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:
Super-critical 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 Tijsen'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. With respect to the speed of analysis in SFC, 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]. Tijsen 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.

\[ H = \frac{2 D_m}{u} + 2 \frac{R^2}{D_m} f(k) \frac{u}{R} + \frac{2 k D_m}{3 (1 + k)^2 D_s} \]  

with:

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

Here \( H \) is the plate height, \( u \) is the average linear velocity, \( D_m \) and \( D_s \) are the diffusion coefficients in the mobile phase and the stationary phase, respectively. \( R \) is the column radius. \( \kappa \) is the so-called velocity profile factor which is 1/48 for straight columns. In case of zero pressure drop the average velocity 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:

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

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

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

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 \( C_m \)-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:

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

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

According to basic flow theory, the values of \( \kappa \) and \( D_t \) mainly depend on the velocity parameter \( De^2Sc \). Here \( De \) (Dean number) and \( Sc \) (Schmidt number) are dimensionless numbers defined as:

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

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

\[ Re = u \frac{R_c}{\eta} \]  

The Schmidt number (Sc) is defined as:

\[ Sc = \frac{\eta}{\rho D_m} \]  

Tijssen [10] gave qualitative and quantitative descriptions of the plate height and the radial dispersion in coiled columns as a function of the \( De^2Sc \) number. Qualitatively, 4 regions were distinguished. At low mobile phase velocities (\( De^2Sc < 10 \)) secondary flow does not contribute significantly to radial dispersion. The plate height equals that of a straight column. At \( De^2Sc > 10 \) secondary flow starts to develop and is fully developed at \( De^2Sc > 10^4 \). 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 \( De^2Sc \) number. A number of expressions and their regions of applicability are given in Table 1. Eqs. (1) 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^2 \cdot u \cdot f(k)}{24 D_m} ]</td>
<td>( De^2 Sc = 0 )</td>
</tr>
<tr>
<td>II. [ H = \frac{R^2 \cdot u \cdot f(k)}{24 D_m} \cdot \frac{1}{(1 + \frac{De^2 Sc}{542})} ]</td>
<td>( \lambda = 0 ). Straight column</td>
</tr>
<tr>
<td>III. [ H = \frac{R^2 \cdot u \cdot f(k)}{24 D_m} \cdot \frac{1}{6.39} ]</td>
<td>( De^2 Sc &lt; 3 \times 10^3 )</td>
</tr>
<tr>
<td>IV. [ H = \frac{2.84 R_c f(k)}{De^{0.5} \lambda^{0.5} Sc^{10.7}} ]</td>
<td>( De &lt; 17 )</td>
</tr>
<tr>
<td>V. [ H = \frac{666.67 R_c f(k)}{De^{0.3} \lambda^{0.3} Sc^{10.7}} ]</td>
<td>( De^2 Sc &gt; 2300 )</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 led 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 μm i.d. and on a 10 m x 50 μm fused silica column coated with CP-si15 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 μm film of cross-linked octadecene. The columns were coiled around metal rods with various diameters. Cyclohexane and the normal alkanes C_{13}, 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 μm 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 \( 4.1 \times 10^{-5} \text{m}^2/\text{s} \) 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 (\( De^2 Sc = 300 \)). 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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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 bar, T = 120 °C.

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.

Reduction of the plate height due to secondary flow in coiled columns. Column: 210 μm i.d. L = 10 m; P = 154 bar; T = 120 °C. □: I = 1/48, x: λ = 1/19, ▼: λ = 1/8. Drawn lines: calculated using eqs. (II) and (III) from Table 1. The numerical constant in eq. (II) was changed into 3500.
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Table 2 Effects of coiling on the detection limits. \( Q_m \) and \( C_m \) are the minimum detectable amount and concentration, respectively. The superscript \( m \) refers to mass flow sensitive detection and \( c \) to concentration sensitive.

