a significant pressure drop cause the plate height to increase along the column.**

**The effect of fluid decompression along the length of the column on the speed of analysis in SFC has been studied and numerical expressions derived which enable calculation of compressibility correction factors for the plate height. Both the  $f_1$  and  $f_2$  correction factors remain very close to unity for acceptable pressure drops, which means that the pressure drop has virtually no effect on the number of plates generated per unit time for an unretained component. For retained species, the decompression of the mobile phase across the column causes the capacity factor to increase and hence leads to increased analysis times.**

## 1 Introduction

The various forms of chromatography have in common the use of a mobile phase which carries the analytes through the column. A pressure difference across the column is required to maintain the flow of mobile phase: such pressure drops are generally low if open tubular columns are used, whereas significantly higher pressure drops are encountered with packed columns. Pressure, and hence pressure drop, is of utmost importance in supercritical fluid chromatography (SFC) because the mobile phase is both highly compressible and a highly non-ideal fluid. In many respects, SFC is a technique intermediate between GC and LC. The influence of pressure on the chromatographic process, however, reaches an extreme when the mobile phase is a supercritical fluid. Because of the high compressibility, all properties of supercritical fluids are very strong functions of pressure (and temperature).

The effects of pressure on retention have been studied in both HPLC and GC. Although the mobile phase in LC is generally considered to be incompressible, it was shown by McGuffin and Evans [1] that the local pressure can have a significant effect upon solute retention. In that study the observed influence of pressure on retention was shown to correlate well with the unified theoretical model proposed by Martire [2].

The effects of the column pressure drop on retention in GC have been studied by a number of authors [3, 4]. As in LC, pressure in GC was shown to have a small, but measurable influence on retention. The effects of gas compressibility on efficiency and plate height in GC were first described by Giddings [5]; he and James and Martin [6] introduced the  $f_1$  and  $f_2$  pressure drop correction factors to account for the effect of fluid compressibility on the plate height in GC.

The influence of the pressure gradient along packed columns in SFC has been the subject of numerous studies [e.g. 7–12]. Poe and Martire published a unified theoretical study into the effect of the pressure drop on efficiency [12]: their predictions were well in agreement with the trends generally observed in experiments. No direct comparison with experimental data was, however, given.

We recently presented numerical methods which enable the prediction of pressure gradients along packed and open tubular columns in SFC [13]: the hold-up times and pressure drops predicted were in excellent agreement with experimental data. These methods could also be used to calculate the variation of the density, the diffusivity, and the local capacity factor and plate height along the length of the column.

In this work the effect of mobile phase compressibility on the performance of packed and open tubular columns in SFC is discussed. Compressibility effects in GC are briefly discussed for reasons of comparison. The influence of fluid decompression along the length of the column on the speed of analysis in SFC is also studied. Numerical methods are described which enable the calculation of compressibility correction factors, similar to the  $f_1$  and  $f_2$  factors in GC, for use in SFC.

## 2 Theory

### 2.1 Numerical Plate Height Calculations for Compressible Fluids

In previous work we have described methods of calculating the variation of pressure, density, velocity, capacity factors, and diffusion coefficients along packed or open tubular columns in

SFC [13]. The following equation was derived for the pressure gradient along the length of the column:

$$P(l) = P_{in} - \int_0^l \frac{4 \cdot B_0 \cdot \eta(l) \cdot F_m}{\pi \cdot \varrho(l) \cdot d_c^2} dl \quad (1)$$

where  $P(l)$ ,  $\eta(l)$ , and  $\varrho(l)$  are, respectively, the pressure, viscosity, and the density at position  $l$ ,  $P_{in}$  is the inlet pressure,  $F_m$  the column mass flow rate,  $d_c$  the column diameter,  $L$  the column length, and  $B_0$  the specific permeability coefficient of the column. For open tubular columns  $B_0$  is given by  $32/d_c^2$  whereas for packed columns  $B_0$  equals  $\varphi_0/d_p^2$ , where  $\varphi_0$  is the column resistance parameter and  $d_p$  is the particle size for packed columns.

Because accurate equations describing the density and viscosity of carbon dioxide as a function of pressure are extremely complex, the integral in eq. (1) can only be solved numerically by dividing the column into  $n$  segments of equal length  $\Delta L$ . If the segments chosen are sufficiently small, eq. (1) can be rewritten:

$$P_j = P_{in} - \sum_{i=1}^{j-1} \frac{4 \cdot B_0 \cdot \eta_i \cdot F_m \cdot \Delta L}{\pi \cdot \varrho_i \cdot d_c^2} \quad (2)$$

Where  $P_j$  is the pressure in segment  $j$ . The subscripts  $i$  indicate that the value of these parameters pertain to the conditions in segment  $i$ . The pressure at any point in the column can be calculated from this equation, and the variation in density along the length of the column can thus be calculated by substituting the pressure data in an appropriate equation of state (e.g. the IUPAC equation [14]).

