On-line sample enrichment - capillary gas chromatography of aqueous samples using geometrically deformed open-tubular extraction columns

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On-Line Sample Enrichment–Capillary Gas Chromatography of Aqueous Samples Using Geometrically Deformed Open-Tubular Extraction Columns

Eindhoven University of Technology, Laboratory of Instrumental Analysis, P.O. Box 513, 5600 MB Eindhoven, The Netherlands

Udo A.Th. Brinkman
Free University, Department of Analytical Chemistry, De Boelelaan 1083, 1081 HV Amsterdam, The Netherlands

Abstract. The effect of geometrical deformation of open-tubular extraction columns on peak dispersion of retained solutes is evaluated. By coiling or stitching of the columns peak dispersion is decreased, with a factor of two and more than five, respectively, due to secondary flow enhanced radial dispersion. This enables the increase of sampling flow rates in on-line extraction-GC using open-tubular extraction columns up to 4 mL/min while still obtaining quantitative trapping of the analytes.

INTRODUCTION

On-line sample enrichment of aqueous samples for GC analysis is often based on solid-phase extraction. Here the analytes from 1–10 mL of an aqueous sample are first trapped on an extraction column and then desorbed by a small volume of organic solvent (typically 75–125 µL) which is directly introduced into the GC system. Before desorption can take place, water remaining in the extraction column after sampling, has to be removed rigorously. This is necessary for efficient desorption and to prevent the transfer of water into the GC as this can deteriorate the performance of the system [1].

The removal of water from the extraction column can be performed by purging with nitrogen gas. For packed extraction columns drying with a gas can take 30 min or more [2] and complete water elimination is sometimes difficult to achieve due to channel formation in the packing [3]. Moreover, due to the high nitrogen flows used (> 100 mL/min) loss of volatile analytes may occur [4]. Therefore, as an alternative to drying with a gas, the use of a drying column has been proposed [5]. In this case sampling is immediately followed by desorption with an organic solvent in which water is (slightly) soluble. Water from the extraction column is led to waste via a valve until the front of the desorption solvent has reached the valve. Then the valve is switched and the solvent is directed to a column packed with a drying agent (an anhydrous salt or silica) which removes water from the solvent before introduction into the GC. Although the incorporation of a drying column prevents the introduction of water into the GC system, several limitations were also reported. Silica reacted with some highly chlorinated phenols, and with sodium sulphate disintegrated particles were transferred to the GC system when using the drying column for more than 20 analyses.

In contrast to the situation for packed extraction columns, complete removal of water is easily achieved when open-tubular extraction columns are used [6]. Here the analytes are trapped in the stationary phase of a short piece
of GC column. Water is efficiently removed by purging briefly with a low flow of nitrogen gas and losses of volatile analytes (toluene) do not occur [7]. On the other hand, the use of open-tubular extraction columns has, in principle, two disadvantages compared with the use of packed columns: i) the retention power is generally weaker and ii) the sampling flow rate is limited due to slow diffusion of the analytes in the water. In previous work we demonstrated that the retention power of an open-tubular extraction column—in fact a 2 m piece of the GC column—can be greatly enhanced by swelling the stationary phase with an organic solvent prior to sampling [7]. This enabled the practical use of open-tubular traps for on-line extraction-GC of aqueous samples up to some 2.5 mL. For larger sample volumes the sampling time became unacceptably long due to the low sampling flow rate (ca. 100 µL/min) that had to be used.

The low sampling flow rate, needed to prevent immediate breakthrough of the analytes in the open-tubular extraction columns, stems from the slow radial mass transfer in the tube. Radial mass transfer in open tubes can be enhanced by geometric deformation (e.g., coiling, stitching, waving) of the tube [8-10]. The explanation for this is that in deformed tubes centrifugal forces are active which generate a so-called secondary flow in radial direction. As a consequence, the analytes are transported to the column wall not only by molecular diffusion but also by convection. Detailed theoretical and experimental descriptions of peak dispersion in helically coiled columns have been published by Tijssen [8,9]. Hofmann and Halász [10] also evaluated peak dispersion in squeezed, twisted, and waved tubes. In chromatographic practice geometrically deformed tubes are applied to reduce peak dispersion in open-tubular reactors used in post-column reaction systems in LC [11] and in flow injection analysis [12,13].

