Possibilities and limitations of coiling induced secondary flow in capillary supercritical fluid chromatography

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Possibilities and Limitations of Coiling Induced Secondary Flow in Capillary Supercritical Fluid Chromatography

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Key Words:
Supercritical fluid chromatography, SFC
Speed of analysis
Secondary flow
Pressure drop

Summary
The possibility of enhancing radial mass transfer in capillary SFC by tightly coiling the column is discussed. The influence of coiling-induced secondary flow on the plate height and the speed of analysis in capillary SFC is investigated. It is shown that the experimental plate height in tightly coiled metal or fused silica columns departs from the Goay theory for laminar flow. The effect of the pressure drop associated with the use of higher mobile phase linear velocities is studied. The capacity factors of retained components are used as sensitive probes for pressure drop over the column. Experimental plate heights in coiled columns are compared with values calculated from Tijssen's theory for coiling induced secondary flow. At low velocities a good quantitative agreement was observed between the theory and the experimental results. At intermediate velocities only a qualitative agreement is found. The speed of analysis in coiled columns was found to be up to 5 times higher than in straight capillaries. The largest gain in analysis speed was obtained for solutes with low capacity factors. It is shown that coiling the column can have a positive influence on the detectability. For tightly coiled 210 μm i.d. columns the advantages of coiling-induced secondary flow could be fully exploited without adverse effects of the column pressure drop. For 50 μm columns the possibility to increase the speed of analysis by coiling was limited due to the high pressure drop.

1 Introduction

The intermediate position of Supercritical Fluid Chromatography (SFC) between Gas Chromatography (GC) and Liquid Chromatography (LC) is inter alia reflected in the choice of the column type. Whereas LC is almost exclusively performed using packed columns and GC with capillary columns, both packed and capillary columns are routinely used in SFC. Within respect to the speed of analysis in SPC, packed columns are superior to contemporary open capillaries. Capillary columns are favorable when high plate numbers are necessary [1, 2]. Plate numbers exceeding approximately 20,000 are generally not readily obtainable using packed columns, because the length of the column is limited by the maximum allowable pressure drop [3].

To obtain reasonable analysis times in capillary SFC, columns with inner diameters in the range of 50 μm to 100 μm are used far above the optimum velocity. Even with these narrow-bore columns the number of plates generated per second is considerably lower than that obtained in GC with standard-bore columns (e.g. 320 μm). The use of columns with inner diameters lower than 100 μm poses severe requirements on the instrumentation. Besides these technical problems, the use of narrow-bore columns is severely hindered by the low sample capacity of these columns. The dynamic range, being the concentration region between the minimum detectable amount and the maximum sample capacity is too low for many practical applications. Either columns with larger sample capacities or more sensitive detectors are required to enlarge the dynamic range. As stated before capillary columns in SFC are generally operated far above the optimum linear velocity. In this case, the only contribution to chromatographic band broadening for an unretained component is the contribution of the velocity profile. The velocity profile under normal operating conditions is parabolic. The mobile phase velocity close to the wall approaches zero and reaches a maximum at the center of the column. Solute bands moving through the column are broadened because the solute molecules near the column wall have a lower effective velocity than the molecules in the center of the column. Solute molecules can only change locations within the velocity profile by radial diffusion. If the time required for radial mass transport between the fluid layers with the different velocities is relatively long compared to the residence time in the column, a considerable broadening of the solute bands takes place.

Several methods have been proposed to obtain velocity profiles which are more favorable with regard to radial transport of solutes in capillary columns. The use of turbulent flow in gas chromatography has been reported by several authors [4–6]. With turbulent flow the velocity profile is largely flattened thereby reducing flow inequalities across the column radius. Furthermore, radial mass transfer is enhanced by the introduction of a radial velocity component. Another approach to change the velocity profile is to coil the column in a tight helix. This introduces a secondary flow perpendicular to the column axis. Fluid flow in coiled columns was first described by Dean who gave approximate expressions for the velocity profile in coiled open tubes [7]. Tijssen et al. [8–11] have published a series of articles describing the effects of secondary flow in helically coiled columns or both GC and LC.

Novotny et al. [12, 13] demonstrated the effect of coiling in capillary LC and SFC. The advantageous effects of secondary flow have also been demonstrated in post-column reaction systems for LC [14, 15] and in flow injection analysis [16].