<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_m )</th>
<th>( C_m )</th>
<th>( Q_c )</th>
<th>( C_c )</th>
</tr>
</thead>
<tbody>
<tr>
<td>L d straight</td>
<td>N</td>
<td>t</td>
<td>a</td>
<td>F</td>
<td>( W_0 )</td>
<td>( C_0 )</td>
<td>( W_0 )</td>
<td>( C_0 )</td>
</tr>
<tr>
<td>L d coiled</td>
<td>4N</td>
<td>t</td>
<td>a/2</td>
<td>F</td>
<td>( W_0/2 )</td>
<td>( C_0 )</td>
<td>( W_0/2 )</td>
<td>( C_0 )</td>
</tr>
<tr>
<td>L/4 d coiled</td>
<td>N</td>
<td>t/4</td>
<td>a/4</td>
<td>F</td>
<td>( W_0/4 )</td>
<td>( C_0 )</td>
<td>( W_0/4 )</td>
<td>( C_0 )</td>
</tr>
<tr>
<td>L/4 d/2 straight</td>
<td>N</td>
<td>t/4</td>
<td>a/4</td>
<td>F/4</td>
<td>( W_0/16 )</td>
<td>( 4C_0 )</td>
<td>( W_0/16 )</td>
<td>( C_0 )</td>
</tr>
</tbody>
</table>

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 coiling 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 coiling a column is equivalent to using straight columns with a two times lower inner diameter. In our situation, an approximately 100 \( \mu \)m uncoiled column would be required to give an analysis speed equal to that of a 210 \( \mu \)m coiled column. From the point of view of sample capacity, the 210 \( \mu \)m coiled column is preferable over a 100 \( \mu \)m column. The use of columns with higher inner diameters permits the use of larger detector cell volumes in order to increase the detectability. If already large cell volumes are used (e.g., FT-IR) the resolution loss is reduced. In addition, the larger bore column is less sensitive for dead volumes in the injector.

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 coiling leads to a 4 times higher analysis speed. For the calculation of the detection characteristics in the table the following expressions were used [22].

\[
Q_m = \sqrt{2\pi} \frac{4R_n}{S} \cdot \alpha_i = K_1 \cdot \sigma_i \quad (10)
\]

\[
Q_c = \sqrt{2\pi} \frac{4R_n}{S} \cdot \alpha_i \cdot F = K_2 \cdot \sigma_i \cdot F \quad (11)
\]

\[
C_m = \frac{4R_n}{S} \cdot \frac{\sigma_i}{\alpha_i} \cdot \frac{1}{F} = K_3 \cdot \frac{1}{F} \quad (12)
\]

\[
C_c = \frac{4R_n}{S} \cdot \frac{\sigma_i}{\alpha_i} = K_4 \quad (13)
\]

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.

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 (\( De^2Sc < 5 \times 10^3 \)), 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 coiling induced secondary flow on the efficiency in a given chromatographic set-up. For the velocity parameter we can write:

\[
De^2Sc = \frac{4 \cdot \varphi \cdot a^2 \cdot R_d^2}{\eta \cdot H_{coil} \cdot D_m} \quad (14)
\]

After substitution of the appropriate values for the various parameters, the gain in efficiency due to the coiling can be obtained from Figure 4. From eq. (14) it can be seen that the effects of coiling 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
For unretained components a significantly improved efficiency on a coated column. The uncoated column used in the previous experiments was disconnected from the injector and the T-piece 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. So far, all experiments were performed using an uncoated column. Although a pressure drop over the column is not necessarily detrimental for the efficiency [3], we limited ourselves in the experiments to a maximum velocity of 40 cm/s.

The influence of the capacity factor on the plate height in coiled columns is demonstrated in Figure 6. A plot of the ratio of the theoretical plate height over the experimental plate height is given for 3 components with different capacity factors. The theoretical plate height was calculated according to the Goiay equation. The diffusion coefficients were estimated using the Wilke-Chang method [23]. So far the resistance to mass transfer in the stationary phase has been neglected. Here we have to test the reliability of this assumption. If we assume a diffusion coefficient in the stationary phase of 4 x 10^{-11} m^2/s [24], we find a stationary phase contribution to the plate height of only 16 pm at a linear velocity of 30 cm/s and a capacity factor of 1.5. This may be considered negligible in the foregoing results.

The reduction in the plate height due to the coiling appears to be largest for components with low capacity factors. For C_{22} (k = 0.29) at 45 cm/s, the experimental plate height in the coiled column is less than one fifth of that in a straight column. For C_{28} (k = 1.4), the gain is only about a factor 3.5. Apparently, the influence of the capacity factor on the plate height in coiled columns is larger than in straight columns. This is in conflict with the theory from Tijssen. Tijssen’s theory predicts that the influence of the capacity factor on the plate height in coiled columns with secondary flow would be lower than in straight columns with normal, laminar flow. According to van Es [6], 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 7 A and B. Figure 7 A 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 C_{22}/C_{24} in a total analysis time of 1800 seconds. Figure 7 B 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 coiled 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 densities, however, also lead to higher viscosities which tend to decrease the De^2Sc value.
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Figure 7

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

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 departs 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.

References


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