In the majority of the publications dealing with deformed tubes the solutes have no interaction with the column wall, i.e., the analytes are not or only weakly retained in the tube (retention factor, k < 2). In this work peak dispersion of retained solutes (k > 2) in geometrically deformed extraction columns is compared with that in straight extraction columns. The aim is to increase the maximum allowable sampling flow rates in on-line extraction-GC using open-tubular extraction columns.

**EXPERIMENTAL**

**Chemicals.** Methanol and acetonitrile (HPLC grade) were obtained from Merck (Darmstadt, Germany). Water was demineralized and purified using a Milli-Q water purification system (Millipore, Bedford, USA). Hexane (P.A., Merck) was freshly distilled before use. Polycyclic aromatic hydrocarbons (PAH) were from K & K Laboratories (Plainview, NY, USA) and organochlorine pesticides were from Polyscience (Niles, IL, USA).

**Determination of peak dispersion.** For the determination of peak dispersion an LC system was used consisting of a gradient LC pump (model PU 4100 LC, Unicam, Eindhoven, The Netherlands), a six-port valve with a 20 µL loop, an open-tubular extraction column, and a UV detector (model 785A, Separations, Hendrik Ido Ambacht, The Netherlands). Different lengths (1-5 m) of the following GC columns were used as extraction column: 0.32 and 0.15 mm i.d. fused silica capillaries coated with 5 and 2 µm CP-Sil-5-CB, a methyl silicone, respectively (Chrompack, Middelburg, The Netherlands), 0.50 mm i.d. Ultimetal capillaries coated with 5 or 13 µm CP-Sil-5-CB (generous gift of Chrompack). Further a 0.21 mm i.d. stainless steel capillary was dynamically coated with 0.6 µm of crosslinked SE-54. In experiments in which straight columns are evaluated, the columns are in fact bent into one single loop for practical reasons. Experiments with tightly coiled columns were performed using metal columns. The metal columns were coiled around ca. 2 mm o.d. iron rods or stitched through a plastic frame as shown in Figure 1. Peak dispersion was calculated from the band width of the PAH eluting from the extraction columns after injection of 4-8 µg/mL solutions of PAH dissolved in the mobile phase.

**Figure 1. Geometry of coiled and stitched open-tubular extraction columns.**
**On-line extraction.** The system used for on-line extraction-GC is schematically depicted in Figure 2. The extraction unit was built around two 10-port valves (Valco, Houston, TX, USA). It consisted of a sampling pump P1 (LC pump, see above) and a pump P2 used for desorption/introduction of the analytes into the GC system (Digisampler, Gerstel, Mülheim a/d Ruhr, Germany). A 0.5 mL sample loop was connected between two ports of valve 1. The open-tubular extraction columns were connected between two ports of valve 2. In Figure 2 the position of the valves at the start of an extraction cycle is shown. The content of the sample loop is transferred to the extraction column by pump 1 and the column is flushed with an additional 0.5 mL of methanol/water (20/80). Then valve 1 is switched and nitrogen (1 mL/min) slowly pushes the remaining water out of the trap (0.5–2.5 min depending on the dimensions of the extraction column). Next, pump 2 is started and valve 2 is switched. Now the analytes are desorbed from the trap with hexane (225 μL/min) which is directly introduced into a PTV injector. For desorption 50 to 280 μL of hexane were needed, depending on the column dimensions. Half a minute before the next extraction, valve 2 is switched again in order to remove the organic solvent (remaining in the column after desorption) by nitrogen. Meanwhile the sample loop is filled again and the next extraction can take place. For extraction of 10 mL samples the loop was removed. In this case one of the eluent bottles of the gradient LC pump was filled with the sample and pump 1 was connected to the port positioned on the left-hand side of the port with the transfer line to valve 2.