In this work we will systematically study the effects of coiling induced secondary flow on the plate height and the speed of analysis in capillary SFC. A recently developed system for flow rate variation in capillary SFC is used for the convenient measurement of plate height curves [19]. The influence of the coil diameter on the plate height is studied. Experimental plate heights in coiled columns are compared with values calculated from Tijssen’s theory for coiling induced secondary flow. The effects of the pressure drop associated with the use of high mobile phase linear velocities are investigated.

2 Theory

The plate height in straight, open-tubular columns for SFC under the conditions of laminar flow is described accurately by the well-known Golay plate-height equation.

\[
H = \frac{2 \cdot D_m}{\overline{u}} + 2 \times R^2 \frac{f(k)}{D_m} \overline{u} + \frac{2 \cdot k \cdot q^2}{3 (1 + k)^2} \overline{u} \tag{1}
\]

with:

\[
f(k) = 1 + 6k + 11k^2
\]

Here \(H\) is the plate height, \(\overline{u}\) is the average linear velocity, \(D_m\) and \(D_s\) are the diffusion coefficients in the mobile phase and the stationary phase, respectively. \(R_c\) is the column radius. \(\lambda\) is the so-called velocity profile factor which is 1/48 for straight columns. In case of zero pressure drop the average velocity \(\overline{u}\) can be replaced by the symbol \(u\). If we neglect the stationary phase contribution to chromatographic band broadening and if we work at velocities far above the optimum, eq. (1) can be rewritten as:

\[
H = \frac{2 \times R^2 f(k) u}{D_m} \tag{2}
\]

The speed of analysis \(N_t\) can now be expressed as:

\[
N_t = \frac{u}{H} = \frac{D_m}{2 \times R^2 f(k)} \tag{3}
\]

Here \(N_t\) represents the number of plates that is generated per second. From eq. (3), two approaches towards higher analysis speeds and hence reduced analysis times become apparent. A common approach is the reduction of the column inner diameter (e.g. 17, 18). Columns with lower inner diameters give more plates per unit time. The second approach is based on enhancing the radial transport of solutes in the column, by increasing \(D_m\) and \(\lambda\).

When a parabolic flow in a capillary column is forced to bend, the central stream parts are subjected to great centrifugal forces and will hence be forced to the outer wall. This generates a secondary flow perpendicular to the main flow and augments radial dispersion. In this case, radial dispersion is the combined effect of molecular diffusion and convection by the secondary flow. The radial dispersion coefficient \(D_r\) is now given by:

\[
D_r = D_m + D_s \tag{4}
\]

where \(D_m\) is the molecular diffusion coefficient and \(D_s\) is the secondary flow dispersion coefficient. At low linear velocities, the centrifugal forces are weak and no significant contribution to radial diffusion occurs by the convective flow. At intermediate velocities the velocity profile changes when the secondary flow starts to develop. The secondary flow tends to divide the main flow into two equal halves. Roughly stated, the column can be looked upon as consisting of two equal parallel columns where diffusion distances are halved and the \(C_r\)-term contribution to the plate height (see eq. (1) and (2)) is reduced by a factor 4. Eq. (2) can be rewritten to take into account the enhanced radial mass transport. The modified plate height equation reads:

\[
H = \frac{2 \times R^2 f(k) u}{D_t} \tag{5}
\]

In case of tightly coiled columns, the velocity profile factor \(\lambda\) and the radial dispersion coefficient \(D_r\) depend on the velocity. Also the function \(f(k)\) depends on the velocity.

According to basic flow theory, the values of \(\lambda\) and \(D_r\) mainly depend on the velocity parameter De\(Sc\). Here De (Dean number) and Sc (Schmidt number) are dimensionless numbers defined as:

\[
De = Re \cdot \sqrt{\lambda} \tag{6}
\]

where \(Re\) is the dimensionless Reynolds number defined as:

\[
Re = \frac{\rho \cdot u \cdot 2R_c}{\eta} \tag{7}
\]

with \(\rho =\) mobile phase density, \(u = \) the linear velocity, \(R_c = \) column radius and \(\eta = \) dynamic viscosity. The parameter \(\lambda\) is the aspect ratio, being the ratio of the column radius and the coil radius:

\[
\lambda = \frac{R_c}{D_{coli}} \tag{8}
\]

The Schmidt number \(Sc\) is defined as:

\[
Sc = \frac{\eta}{\rho \cdot D_m} \tag{9}
\]

Tijssen [10] gave qualitative and quantitative descriptions of the plate height and the radial dispersion in coiled columns as a function of the De\(Sc\) number. Qualitatively, 4 regions were distinguished. At low mobile phase velocities \((DeSc < 10)\) secondary flow does not contribute significantly to radial dispersion. The plate height equals that of a straight column. At \(DeSc > 10\) secondary flow starts to develop and is fully developed at \(DeSc > 10^4\). In the latter case the plate height reaches a kind of plateau. At still higher velocities, the plate height drops approximately linearly with the velocity and largely reduced plate heights in comparison with straight columns can be obtained.