Because of the decrease of the density along the column, the linear velocity increases. The linear velocity in segment  $i$  is given by:

$$u_i = \frac{4 \cdot F_m}{\pi \cdot \varrho_i \cdot d_c^2 \cdot \varepsilon} \quad (3)$$

where  $\varepsilon$  is the void fraction of the column (porosity). For open tubular columns  $\varepsilon$  equals unity. The residence time in segment  $i$  is now given by:

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

The local capacity factor in segment  $i$  can be obtained by substituting  $\varrho_i$  in an equation relating  $k$  to  $\varrho$ . The capacity factor is, in general, accurately described by an equation of the form:

$$\ln(k_i) = a + b \cdot \varrho_i + c \cdot \varrho_i^2 \quad (5)$$

where  $a$ ,  $b$ , and  $c$  are constants which must be established experimentally. The residence time of a retained solute in the  $i$ th segment,  $t_{r,i}$ , is now given by:

$$t_{r,i} = t_{0,i} \cdot (1 + k_i) \quad (6)$$

The variation of the diffusion coefficient along the length of the column can be estimated using the Wilke and Chang equation [15]:

$$D_{m,i} = 7.4 \cdot 10^{-8} \cdot \frac{\sqrt{M_b} \cdot T}{\eta_i \cdot V_a^{0.6}} \quad (7)$$

Where  $M_b$  is the molecular mass of the solvent,  $T$  the absolute temperature, and  $V_a$  the molar volume of the solute at its boiling point [cm<sup>3</sup>/mole].

In previous work we described the effects of variations in  $k$ ,  $u$ , and  $D_m$  on the plate height in open tubular columns for SFC [13]. For this type of column, the well known Golay equation can be used to calculate the local plate height in every segment:

$$H_i = \frac{2 \cdot D_{m,i}}{u_i} + \frac{(1 + 6k_i + 11k_i^2) \cdot d_c^2 \cdot u_i}{96 \cdot (1 + k) \cdot D_{m,i}} \quad (8)$$

In this expression the contribution of the stationary phase to band broadening is neglected. The values of the input parameters can be calculated from eqs (3), (5), and (7). From eq. (8) it is apparent that the plate height observed in open tubular columns is affected by the diffusion coefficient of the solute in the mobile phase and by its capacity factor. Changes in the linear velocity will, furthermore, affect the plate height. From the studies presented previously, two important conclusions could be drawn: (i) the ratio of  $u$  to  $D_m$  is almost constant along the column, and (ii) the variation of the local plate height along an open tubular column is mainly a result of variations in the capacity factor. In earlier studies we limited our efficiency studies to open tubular columns. In this work the plate height studies are extended to packed columns.

Several expressions [e.g. 16–19] have been proposed for calculating the plate height of packed columns in liquid chromatography, where the mobile phase is incompressible. All these equations contain empirical coefficients which must be established experimentally. Using the approach we described in previous publications, these equations, which were originally derived for incompressible fluids, can be used in packed column SFC where the mobile phase is highly compressible. Here we opted for the use of the Horvath and Lin equation [19], which, for use in SFC, can be simplified to [20]:

$$H_i = \frac{2\gamma D_{m,i}}{u_i} + \frac{2\lambda d_p u_i^{1/3}}{u_i^{1/3} + \omega(D_{m,i}/d_p)^{1/3}} + \frac{2k_i^2 u_i}{(1 + \psi)(1 + k_i)^2 \beta k_a} \quad (9)$$

where  $\gamma$ ,  $\lambda$ ,  $\omega$ ,  $\psi$ , and  $\beta$  are column constants,  $u_i$  is the interstitial mobile phase velocity, and  $k_a$  is the rate constant for adsorption. The subscripts  $i$  again indicate that the values of these parameters pertain to the conditions in segment  $i$ . For a solute with a capacity factor above approximately unity the third term on the right hand side of eq. (9) is the prevalent term. This term expresses the contribution of slow adsorption/desorption kinetics to the overall plate height.

If we assume the Horvath and Lin equation to be valid, it can be concluded that variations in the local plate height along a packed column can arise from variations in the diffusion coefficient, linear velocity, and capacity factor of the solute. This is similar to the situation in open tubular columns. In the first term of the simplified Horvath and Lin equation (eq. (9)), the increase in  $D_m$  is effectively cancelled by an increase in  $u_i$  and also the second term remains (almost) constant along the column because variations in  $u_i$  are again outweighed by changes in  $D_m$ .

The first two terms do not contain the capacity factor and so are unaffected by the increase in  $k$  along the column. For the last term the situation is more complicated. Because the increase in  $u_i$  is no longer compensated by an increase in  $D_m$ , this term increases along the column owing to the increase in the linear velocity. In addition, because the third term of the simplified Horvath and Lin equation is capacity factor-dependent, if there is a significant

pressure drop across the column the increase in the capacity factor will cause an increase of the plate height along the column. This increase can be especially significant for capacity factors below 5.

In conclusion, the local plate height along a packed column in SFC will increase because of the increasing value of the kinetic resistance term. Two parameters affect the increase of this term, the increase in the linear velocity and the increase of the capacity factor. In most circumstances, the second effect will be predominant. Eqs (8) and (9) give expressions for the local plate heights in open tubular and packed columns, respectively. The overall plate height,  $H_{obs}$ , is then given by:

$$H_{obs} = \frac{L \cdot \sum_{i=1}^n H_i \cdot t_{r,i}^2}{\Delta L \cdot \left[ \sum_{i=1}^n t_{r,i} \right]^2} \quad (10)$$