**Large volume injection/GC analysis.** For large volume injection/GC analysis a gas chromatograph (Model 5890, Hewlett Packard, Avondale, PA, USA) with flame ionization detection (FID) and equipped with a programmed temperature injection system (PTV injector) (CIS-3, Gerstel) was used. The PTV injector was equipped with a porous glass bed liner and the split vent was modified as described previously [14]. Hexane entering the PTV injector (25°C) was vaporized and eliminated via the open split exit (split flow 600 mL/min). When desorption was complete, the analytes concentrated in the liner were splitlessly transferred (splitless time 1.5 min) to the GC column by heating the PTV at 12°C/s to 300°C. GC separation was performed on a 25 m × 0.32 mm i.d. column coated with 0.52 μm Ultra-1 (Hewlett Packard), temperature programme: from 50°C (1 min) at 20°C/min to 300°C (1.5 min). Helium was used as the carrier gas (100 kPa). For data collection, an Omega integration system (Perkin Elmer, Norwalk, CT, USA) was used.

**THEORETICAL**

Flow profiles. In coiled tubes centrifugal forces produce a secondary flow in radial direction [8,9]. At low velocities these forces are still weak and the secondary flow manifests itself in the formation of two radial circular patterns which tend to divide the cross section of the tube into two equal parts, i.e., two parallel identical columns with d = 0.5 · d, are formed. The axial velocity profile at these low velocities still resembles the parabolic profile after Poiseuille. At higher velocities the centrifugal forces increase sharply which results in a more linear axial velocity profile. At very high velocities the axial profile tends to plug flow while turbulence sets in. In practice, for the open-tubular extraction columns (0.25–0.50 mm i.d., flow rates 0.1–4.0 mL/min) the velocities are low to intermediate (0.85-135 cm/s). As the Reynolds number (Re, see Equation 7) under

---

**Figure 2.** Schematic diagram of the set-up used for on-line extraction. V1 and V2 are valves, L = 0.5 mL loop, P1 and P2 are pumps filled with methanol/water (20/80) and hexane, respectively.
these conditions is below 340, for the experiments described in this work, the flow profile is laminar.

**Peak dispersion** in straight open-tubular columns under laminar flow conditions can be described by the Golay equation:

\[
H = \frac{2 \cdot D_M}{u} + \frac{\kappa \cdot f(k) \cdot d_e^2}{2 \cdot D_M} \cdot u
\]

or

\[
H = \frac{B}{u} + C_M \cdot u + C_S \cdot u
\]

with

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

where \(H\) is the plate height (m), \(u\) the linear velocity (m·s⁻¹), \(D_M\) and \(D_S\) (m²·s⁻¹) are diffusion coefficients of the analyte in the mobile phase and the stationary phase, respectively, and \(k\) is the retention factor. \(\kappa\) is a function of the shape of the velocity profile and is called the velocity profile factor (= 1/48 for straight columns), \(d_e\) is the column diameter, and \(d_f\) the film thickness of the stationary phase. The \(B\) term in Equation 1b represents axial molecular diffusion. The \(C\) terms represent resistance to mass transfer in the mobile phase \((C_M)\) and stationary phase \((C_S)\). At the velocities applied during extraction the contribution of axial molecular diffusion to peak dispersion can be neglected. If we further neglect the (relatively small) stationary phase contribution to chromatographic band broadening, Equation 1a can be simplified to:

\[
H = \frac{\kappa \cdot f(k) \cdot d_e^2}{2 \cdot D_M} \cdot u
\]

In straight tubes radial dispersion is determined by \(D_M\) alone. In deformed tubes radial dispersion is the combined effect of molecular diffusion and convection by the secondary flow. The radial dispersion coefficient, \(D_R\), is given by [8]:

\[
D_R = D_M + D_{SF}
\]

where \(D_{SF}\) is the secondary-flow dispersion coefficient. Taking the enhanced radial mass transport into account one has to write Equation 3 as:

\[
H = \frac{\kappa \cdot f(k) \cdot d_e^2}{2 \cdot D_R} \cdot u
\]

\(D_R\) and \(\kappa\) are both functions of the velocity. In coiled open-tubular columns theory predicts [9] that both \(\kappa\) and \(D_R\) are mainly dependent on the velocity parameter \(D_{e^2}S_c\). 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:

\[
Re = \frac{\rho \cdot u \cdot d_e}{\eta}
\]

with \(\rho\) (kg·m⁻³) and \(\eta\) (cPoise = 10⁻³ kg·m⁻¹·s⁻¹) being the mobile phase density and dynamic viscosity, respectively. The parameter \(\lambda\) (aspect ratio) is the ratio of the column radius and the coil radius:

\[
\lambda = \frac{r_c}{R_{coil}}
\]