In a quantitative theoretical study, Tijssen [11] derived mathematical expressions for the plate heights and the radial dispersion coefficients in coiled columns as a function of the \(DeSc\) number. A number of expressions and their regions of applicability are given in Table 1. Eqs. (I) to (III) cover the experimental region in the present study on capillary SFC. The expressions given in this table were derived for gaseous and liquid mobile phases. One of the intentions of the present work is to test the applicability of this set of expressions to chromatographic systems using supercritical fluids as the mobile phase. It follows from these expressions that a significantly enhanced radial mass transfer can be obtained in coiled columns. For instance according
Table 1
Mathematical expressions and their regions of applicability for the plate height in coiled columns according to Tijssen [11].

<table>
<thead>
<tr>
<th>Plate height equation</th>
<th>Application range</th>
</tr>
</thead>
<tbody>
<tr>
<td>I. ( H = \frac{R_u \cdot u \cdot f(k)}{24 \cdot D_m} )</td>
<td>( \text{De}^2 \text{Sc} = 0 )</td>
</tr>
<tr>
<td>II. ( H = \frac{R_u \cdot u \cdot f(k)}{24 \cdot D_m} \cdot \frac{1}{1 + \frac{\text{De}^2 \text{Sc}}{542}} )</td>
<td>( \text{De}^2 \text{Sc} &lt; 3 \times 10^3 )</td>
</tr>
<tr>
<td>III. ( H = \frac{R_u \cdot u \cdot f(k)}{24 \cdot D_m} \cdot \frac{1}{6.39} )</td>
<td>( \text{De}^2 \text{Sc} &gt; 2300 )</td>
</tr>
<tr>
<td>IV. ( H = \frac{2.84 \cdot R_u \cdot f(k)}{\text{De}^{0.4} \cdot \text{Sc}^{0.13}} )</td>
<td>( 3 &lt; \text{De} &lt; 17 )</td>
</tr>
<tr>
<td>V. ( H = \frac{666.67 \cdot R_u \cdot f(k)}{\text{De}^{0.05} \cdot \text{Sc}^{0.14}} )</td>
<td>( \text{De} &gt; 100 )</td>
</tr>
</tbody>
</table>

Retention in SFC strongly depends on the mobile phase pressure or density. Under normal operating conditions in capillary SFC, the column pressure drop is negligible. The pressure drop in coiled columns under secondary flow conditions, however, might be larger because some additional pressure drop is required for the secondary flow. According to Tijssen, this additional pressure drop is generally small and does not cause serious problems in LC. In SFC, however, an additional significant pressure drop could result in increased capacity factors. The capacity factors of the test solutes provide a sensitive probe for pressure drop. In this case the capacity factors of the solutes will no longer be independent from the linear velocity, because the pressure drop is higher for the higher velocities.

3 Experimental

All experiments were performed on a home-built SFC instrument. The mobile phase delivery system consists of a Varian 8500 syringe pump (Varian Associates, Walnut Creek, CA, USA) modified to allow constant pressure operation. Sample introduction was accomplished at ambient temperature using a pneumatically actuated sample valve (model A-3-Ni4W, VICI AG, Schenkon, Switzerland). The injection valve was equipped with a 60 nL rotor and was used in the combined timed-split/flow-split mode. A Varian 3300 Gas Chromatograph was used to provide temperature control and flame ionization detection. A system previously developed for flow rate control in pressure programmed capillary SFC was used to vary the linear velocity in the column at a fixed pressure and temperature. The system allows variation of the linear velocity without replacement of the restrictor [19]. The set-up for flow rate variation is based on column-effluent splitting in a low dead volume T-piece at the column exit just before detection. The column flow was split into two streams. One stream is fed to the FID, and the second is used to control the total mass flow through the column. Flow rate control through the second branch was accomplished by regulating a back pressure of carbon dioxide supplied by a second Varian 8500 pump also modified for constant pressure operation. The mobile phase used in the experiments was 99.996 % carbon dioxide (Intermar B.V., Breda, The Netherlands). The experiments were carried out on uncoated and coated stainless steel capillary columns of 10 m x 210 \( \mu \)m i.d. and on a 10 m x 50 \( \mu \)m fused silica column coated with CP-sil 5 CB (phase ratio: 250). In the first series of experiments an uncoated stainless steel column was used which was subsequently coated dynamically with an approximately 0.1 \( \mu \)m film of cross-linked octadecene. The columns were coiled around metal rods with various diameters. Cyclohexane and the normal alkanes C\(_{22}\), C\(_{24}\), and C\(_{26}\) were used as the test solutes. Cyclohexane was injected as vapor. The other solutes were injected dissolved in cyclohexane. Plate heights were calculated from the second moments of the peaks. Statistical evaluation of the peak was performed using the peak summary software of the Nelson Analytical integration system (Nelson Analytical, Cupertino, CA, USA).