## 2.2 Compressibility Effects in Gas and Supercritical Fluid Chromatography

### 2.2.1 Gas Chromatography

In gas chromatography the speed of analysis is significantly affected by the pressure drop along the column. The relationship between analysis time, pressure gradient, and column i.d. has been extensively studied by *Schutjes* [21]: in that study it was shown that if the pressure drop across the column is negligible, the analysis time in GC is proportional to the square of the column diameter. Because of the adverse effects of the pressure drop, when it is large (e.g. when long and/or low i.d. columns are used) the analysis time no longer remains proportional to  $d_c^2$ , but simply to  $d_c$ . According to *Schutjes* the relationship between analysis time and column diameter is given by

$$t_r = \frac{(1 + 6k + 11k^2) \cdot N \cdot d_c^2}{48 \cdot (1 + k) \cdot D_m} \cdot \frac{f_1}{f_2} \quad (11)$$

where

$$f_1 = \frac{9}{8} \cdot \frac{(P_R^4 - 1)(P_R^2 - 1)}{(P_R^3 - 1)^2} \quad (12)$$

and

$$f_2 = \frac{3}{2} \cdot \frac{(P_R^2 - 1)}{(P_R^3 - 1)} \quad (13)$$

$f_1$  and  $f_2$  are pressure drop correction factors which take into account the volumetric expansion of the gas along the length of the column.  $P_R$  is the ratio of the column inlet pressure to that at the outlet.

When the pressure drop is zero,  $f_1/f_2 = 1$ , otherwise the analysis time increases by a factor  $f_1/f_2$  in comparison with the hypothetical case in which pressure drop is absent. Substitution of eqs (12) and (13) into eq. (11) gives

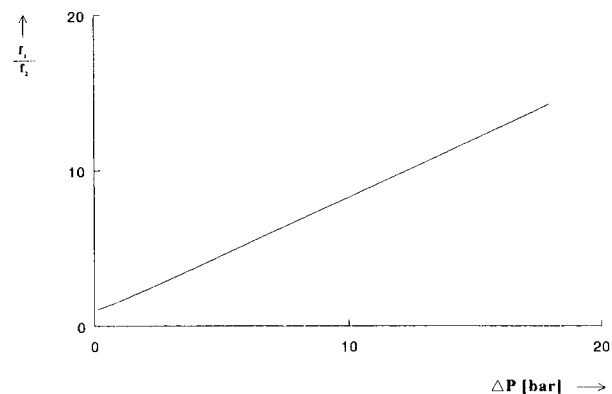
$$t_r = \frac{(1 + 6k + 11k^2) \cdot N \cdot d_c^2}{48 \cdot (1 + k) \cdot D_m} \cdot \frac{3(P_R^4 - 1)}{4(P_R^3 - 1)} \quad (14)$$

The optimum inlet pressure of a capillary GC column,  $P_{R,opt}$ , is given by

$$P_{R,opt} = \sqrt{\frac{256 \cdot D_{m,0} \cdot \eta \cdot N \cdot f_1}{\rho_o \cdot d_c^2} + 1} \quad (15)$$

where  $p_o$  is the outlet pressure (usually 100 kPa) [21]. By substituting eq. (15) into eq. (14) the relationship between analysis time and column diameter can be evaluated. Because of their complexity, these equations cannot be solved analytically: only numerical evaluation is possible.

The influence of the pressure drop on the speed of analysis is illustrated in **Figure 1**, in which the ratio [true analysis time] :



**Figure 1**

**Calculated influence of the pressure drop on the speed of analysis in capillary GC. Input data for calculation:**  
 $D_m = 2 \cdot 10^{-5} \text{ m}^2/\text{s}$ ,  $\eta = 2 \cdot 10^{-5} \text{ kg}/(\text{m}\cdot\text{s})$ ,  $k = 3$ , and  $N = 10^5$ .

[analysis time for the hypothetical situation in which there is no pressure drop] (i.e. the value of the ratio  $f_1/f_2$ ) is plotted against the pressure drop across the column.

For a 50  $\mu\text{m}$  i.d. column, for example, the true analysis time is ca three times longer than under the hypothetical conditions of zero pressure drop. Despite the inherently higher pressure drop, however, narrow-bore columns are still significantly faster than columns with larger inner diameters.

### 2.2.2 Supercritical Fluid Chromatography

In SFC, the interrelationship between analysis time, column diameter, and pressure drop is even more complicated than in GC. In contrast with the situation in gas chromatography, the pressure drop in SFC will affect the capacity factor of the solutes, and this will also influence the analysis time. The latter effect has to be included in a thorough study of the relationship between column diameter, pressure drop, and analysis time in SFC.

From this it is clear that two effects influence the analysis time in SFC systems with a significant pressure drop: (i) fluid compressibility effects, which, as in GC, can be taken into account by introduction of appropriate compressibility correction factors, and (ii) the capacity factor increase. In GC the latter effect is absent because the capacity factor is virtually pressure independent. In SFC, it is not possible to derive exact analytical expressions which describe  $f_1$  and  $f_2$  as a function of the pressure drop or the ratio of the inlet and outlet pressures. The values of these factors can, however, be calculated numerically, as will be shown below.

#### $f_1$ Correction Factor

The  $f_1$  correction factor relates the overall observed plate height,  $H_{obs}$ , to the local plate height,  $H_i$ , i.e. the plate height at a certain position in the column [22]:

$$H_{obs} = f_1 \cdot H_i \quad (16)$$

In order that an expression for  $f_1$  may be derived, it is a prerequisite that the local plate height,  $H_i$ , should not vary along the column. For  $H_i$  to be constant, two demands must be met: (i) the ratio of  $D_m$  to  $u$  must be constant along the column, and (ii) the capacity factor must be constant throughout the column. The first demand is valid for ideal gases and, to a rough approximation, for supercritical fluids also [13]. The second demand can **never** be true in SFC except for unretained species. Pressure is the key parameter controlling retention in SFC. The requirement that  $k$  be independent of pressure conflicts with the basic principles of SFC.