The Schmidt number is defined as:

\[
Sc = \frac{\eta}{\rho \cdot D_M}
\]

When the linear velocity in Equation 7 is substituted by \(u = F/(0.25 \cdot \pi \cdot d_e^2)\), \(F\) being the flow rate, and Equations 6–9 are combined, the following expression for \(D_{e^2}S_c\) can be found:

\[
D_{e^2}S_c = \frac{8 \cdot \rho \cdot F^2}{\pi^2 \cdot \eta \cdot D_M \cdot d_e \cdot R_{coil}}
\]

Tijssen gave qualitative and quantitative descriptions of the plate height and the radial dispersion in coiled columns as a function of \(D_{e^2}S_c\). For \(D_{e^2}S_c < 10\), i.e., at low flow rates and/or large coil diameters, secondary flow does not contribute to radial dispersion. Hence, the plate height equals that of a straight column. For \(D_{e^2}S_c > 10\) secondary flow develops gradually and is well established at \(D_{e^2}S_c >\)
Roughly, for De$^2$Sc numbers between $10^4$ and $10^5$ the plate height has a plateau value equal to ca. $H_{\text{straight}}/4$. This is explained by the formation of the two identical parallel column halves which reduces the column diameter by a factor of two. At still higher values of De$^2$Sc, peak dispersion decreases more or less linear to $H_{\text{coll}}/H_{\text{straight}} = 10^4$ at De$^2$Sc = $10^9$.

In previous work [7] a 2 m × 0.32 mm i.d. × 0.45 mm o.d. open-tubular extraction column was used. This column was coiled around a standard GC-column frame ($R_{\text{coil}} = 80$ mm). The maximum allowable sampling flow rate for this column was found to be approx. 100 $\mu$L/min. If the diffusion coefficient of the solutes in water is estimated to be $0.5 \times 10^{-5}$ cm$^2$/s it can be calculated that De$^2$Sc equals 176. This means that in this case radial dispersion is hardly increased compared with the situation encountered for straight columns. By coiling the column very tightly around a 2 mm o.d. rod ($R_{\text{coil}} = 1.225$ mm), one can increase De$^2$Sc to approx. $10^4$ which should correspond with a reduction of peak dispersion by a factor of about four. Alternatively, and more important for the present work, the sampling flow rate can be increased by a factor of four without affecting the breakthrough volume. This will be experimentally verified in the next section.

RESULTS AND DISCUSSION

Peak dispersion in coiled extraction columns. For evaluation of the effect of coiling on peak dispersion, two short metal GC columns of different length and diameter were used. Three polycyclic aromatic hydrocarbons (naphthalene, phenanthrene, and pyrene) were used as test compounds. First the band broadening was measured for the "straight" ($R_{\text{coil}} > 300$ mm) columns. Then the columns were tightly coiled and the band broadening was measured again applying the same experimental conditions. In Figure 3 the calculated and experimental plate height for a straight column, and the experimental plate height for the same, but now tightly coiled column, are shown as a function of the flow rate. For the straight columns the experimental values for the plate height were generally in good agreement with the theoretical values although, for low k values (k ≈ 2), experimental plate heights were sometimes lower (1.3–1.6 times) than calculated. Coiling clearly reduced band broadening and, as expected, the effect was more pronounced at higher flow rates (Equation 10). The reduction in peak dispersion for naphthalene and the more strongly retained phenanthrene was found to be similar.