4 Results and Discussion

In Figure 1 the variation of the plate height with the linear velocity is illustrated for an uncoated 210 \( \mu \)m i.d. stainless steel capillary column coiled around a 1.05 cm rod (aspect ratio \( \lambda = 1/48 \)).

The solid line gives the theoretical plate height calculated according to the Golay plate height equation for straight columns. A binary diffusion coefficient of \( 4.1 \times 10^{-8} \text{ m}^2/\text{s} \) was used in the calculation of this line [19]. In the figure it is seen that the experimental plate height closely follows the Golay equation up to linear velocities of 5 cm/s (\( \text{De}^2 \text{Sc} = 300 \)). Up to here the coiled column cannot be distinguished from a straight column. Beyond this point a rather abrupt departure from the Golay equation occurs. The slope of the plate height curve decreases. This transition point indicates the onset of coiling induced secondary

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Figure 1
Plate height curve for a coiled column. The solid line was calculated using the Golay equation for straight columns. Column diameter: 210 μm (uncoated). Coil diameter: 1.05 cm. Test solute: Cyclohexane. Conditions: \( P = 154 \text{ bar}, T = 120 \, ^\circ \text{C} \).

Figure 2
Influence of the coil diameter on the plate height in coiled columns. Coil diameters: \( \square = 10.5 \text{ mm}, \, x = 4 \text{ mm}, \, \uparrow = 1.6 \text{ mm} \). \( \lambda = 1/48, 1/19, \) and \( 1/8 \), respectively. Further experimental conditions as in Figure 1.

Flow. At velocities exceeding 5 cm/s the slope of the plate height curve decreases which indicates an increased radial dispersion. The influence of the coil diameter on the plate height for cyclohexane is illustrated in Figure 2. Different coil diameters were obtained by coiling the column around metal rods with various diameters. In order to avoid dead volume effects due to reinstallation, the coil diameter was changed without disconnecting the column from the injector and from the T-piece at the column exit.

From Figure 2, two interesting conclusions can be drawn. First, the onset of coiling-induced secondary flow appears to occur at lower linear velocities if the column is coiled to give a lower coil diameter. Secondly, the slope of the line of the experimental plate height versus the linear velocity appears to be lower when using lower coil diameters. For the column with the lowest coil diameter the experimental plate height at a linear velocity of 28 cm/s was reduced by a factor 4 in comparison with a straight column.

In Figure 3 the consequences of coiling the column on the speed of analysis are illustrated. In this figure the number of plates generated per second is plotted as a function of the linear velocity for a coiled and a straight column. The test solute was cyclohexane.
The value of the radial dispersion coefficient $D_r$ is mainly determined by the value of the velocity parameter $De^2Sc$. Janssen [20] and Akiyama et al. [21] proposed plotting the ratio of the experimental plate height over the theoretical plate height vs. the velocity parameter $De^2Sc$. A single curve should then be obtained regardless of the column diameter, the aspect ratio, the density or the diffusivity. In Figure 4, the results from Figure 2 are replotted to give a plot of $H_{exp}/H_{theory}$ vs. $De^2Sc$.

As can be seen from Figure 4, the proposition of Janssen and Akiyama appears to be correct, although some spread in the data is seen to occur. The drawn lines give the theoretical values calculated from the equations derived by Tijssen (eq. (II) and (III) from Table 1). In the low $De^2Sc$ range ($De^2Sc < 5 \times 10^2$), a reasonable fit could be obtained by changing the numerical constant from eq. (II) into 3500. It was already anticipated by Tijssen that the numerical constants in the equations might require fitting to the experimental results. Eq. (III) predicts a constant deviation from the Golay equation for $De^2Sc > 2300$. The data in Figure 4 indeed show the tendency to level off to a constant value, about a factor 5 or 6 below the plate height calculated from the Golay equation. More experiments at higher values for the velocity parameter, however, are necessary to draw sound conclusions.