Although the  $f_1$  factor is thus of limited practical importance for SFC, it can be used to gain some insight into the effects of the volume expansion along an SFC column on the observed plate height. An expression for the  $f_1$  factor in SFC will be derived below.

Substituting eq. (10) into eq. (6) and transformation yields

$$f_1 = \frac{L \cdot \sum_{i=1}^n t_{r,i}^2}{\Delta L \cdot \left[ \sum_{i=1}^n t_{r,i} \right]^2} \quad (17)$$

Expressed in terms of the velocities in the various segments this becomes:

$$f_1 = \frac{L \cdot \sum_{i=1}^n \left( \frac{1}{u_i} \right)^2}{\Delta L \cdot \left( \sum_{i=1}^n \frac{1}{u_i} \right)^2} \quad (18)$$

or in the analytical form:

$$f_1 = \frac{L \cdot \int_0^L \frac{1}{u^2} dl}{\left( \int_0^L \frac{1}{u_i} dl \right)^2} \quad (19)$$

where  $l$  is the position along the column and varies between 0 at the column inlet to  $L$  at the outlet. Evaluation of the  $f_1$  factor requires knowledge of the entire velocity gradient across the column.

To get an impression of the order of magnitude of the  $f_1$  factor, a simple relationship for the linear velocity profile can be substituted into eq. (19). In earlier work [13], the density gradient across the column was shown to be almost linear, and this leads to the following expression for the linear velocity,  $u_i$ , as a function of the position along the column:

$$u_i = \frac{\varrho_0 \cdot u_0 \cdot L}{\varrho_0 \cdot L - (\varrho_0 - \varrho_L) \cdot l} \quad (20)$$

In this equation the subscripts refer to the position along the column (0 = inlet,  $L$  = outlet). Substitution of eq. (20) into eq. (19) and subsequent integration yields, after some (tedious) algebra:

$$f_1 = \frac{4 \cdot (\varrho_0 \varrho_L + \varrho_0^2 + \varrho_L^2)}{3 \cdot (2\varrho_0 \varrho_L + \varrho_0^2 + \varrho_L^2)} \quad (21)$$

From this equation the value of the  $f_1$  factor can be calculated as a

function of the fractional density loss across the column,  $v$ , which can be defined as:

$$v = \frac{\varrho_0}{\varrho_L} \quad (22)$$

Note that  $v$  is very similar to  $P_R$ , =  $P_{in}/P_{out}$ , in GC. Both parameters reflect the ratio of the density at the inlet to that at the outlet. Introduction of this equation into eq. (21) yields, for the  $f_1$  factor:

$$f_1 = \frac{4 \cdot (1 + v + v^2)}{3 \cdot (1 + 2v + v^2)} \quad (23)$$

### $f_2$ Correction Factor

The  $f_2$  correction factor relates the velocity at the column outlet to the experimentally more readily measurable average velocity. Numerically, the  $f_2$  factor is readily expressed as

$$f_2 = \frac{L}{\sum_{i=1}^n t_i} \bigg/ \frac{\Delta L}{t_n} = \frac{n \cdot t_n}{\sum_{i=1}^n t_i} \quad (24)$$

or, in terms of the linear velocities in the segments,

$$f_2 = \frac{n}{u_n \cdot \sum_{i=1}^n \frac{1}{u_i}} \quad (25)$$

or, in the analytical form,

$$f_2 = \frac{L}{u_L \cdot \int_0^L \frac{1}{u_i} dl} \quad (26)$$

If we again assume that the density profile in the column is linear, eq. (20) can be substituted into the above equation. After integration, this gives

$$f_2 = \frac{2 \cdot \varrho_0 \cdot u_0}{(\varrho_0 + \varrho_L) \cdot u_L} \quad (27)$$

Realizing that:

$$\frac{u_0}{u_L} = \frac{\varrho_L}{\varrho_0} \quad (28)$$

We finally find, for the  $f_2$  factor:

$$f_2 = \frac{2}{1 + v} \quad (29)$$

Where  $v$  is, again, the fractional loss of density.

## 3 Results and Discussion

From the expressions for the  $f_1$  and  $f_2$  compressibility correction factors it is possible to calculate the influence on the plate height of the decompression of the fluid along the column, although it should be emphasized that these equations do not take into account the effect on the plate height of the capacity factor increase along the length of the column, an effect which can only be calculated numerically, as will be shown below. A plot of the  $f_1$  and  $f_2$  factors against  $v$  is presented in **Figure 2**.

It is difficult to define a limit for the maximum allowable density drop in SFC: good separations can be obtained even with pressure drops of almost 200 bar [23] (although very high inlet pressures, far beyond the limits of current instrumentation, are then required to elute high molecular weight solutes with capacity factors in the optimum range). A density drop of 20% ( $\nu = 1.2$ ) appears to be a reasonable estimate for the maximum permissible density drop under average practical conditions and it can, therefore, be concluded from Figure 2 that the  $f_1$  and  $f_2$  factors are both always very close to unity. This implies that the expansion of the fluid along the column length does not cause a significant increase of the observed plate height.

It is interesting to compare the value of  $\nu$  with typical values for  $P_R$  in GC. The decompression effect in SFC is extremely low when compared with the situation in GC. Routine GC columns (25 m, 320  $\mu\text{m}$  i.d.) are typically operated at a column head pressure of

about 1.5 bar, which means that  $P_R$  already equals 1.5. For narrow bore GC columns of, for example, ca 10 meter length and 50  $\mu\text{m}$  i.d. this increases to about 25. Under vacuum outlet conditions in GC,  $P_{\text{in}}/P_{\text{out}}$  can easily be as large as  $10^5$ .