According to Tijssen [8,9] radial dispersion in coiled columns mainly depends on the velocity parameter De$^2$Sc. It should therefore be possible to obtain a single curve, irrespective of the values of $d_c$, $\lambda$, and $D_M$, by plotting the relative plate height, ($H_{\text{coll}}/H_{\text{straight}}$), against De$^2$Sc. For De < $10^3$ this curve should also be independent of the retention factor. This should enable us to fit the plate height data obtained for the different PAHs and trapping columns into a single graph. The resulting plot is depicted in Figure 4. Up to De$^2$Sc values of $10^3$ no reduction of band broadening was observed. For higher De$^2$Sc values the relative plate height for the coiled columns decreases with

![Figure 3](image)

Figure 3. Theoretical (dashed line) and experimental (solid line) peak dispersion in straight and tightly coiled ($R_{\text{coil}} = 1.13$ mm) open-tubular extraction columns. Column: 550 cm × 0.50 mm i.d., 5$\mu$m CP-Sil-5 CB, mobile phase acetonitrile/water (20/80). For theoretical peak dispersion in straight columns $D_M$ was calculated using the modified Wilke-Chang equation [15].
increasing De$^2$Sc to reach a value of ca. 0.5 at De$^2$Sc $\approx 5 \cdot 10^4$. This obviously is more or less a plateau situation. Qualitatively, the plot of Figure 4 is rather similar to the one presented by Tijssen [13]. Quantitatively, the main difference is that the plateau value of $H_{coil}/H_{straight}$ found for De$^2$Sc $= 10^4$-$10^6$, is approx. 0.50 rather than 0.25 as reported by Tijssen. Another difference is that Tijssen reported a strong increase in $H_{coil}/H_{straight}$ when the retention factor of the solutes increased from 0 to 1.3 [9].

In the present study, where the retention factors varied between 2.3 and 8.7, such an increase was not observed. Tijssen attributed the unfavorable effects found for retained solutes to so-called interphase effects. Interphase effects arise from the existence of a sublayer of mobile phase along the column wall in which no radial dispersion due to convection takes place. In the sublayer, interphase mass transfer is only caused by molecular diffusion. To account for the resistance to mass transfer in the sublayer an extra term, $C_1$, has to be added to the $C$ term of the Golay equation [9]:

$$H = \frac{B}{u} + (C_M + C_S + C_1) \cdot u$$

with

$$C_1 = \frac{d^2}{16} \cdot \left( \frac{1}{D_M} - \frac{1}{D_R} \right) \cdot \left( \frac{k}{1 + k} \right)^2$$

In coiled tubes and at higher velocities, $C_M$ is reduced due to secondary flow enhanced radial dispersion (Equation 5) and, hence, the $C_1$ term can become the dominating contribution to band broadening [9,16]. $C_1$ increases with the retention factor $(k/(1 + k))^2$ term which explains the strong dependence of the plate height on $k$ found by Tijssen. It probably also explains the absence of such a dependence in our study as for $k > 2.3$ the $C_1$ term is not anymore strongly dependent on the retention factor. As a consequence, for solutes which are stronger retained than those of Figure 4, similar values for $H_{coil}/H_{straight}$ may be expected.

The effect of coiling on band broadening for De$^2$Sc values larger than $10^6$ was not examined. Higher flow rates and/or much smaller column diameters would be necessary for obtaining these De$^2$Sc values (see Equation 10). Such conditions are not very practical, e.g., with regard to column pressure drop, when applying open-tubular capillaries as extraction columns.

![Figure 4](image-url)

**Figure 4.** Relative peak dispersion in coiled open-tubular extraction columns. (●) naphthalene ($k = 2.4$) and (▼) phenanthrene ($k = 8.7$) mobile phase: acetonitrile/water (20/80), (▲) phenanthrene ($k = 2.3$) acetonitrile/water (30/70), column: 205 cm × 0.21 mm i.d., 0.6 μm SE-54, $R_{coil} = 1.03$ mm; (○) naphthalene ($k = 2.8$) and (△) phenanthrene ($k = 7.7$) mobile phase acetonitrile/water (20/80), column: 550 × 0.50 mm i.d., 5 μm CP-Sil-5 CB, $R_{coil} = 1.13$ mm.
Obviously, peak dispersion for retained solutes in coiled open-tubular columns can be decreased by a factor of approx. two. Although this is less than expected, which is probably due to slow interphase mass transfer, coiling of the extraction column should nevertheless enable the use of 2-fold higher maximum allowable sampling flow rates.