Figure 4 provides a good guideline for the calculation of the influence of coating-induced secondary flow on the efficiency in a given chromatographic set-up. For the velocity parameter we can write:

$$De^2Sc = \frac{\varphi u^2 R_m^2}{\eta R_{coli} D_m}$$

(14)

After substitution of the appropriate values for the various parameters, the gain in efficiency due to the coating can be obtained from Figure 4. From eq. (14) it can be seen that the effects of coating-induced secondary flow are most pronounced when working at high densities, i.e. close to the liquid region. Apart from the direct influence of $\varphi$ on the velocity parameter, the density also has an indirect influence via the diffusion coefficient. At high densities, the binary diffusion coefficients in the mobile phase are low which also leads to high $De^2Sc$ values. Higher

<table>
<thead>
<tr>
<th>Length diam.</th>
<th>Plate number</th>
<th>Anal. time</th>
<th>Peak width</th>
<th>Volum. flow rate</th>
<th>$Q_{in}^m$</th>
<th>$C_{in}^m$</th>
<th>$Q_{in}'$</th>
<th>$C_{in}'$</th>
</tr>
</thead>
<tbody>
<tr>
<td>L</td>
<td>d</td>
<td>straight</td>
<td>$N$</td>
<td>t</td>
<td>$\sigma$</td>
<td>$W_0$</td>
<td>$C_0$</td>
<td>$W_0'$</td>
</tr>
<tr>
<td>L</td>
<td>d</td>
<td>coiled</td>
<td>$4N$</td>
<td>t</td>
<td>$\sigma/2$</td>
<td>$W_0/2$</td>
<td>$C_0$</td>
<td>$W_0/2'$</td>
</tr>
<tr>
<td>L/4</td>
<td>d</td>
<td>coiled</td>
<td>$N$</td>
<td>$t/4$</td>
<td>$\sigma/4$</td>
<td>$W_0/4$</td>
<td>$C_0$</td>
<td>$W_0/4'$</td>
</tr>
<tr>
<td>L/4</td>
<td>d/2</td>
<td>straight</td>
<td>$N$</td>
<td>$t/4$</td>
<td>$\sigma/4$</td>
<td>$F/4$</td>
<td>$W_0/4$</td>
<td>$C_0'$</td>
</tr>
</tbody>
</table>

Here $R_n$ is the detector noise, $S$ is the sensitivity, $\sigma_i$ is the peak width, $\alpha_i$ is the injection band width and $F$ is the column flow. $K_1$ to $K_4$ are constants. In the table it can be seen that the coiled column not only has a 4 times higher analysis speed, but also has favourable detection characteristics in comparison with a straight column with an equivalent inner diameter and plate number. Compared with the straight column with the 2 times lower inner diameter, the coiled column is advantageous with regard to the minimum detectable concentration on mass flow sensitive detectors.

In Table 2 a comparison of the detection limits is given for coiled columns and straight columns. The table was calculated for the case that coating leads to a 4 times higher analysis speed.

For the calculation of the detection characteristics in the table the following expressions were used [22]:

$$Q_{in}^m = \sqrt{2\pi} \frac{4R_n}{S} \cdot \frac{\sigma_i}{F} \cdot K_1 \cdot \sigma_i$$

(10)

$$Q_{in}' = \sqrt{2\pi} \frac{4R_n}{S} \cdot \frac{\sigma_i}{F} \cdot F$$

(11)

$$C_{in}^m = 4R_n \cdot \frac{\sigma_i}{\alpha_i} \cdot \frac{1}{F} = K_3 \cdot \frac{1}{F}$$

(12)

$$C_{in}' = 4R_n \cdot \frac{\sigma_i}{\alpha_i} = K_i$$

(13)

For the straight column the number of plates generated per second is approximately 90 and is independent from the linear velocity. For the coiled column, the number of plates per second increases with increasing linear velocity. This is caused by the more pronounced effect of the coating-induced secondary flow at higher velocities. At a low velocity (e.g. 1 cm/s), no enhanced radial mass transfer is observed for the coiled column. At higher velocities, however, secondary flow starts to develop and the number of plates obtained per second increases. At a velocity of 28 cm/s, the speed of analysis in the coiled column is approximately 4 times higher than in the uncoiled column. If we assume that the analysis time in capillary chromatography is inversely proportional to the square of the column diameter [17], we can conclude that coating a column is equivalent to using straight columns with a two times lower inner diameter. In our situation, an approximatively 100 µm uncoiled column would be required to give an analysis speed equal to that of a 210 µm coiled column.