In conclusion, some volume compressibility effects occur in supercritical media. In general, however, it seems that the behavior of supercritical media closely resembles that of incompressible media: under practical conditions, only small errors are introduced by neglecting the compressibility of the fluid. At this point it should be emphasized that the compressibility correction factors, as discussed above, correct only for the velocity gradient which occurs along the length of the column: the increase of the capacity factor that occurs as a result of the decreasing density should be treated separately. It will be shown below that the increase of the capacity factors along the column can seriously influence the speed of analysis in SFC.

Table 1

**Calculated column length ( $L$ ), analysis time ( $t$ ), and pressure drop ( $\Delta P$ ) required to generate 100000 plates for an unretained component in columns of different i.d. Conditions: pure carbon dioxide;  $T = 70^\circ\text{C}$ ;  $P_{\text{in}} = 160$  bar; molar volume for  $D_m$  calculations,  $644$   $\text{cm}^3/\text{mole}$ ;  $F_m =$  mass flow rate.**

Column i.d. 100 $\mu\text{m}$						
Velocity	$F_m$ [kg/s]	$L$ [m]	$t$ [s]	$\Delta P$ [bar]	$f_1$	$f_2$
$u_{\text{opt}}$	$5.03 \cdot 10^{-9}$	2.89	3111	0.00	1.00000	1.000
$2u_{\text{opt}}$	$1.01 \cdot 10^{-8}$	3.61	1944	0.01	1.00000	1.000
$3u_{\text{opt}}$	$1.51 \cdot 10^{-8}$	4.81	1727	0.02	1.00000	1.000
$5u_{\text{opt}}$	$2.52 \cdot 10^{-8}$	7.54	1620	0.06	1.00000	1.000
$10u_{\text{opt}}$	$5.03 \cdot 10^{-8}$	14.56	1570	0.22	1.00000	1.000
Column i.d. 50 $\mu\text{m}$						
Velocity	$F_m$ [kg/s]	$L$ [m]	$t$ [s]	$\Delta P$ [bar]	$f_1$	$f_2$
$u_{\text{opt}}$	$2.52 \cdot 10^{-9}$	1.46	789	0.02	1.00000	1.000
$2u_{\text{opt}}$	$5.03 \cdot 10^{-9}$	1.81	486	0.05	1.00000	1.000
$3u_{\text{opt}}$	$7.55 \cdot 10^{-9}$	2.40	432	0.09	1.00000	1.000
$5u_{\text{opt}}$	$1.26 \cdot 10^{-8}$	3.72	404	0.23	1.00000	0.999
$10u_{\text{opt}}$	$2.52 \cdot 10^{-8}$	7.26	392	0.89	1.00000	0.997
Column i.d. 25 $\mu\text{m}$						
Velocity	$F_m$ [kg/s]	$L$ [m]	$t$ [s]	$\Delta P$ [bar]	$f_1$	$f_2$
$u_{\text{opt}}$	$1.26 \cdot 10^{-9}$	0.772	195	0.07	1.00000	1.000
$2u_{\text{opt}}$	$2.52 \cdot 10^{-9}$	0.905	122	0.18	1.00000	1.000
$3u_{\text{opt}}$	$3.77 \cdot 10^{-9}$	1.20	108	0.35	1.00000	1.000
$5u_{\text{opt}}$	$6.29 \cdot 10^{-9}$	1.87	101	0.92	1.00000	0.997
$10u_{\text{opt}}$	$1.26 \cdot 10^{-8}$	3.62	97.4	3.55	1.00001	0.992
Column i.d. 10 $\mu\text{m}$						
Velocity	$F_m$ [kg/s]	$L$ [m]	$t$ [s]	$\Delta P$ [bar]	$f_1$	$f_2$
$u_{\text{opt}}$	$5.03 \cdot 10^{-10}$	0.289	30.3	0.45	1.00000	1.000
$2u_{\text{opt}}$	$1.01 \cdot 10^{-9}$	0.364	19.3	1.14	1.00000	1.000
$3u_{\text{opt}}$	$1.51 \cdot 10^{-9}$	0.486	17.1	2.26	1.00000	0.999
$5u_{\text{opt}}$	$2.52 \cdot 10^{-9}$	0.756	15.9	5.87	1.00003	0.991
$10u_{\text{opt}}$	$5.03 \cdot 10^{-9}$	1.45	14.8	22.31	1.00058	0.958

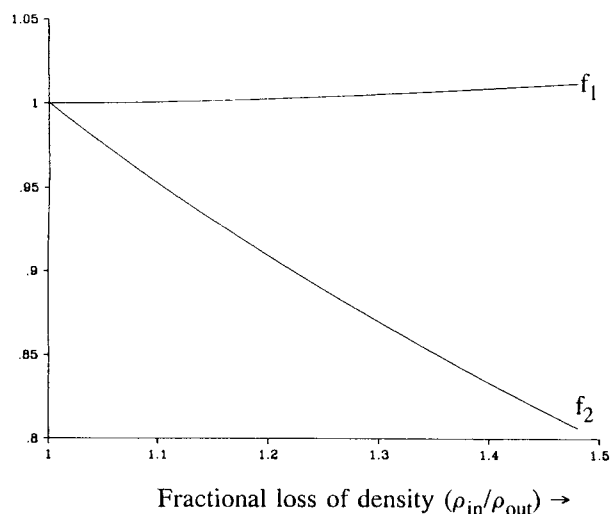


Figure 2

Compressibility correction factors  $f_1$  and  $f_2$  as a function of the fractional loss of density in open tubular SFC with a linear density gradient.