*Peak dispersion in stitched extraction columns.* From the literature [10] it is known that more “exotic” deformation of open tubes than simply coiling can reduce peak dispersion much more efficiently. Geometrically deformed, e.g., squeezed, zig-zag, serpentine, knitted, or stitched tubes are widely used in liquid chromatography in the field of post-column reaction detection [11] and as low-dispersion connecting tubes [17]. As with coiling, the deformation of the tube results in the generation of a secondary flow which enhances radial dispersion. The effect is, however, much more pronounced. It is difficult or even impossible to predict the effect of column geometry on peak dispersion from theory and therefore optimization of the geometry has been done by trial and error. Optimal deformation is relatively easily obtained by knitting or stitching of the tube [11]. The continuous change in coiling direction and the bending of the coil out of the plane leads to a continuous change in direction of the secondary flow. This, apparently, results in a plug-like flow profile which already develops at low velocities. For higher velocities peak dispersion is practically constant.

As with the coiled columns, reduction in peak dispersion with other deformed tubes is much less pronounced (factor 2-10) for even slightly retained solutes [10]. However, for our application even a modest reduction may still be practically useful. To verify this an extraction column was carefully stitched through a plastic frame (see Experimental) and the peak dispersion was measured. In Figure 5 the plate height for naphthalene (k = 3) observed with the stitched column is compared with that observed for a straight and a coiled column. The stitched column is clearly superior to the straight and coiled columns, despite the fact that the plate height (H = 7-40 cm) is much higher than reported in the literature (H < 5 cm [10,11]) for unretained solutes. Next, peak dispersion was studied for stronger retained analytes which is important when using the column as a trap. Peak dispersion was found to increase with the retention factor (Figure 6), e.g., at 1 mL/min the plate height found for naphthalene and pyrene was 30 and 82 cm, respectively. This increase is higher than expected from the $C_M$ term of Equation 1 (theoretically: $H_{pyr}/H_{naf} = 1.75$). As a consequence, the relative plate height, $H_{stitched}/H_{straight}$, increases with k: for example, at 1 mL/min the

![Figure 5.](image-url)  
*Figure 5. Peak dispersion of naphthalene (k = 3) in straight, coiled and stitched 0.5 mm i.d. open-tubular extraction columns. Mobile phase: acetonitrile/water (20/80) for the straight and coiled column (5 µm CP-Sil-5), and (30/70) for the stitched column (13 µm CP-Sil-5).*
relative plate heights were 0.14, 0.17, and 0.22, for naphthalene \((k = 3.3)\), phenanthrene \((k = 4.8)\), and pyrene \((k = 19)\), respectively. Thus, analogous to the situation for coiled columns, there seems to be an extra contribution to band broadening, possibly due to slow interphase mass transfer, for retained compounds in stitched columns. As for the coiled tubes, this contribution levels out with increasing values of \(k\).

In conclusion, peak dispersion for retained compounds in stitched open-tubular columns is much higher than reported in literature for unretained solutes. However, compared with straight and coiled columns, band broadening in stitched columns is a factor of 4.5-7 less. Because peak dispersion is relatively independent of the flow rate, the maximum allowable sampling flow rates during extraction using stitched trapping columns are expected to be at least five times higher than those for straight extraction capillaries.

Recovery versus flow rate in on-line extraction-GC with straight columns. When the breakthrough volume is defined as \(V_B = V_R - 2.326 \sigma_v\), where \(V_R\) is the retention volume and \(\sigma_v\) the standard deviation of a Gaussian shaped peak eluting from the open-tubular trapping column, one can derive that breakthrough of an analyte will occur when [6]:

\[
V_B = V_R \cdot f(N) = V_0 \cdot (1 + k) \cdot f(N) \quad (13)
\]

with

\[
f(N) = 1 - \frac{2.326}{\sqrt{N}} = 1 - 0.89 \cdot \left( \frac{F}{D_M \cdot L} \right)^{-1/2}
\]

\[
(14)
\]

where \(V_0\) is the void volume of the trap. From Equation 13 it is obvious that the flow rate may not exceed a certain threshold value or breakthrough will occur immediately. This maximum allowable sampling flow rate is given by:

\[
F_{\text{max}} = 1.267 \cdot D_M \cdot L \quad (15)
\]