From the point of view of sample capacity, the 210 µm coiled column is preferable over a 100 µm column. The use of columns with higher inner diameters permits the use of larger detector cell volumes. The value of the radial dispersion coefficient $D_r$ is mainly determined by the value of the velocity parameter $De^2Sc$. In the low $De^2Sc$ range ($De^2Sc < 5 \times 10^2$), a reasonable fit could be obtained by changing the numerical constant from $De^2Sc = 3500$. It was already anticipated by Tijssen that the numerical constants in the equations might require fitting to the experimental results. $De^2Sc$ predicts a constant deviation from the Golay equation for $De^2Sc > 2300$. The data in Figure 4 indeed show the tendency to level off to a constant value, about a factor 5 or 6 below the plate height calculated from the Golay equation. More experiments at higher values for the velocity parameter, however, are necessary to draw sound conclusions.

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$$C_{in}^m = 4R_n \cdot \frac{\sigma_i}{\alpha_i} \cdot \frac{1}{F} = K_3 \cdot \frac{1}{F}$$

(12)

$$C_{in}' = 4R_n \cdot \frac{\sigma_i}{\alpha_i} = K_i$$

(13)
For unretained components a significantly improved efficiency on a coated column. The uncoated column used in the previous was observed. In a recent study on turbulent flow in GC, van Es observed a very strong dependence of the plate height on the capacity factor. According to van Es, the strong capacity factor dependence of the plate height in turbulent flow GC is an intrinsic property of turbulent flow, which can be explained from the shape of the velocity profile. In view of the intermediate position of coiling induced secondary flow between normal, laminar flow and turbulent flow the increased capacity factor dependence of the plate height is not surprising.

Representative chromatograms of the separation of a normal alkanes standard obtained under the conditions of coiling induced secondary flow are given in the Figure 7A and B. Figure 7A shows the separation of the alkanes at a low linear velocity where the column behaves as a straight column. Here, a resolution of 3.8 is obtained for the peak pair C22/C24 in a total analysis time of 1800 seconds. Figure 7B shows the same analysis but now at a high linear velocity where the convective flow enhances radial mass transfer. Here, a resolution of 1.6 is obtained in only 70 s. The reduction of the analysis time is much more than can be explained by the loss in resolution. Hence this is a clear example of the potential of coiled columns to give increased analysis speeds at least for low capacity factors.

In a next series of experiments the plate height curve of a 10 m, 50 μm fused silica column coated around a 1 cm diam. metal rod (λ = 1/200) was measured. Due to the fragility of the fused silica, it was impossible to use smaller coil diameters without breakage of...
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Figure 7

Figure 8
A and B illustrate the effect of the linear velocity on the capacity factor and the plate height. Plate height in a coiled column (B). Column: 10 m × 50 μm i.d. Coil diameter: 1 cm.

the material. Using this column, deviations from the Golay equation were only observed at linear velocities above 1 m/s. In this velocity range, however, significant pressure drops occurred. Figure 8 A and B illustrate the effect of the linear velocity on the capacity factor and the plate height.

Unpractically low coil diameters would be required to obtain enhanced radial mass transfer at velocities which would not lead to excessive pressure drops. Thus it appears that the positive effects of coiling induced secondary flow can only be fully exploited in columns with relatively large inner diameters.

5 Conclusions
Radial mass transfer in open capillary columns for SFC can be enhanced by tight coiling of the columns. The plate height curve in a coiled column depart from the Golay equation at higher mobile phase velocities. The resulting curve could be partly described by Tijssen’s theory for coiling induced secondary flow. A quantitative fit is observed at low linear velocities. At higher velocities only a qualitative agreement is observed between the theory and the experimental results. Coiling the column can lead to positive effects on the detectability. The capacity factors of
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retained solutes can be used as sensitive probes for pressure drop over the column. At high mobile phase linear velocities significant effects were observed. The speed of analysis in coiled columns was found to be up to 5 times higher than in straight capillaries. Unfortunately, the dependence of the plate height on the capacity factor is larger than under the conditions of pure laminar flow.

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