### 3.1 Speed of Analysis in Open Tubular SFC

The influence of the pressure drop on the speed of analysis in gas chromatography is accurately described by eq. (11). Here the parameters  $f_1$  and  $f_2$  account for the influence of the pressure drop on the total analysis time. It is clear that eq. (11) cannot be applied to SFC because in the latter not only are  $f_1$  and  $f_2$  a function of the pressure drop, but also the capacity factor  $k$ . Efficiencies and analysis times in SFC can be calculated by means of the numerical procedures described in the first part of Section 2; here we will first consider an unretained component. For such a component the pressure drop across the column affects the efficiency only via the  $f_1$  and  $f_2$  correction factors. **Table 1** lists the calculated column lengths, analysis times, and the pressure drops required to generate 100000 plates for an unretained component at various mass flow rates for open tubular columns of 100, 50, 25, and 10  $\mu\text{m}$  i.d. The lowest mass flow rate represents the minimum in the curve of  $H$  against  $u$  (for a solute with  $k = 0$ ). The values of the  $f_1$  and  $f_2$  factors are also given in the table.

A number of interesting conclusions can be drawn from this table. It can be concluded that columns with lower inner diameters yield shorter analysis times, but only at the expense of an increased pressure drop. It is, furthermore, apparent that operating the columns at velocities above the optimum increases the analysis speed, but again at the expense of an increasing pressure drop. It is also apparent from the table that the effects of the pressure drop

on the plate height are very small: because  $f_1$  and  $f_2$  are very close to unity under all conditions, the plate height is virtually unaffected by compressibility effects.

The deviation of the  $f_1$  factor is below the significance limit of the calculations. The  $f_2$  factor shows a value significantly different from unity only under extreme conditions (10  $\mu\text{m}$  column at 5 or 10 times  $u_{\text{opt}}$ ).

In conclusion, it can be stated that fluid compressibility is unlikely to form a major obstacle in open tubular SFC. Even with 10  $\mu\text{m}$  i.d. columns, compressibility effects are negligible, unless the column is operated extremely far above the optimum.

It is interesting to compare analysis times in the different columns. A summary of these is given in **Table 2** from which it is apparent that the analysis time decreases in proportion to  $d_c^2$ , which is also true for open tubular LC, and GC with low pressure drops [24].

The conclusions given above are valid for unretained components only. For retained species, account must be taken of the possible increase in the capacity factor along the length of the column. This leads to an increase in the analysis time and, if the capacity factor is below approximately 5, to an increase in the plate height also. Both effects will be more pronounced for narrower columns or operation at higher linear velocities.

A series of calculations similar to those summarized in Table 1 were performed in order to investigate the effect of the column pressure drop on the analysis time for retained species. The test component for these calculations was  $n\text{-C}_{28}$ . The coefficients for the relationship between the capacity factor and the density (eq. (5)) were taken from reference 13.

The results of the calculations are shown in **Table 3**. In the first series of calculations the capacity factor was fixed at 0.708, which was the value under column inlet conditions. This means that in these calculations the effect of compressibility on the plate height is included, whereas the effect of the increasing capacity factor was not considered. In such circumstances, the pressure drop affects the plate height only, via the  $f_1$  and  $f_2$  factors. As was already concluded from Table 1 these effects are negligible. The column lengths and mass flow rates from Table 1 were used in the calculations, so that all columns yielded 100000 plates for an unretained component. The calculations were again performed at the optimum mass flow rate ( $k = 0$ ) and at 2, 3, 5 and 10 times the optimum flow. All the calculations neglected the contribution of the stationary phase to band broadening.

In the second series of calculations the variation of the capacity factor along the length of the column was also taken into account. As is apparent from Table 3, the capacity factor increases considerably, especially for small i.d. columns and operation far

Table 2

Analysis time (at  $u_{\text{opt}}$ ) required to generate 100000 plates for an unretained component in open tubular columns with different inner diameters. Conditions as for Table 1.

Column diameter [ $\mu\text{m}$ ]	Analysis time [s]	Relative time	$1/d_c^2$ (normalized)
100	3111	1.00	1.00
50	789	0.25	0.25
25	195	0.063	0.0625
10	30.3	0.0097	0.010

above the optimum velocity. The column on the extreme right of Table 3 represents the ratio of the analysis time calculated taking the capacity factor increase into account to that when it was ignored. The results illustrate that for standard columns (i.d. 50  $\mu\text{m}$ ) the effect of the increasing capacity factor on retention time and plate number is marginal. Only at velocities way above  $u_{\text{opt}}$  do the effects of the increase in capacity factor become

visible. For 25 and 10  $\mu\text{m}$  i.d. columns the effect of the increase of the capacity factor along the column is significant: because of the increase of the capacity factor and the concomitant reduction in the plate number, the analysis time is no longer proportional to  $d_c^2$ . It is interesting to note that for the 10  $\mu\text{m}$  column the effects of pressure drop on retention time and plate number become visible at the optimum velocity, although only at higher velocities are the

**Table 3**  
Influence of the pressure drop on the chromatographic parameters of retained components in open tubular SFC. Conditions: pure carbon dioxide;  $T = 70^\circ\text{C}$ ;  $P_{\text{in}} = 160 \text{ bar}$ ;  $\rho_{\text{in}} = 0.549 \text{ g/mL}$ ; solute,  $\text{C}_{28}$ ; molar volume for  $D_m$  calculations,  $644 \text{ cm}^3/\text{mole}$ ;  $F_m =$  mass flow rate (Table 1);  $k_{\text{obs}} =$  observed capacity factor.

Column i.d. 100 $\mu\text{m}$							
Conditions		k fixed at 0.708		k variation included			Relative time
Velocity	L [m]	$t_r^{\text{fix}}$ [s]	$N^{\text{fix}}$ [ $\times 10^4$ ]	$k_{\text{obs}}$	$t_r^{\text{incl.}}$ [s]	$N^{\text{incl.}}$ [ $\times 10^4$ ]	$\frac{t_r^{\text{incl.}} \cdot N^{\text{fix}}}{t_r^{\text{fix}} \cdot N^{\text{incl.}}}$
$u_{\text{opt}}$	2.89	$4.25 \cdot 10^3$	4.28	0.708	$4.25 \cdot 10^3$	4.28	1.00
$2u_{\text{opt}}$	3.61	$2.66 \cdot 10^3$	3.19	0.708	$2.66 \cdot 10^3$	3.19	1.00
$3u_{\text{opt}}$	4.81	$2.38 \cdot 10^3$	2.96	0.708	$2.38 \cdot 10^3$	2.96	1.00
$5u_{\text{opt}}$	7.54	$2.22 \cdot 10^3$	2.81	0.709	$2.22 \cdot 10^3$	2.81	1.00
$10u_{\text{opt}}$	14.56	$2.14 \cdot 10^3$	2.73	0.711	$2.14 \cdot 10^3$	2.72	1.00

Column i.d. 50 $\mu\text{m}$							
Conditions		k fixed at 0.708		k variation included			Relative time
Velocity	L [m]	$t_r^{\text{fix}}$ [s]	$N^{\text{fix}}$ [ $\times 10^4$ ]	$k_{\text{obs}}$	$t_r^{\text{incl.}}$ [s]	$N^{\text{incl.}}$ [ $\times 10^4$ ]	$\frac{t_r^{\text{incl.}} \cdot N^{\text{fix}}}{t_r^{\text{fix}} \cdot N^{\text{incl.}}}$
$u_{\text{opt}}$	1.46	$1.06 \cdot 10^3$	4.28	0.708	$1.06 \cdot 10^3$	4.28	1.00
$2u_{\text{opt}}$	1.81	$6.59 \cdot 10^2$	3.19	0.708	$6.59 \cdot 10^2$	3.19	1.00
$3u_{\text{opt}}$	2.40	$5.90 \cdot 10^2$	2.96	0.709	$5.91 \cdot 10^2$	2.95	1.00
$5u_{\text{opt}}$	3.72	$5.50 \cdot 10^2$	2.81	0.712	$5.51 \cdot 10^2$	2.80	1.01
$10u_{\text{opt}}$	7.26	$5.33 \cdot 10^2$	2.73	0.723	$5.38 \cdot 10^2$	2.69	1.02

Column i.d. 25 $\mu\text{m}$							
Conditions		k fixed at 0.708		k variation included			Relative time
Velocity	L [m]	$t_r^{\text{fix}}$ [s]	$N^{\text{fix}}$ [ $\times 10^4$ ]	$k_{\text{obs}}$	$t_r^{\text{incl.}}$ [s]	$N^{\text{incl.}}$ [ $\times 10^4$ ]	$\frac{t_r^{\text{incl.}} \cdot N^{\text{fix}}}{t_r^{\text{fix}} \cdot N^{\text{incl.}}}$
$u_{\text{opt}}$	0.772	$2.56 \cdot 10^2$	4.28	0.709	$2.56 \cdot 10^2$	4.28	1.00
$2u_{\text{opt}}$	0.905	$1.67 \cdot 10^2$	3.19	0.711	$1.67 \cdot 10^2$	3.19	1.00
$3u_{\text{opt}}$	1.20	$1.46 \cdot 10^2$	2.96	0.714	$1.47 \cdot 10^2$	2.95	1.01
$5u_{\text{opt}}$	1.87	$1.37 \cdot 10^2$	2.81	0.724	$1.39 \cdot 10^2$	2.77	1.03
$10u_{\text{opt}}$	3.62	$1.32 \cdot 10^2$	2.73	0.775	$1.38 \cdot 10^2$	2.59	1.10

Column i.d. 10 $\mu\text{m}$							
Conditions		k fixed at 0.708		k variation included			Relative time
Velocity	L [m]	$t_r^{\text{fix}}$ [s]	$N^{\text{fix}}$ [ $\times 10^4$ ]	$k_{\text{obs}}$	$t_r^{\text{incl.}}$ [s]	$N^{\text{incl.}}$ [ $\times 10^4$ ]	$\frac{t_r^{\text{incl.}} \cdot N^{\text{fix}}}{t_r^{\text{fix}} \cdot N^{\text{incl.}}}$
$u_{\text{opt}}$	0.289	42.3	4.28	0.715	42.4	4.26	1.01
$2u_{\text{opt}}$	0.364	26.5	3.19	0.727	26.8	3.14	1.03
$3u_{\text{opt}}$	0.468	23.4	2.96	0.748	23.9	2.86	1.06
$5u_{\text{opt}}$	0.756	21.6	2.81	0.824	23.1	2.57	1.17
$10u_{\text{opt}}$	1.45	19.7	2.73	1.55	29.4	1.60	2.55



effects really significant. For columns with larger inner diameters the effect of pressure drop on performance is negligible if velocities are not too far above the optimum. From this it can be concluded that the use of open tubular columns in SFC is limited to those with i.d. > ca 10  $\mu\text{m}$ . For lower i.d. columns it may not be possible to realise the optimum performance owing to the adverse effects of the pressure drop.

It should be emphasized that the minimum allowable column diameter calculated above can be dependent on the operating conditions. Because of the complex interdependence of pressure, density, retention, and plate height it is dangerous to assume the this value is generally applicable: when other experimental conditions are considered, it is, therefore, necessary to repeat the calculations in order to obtain an accurate estimate of the minimum allowable diameter under those specific conditions. A minimum diameter of 10  $\mu\text{m}$  appears to be a reasonable estimate under normal operating conditions.

Because of the combined effect of the pressure drop and the compressibility of supercritical fluids, a density gradient is created along the column. In chromatographic terms this means that there is a negative "solvent strength" gradient along that column. At the column entrance the local capacity factor of a solute, and hence its plate height, is relatively low. At the exit, the capacity factor and the plate height are higher. This can be looked upon as a gradual shift in the column performance from more efficient (lower plate height) at the column entrance, to less efficient (higher plate height) at the exit. This gradual transition

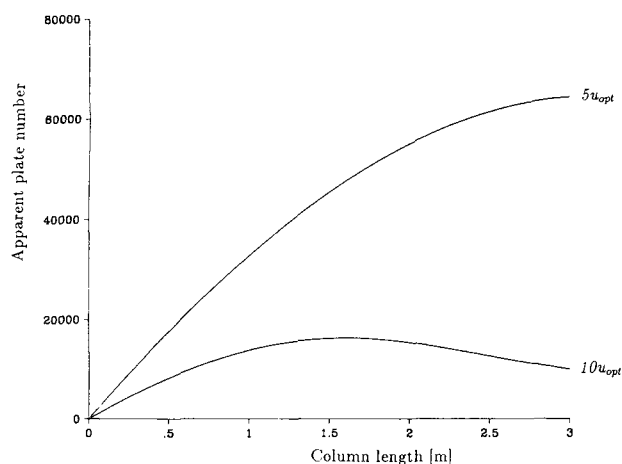


Figure 3

Calculated apparent plate numbers as a function of the column length for a 10  $\mu\text{m}$  open tubular column in SFC.  $5u_{\text{opt}} = 2.52 \cdot 10^{-9}$  kg/s,  $10u_{\text{opt}} = 5.03 \cdot 10^{-9}$  kg/s. The calculated pressure drops over a 3 m column were 23 bar and 48 bar at  $u = 5u_{\text{opt}}$  and  $10u_{\text{opt}}$ , respectively. Further conditions as in Table 3.

has important consequences for the apparent plate number of the column: because of the "downstream deterioration" of the column, the apparent plate number might eventually decrease with increasing column length.

This is illustrated in Figure 3, which shows the calculated apparent plate number as a function of the distance along the column. The data were calculated for a 10  $\mu\text{m}$  column at flows of five and ten times the optimum ( $5u_{\text{opt}}$  and  $10u_{\text{opt}}$ , respectively;

Table 3). All other conditions were as in Table 3. At  $5u_{\text{opt}}$  the plate number increases monotonously with increasing length. At  $10u_{\text{opt}}$  the apparent overall plate number at first increases with increasing column length, up to column lengths of ca 1.5 m, but above this length the plate count starts to decrease owing to the large increase in the capacity factor. Thus for column lengths exceeding 1.5 m the surprising conclusion is that the plate number of a longer column is lower than that of a shorter, but otherwise similar, column.

For packed columns the conclusions are completely analogous to those drawn above for open tubular columns. For very small particles, the detrimental effect of the column pressure drop might begin at low velocities, which would mean that it would not be possible to realise the optimum performance of the system because of the pressure drop. This has been observed experimentally by Schoenmakers and Uunk [10]. From their results they concluded that there was a minimum particle size which can be used in packed column SFC: for operation at low densities the minimum size was about 8 to 10  $\mu\text{m}$ ; under other conditions slightly smaller particles could be used. Under conditions typically applied in packed column SFC, 5  $\mu\text{m}$  appears to be a reasonable lower limit. The influence of the particle size on the performance of packed columns in SFC will be the subject of future research.

## 4 Conclusion

The local plate height along SFC columns varies owing to changes in the linear velocity, the diffusion coefficient, and the local capacity factor. In open tubular columns, the effect of the increased linear velocity is effectively compensated by an increase in diffusion coefficients and as a result, changes in the local plate height arise mainly from variations in the capacity factors. In packed columns, the increase in both linear velocity and capacity factor cause the plate height to increase along the column.

The numerical methods described herein enable the calculation of compressibility correction factors for the plate height equation in open tubular SFC: if certain assumptions are made, mathematical equations for the correction factors can be derived; in most cases, unfortunately, only numerical evaluation is possible. Both  $f_1$  and  $f_2$  remain very close to unity for acceptable pressure drops.

The effect of  $f_1$  and  $f_2$  on the speed of analysis in SFC is negligible. As in open tubular LC and GC with low pressure drops, the analysis speed for unretained components is proportional to  $d_c^2$ . When the pressure drop is significant, the analysis time of retained species increases because of an increase in the capacity factor and the concomitant increase in the plate height. Because of this, the minimum i.d. which can be used in open tubular SFC is about 10  $\mu\text{m}$ ; for packed columns the minimum particle size is about 5  $\mu\text{m}$ . For smaller i.d. columns or smaller particle sizes it may not be possible to realise the optimum performance of the column owing to the adverse effects of the pressure drop.

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