from which equation one readily can deduce that the length of the trapping column is the key parameter. This is illustrated in Figure 7 where the recovery of pyrene after on-line extraction-GC is plotted against the sampling flow rate. The experimental maximum allowable sampling flow rates obtained from this figure are three to four times higher than the theoretical values calculated using Equation 15. This deviation is due to the fact that Equations 14 and 15 are only valid for \(N > 5.4\), which corresponds to flow rates below 28, 56, and 140 \(\mu\text{L/min}\) for the 1, 2, and 5 m columns, respectively. For \(N < 5.4\) the breakthrough volumes can no longer be predicted based on a Gaussian
shaped band. Lövkvist and Jönsson [18] compared several equations for breakthrough curves at very low plate numbers (0.2 < N < 25) and suggested to use an alternative equation for f(N):

\[
f(N) = \left( a_0 + \frac{a_1}{N} + \frac{a_2}{N^2} \right)^{-1/2}
\]

where \( a_0, a_1, \) and \( a_2 \) have values of 0.9801, 13.59, and 17.60, respectively, when accepting breakthrough of 1% of the solute. For a 2 m × 0.32 mm i.d. extraction column, the breakthrough volumes for pyrene at low plate numbers were calculated using both Equations 14 and 16. The results are given in Table I. When using Equation 14 the breakthrough volume is below zero for \( N < 5.4 \). When using Equation 16 the breakthrough volume, even at the extremely low plate number of 0.08, still is 0.75 mL. This implies that for sample volumes of 0.5 mL no breakthrough should occur. The experimental data in Figure 7, however, show that breakthrough does occur for 0.5 mL samples. This is in contradiction with the statement of Lövkvist that, provided that the analytes are strongly retained (\( V_R \) is very large), a sufficiently large breakthrough volume can be obtained even at very low plate numbers. Figure 7 also shows that the losses occur at flow rates which correspond with \( N < 1.5 \) for all three columns. Apparently, for \( N < 1.5 \) the breakthrough volume can not be increased by increasing the retention volume. To verify this, the recovery of pyrene versus sampling flow rate was determined for three extraction columns with different \( V_R \) but identical plate numbers. \( V_R \) was varied by using extraction columns with different internal diameters/stationary phase thicknesses: 0.15 mm/2 \( \mu \)m, 0.32 mm/5 \( \mu \)m, and 0.50 mm/13 \( \mu \)m, respectively. The length was the same for all three columns and hence, as the plate number at constant flow rate is independent of the column diameter, the

Table I. Calculated breakthrough volumes at low plate numbers.

<table>
<thead>
<tr>
<th>F (mL/min)</th>
<th>N*</th>
<th>Equation 14</th>
<th>Equation 16</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>f(N)</td>
<td>( V_B ) (mL)</td>
<td>f(N)</td>
</tr>
<tr>
<td>0.010</td>
<td>30.6</td>
<td>0.579</td>
<td>24.6</td>
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<td>0.060</td>
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<td>&lt; 0</td>
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<tr>
<td>0.25</td>
<td>1.2</td>
<td>&lt; 0</td>
<td>&lt; 0</td>
</tr>
<tr>
<td>0.50</td>
<td>0.61</td>
<td>&lt; 0</td>
<td>&lt; 0</td>
</tr>
<tr>
<td>0.10</td>
<td>0.31</td>
<td>&lt; 0</td>
<td>&lt; 0</td>
</tr>
<tr>
<td>2.0</td>
<td>0.15</td>
<td>&lt; 0</td>
<td>&lt; 0</td>
</tr>
<tr>
<td>4.0</td>
<td>0.08</td>
<td>&lt; 0</td>
<td>&lt; 0</td>
</tr>
</tbody>
</table>

\* Extraction column: 200 cm × 0.32 mm i.d., 5 \( \mu \)m CP-Sil-5-CB. Mobile phase: methanol/water (20/80). Solute: pyrene, \( D_M = 0.37 \cdot 10^{-5} \) cm²/s, \( D_s = 10^{-7} \) cm²/s, \( k = 280 \) [6].
plate numbers were equal. Although $V_r$ differed up to a factor of 21, almost identical curves for recovery versus sampling flow rate were obtained. This leads us to conclude that for quantitative trapping of analytes in an extraction column the plate number should always be above 1.5. On the basis of Equation 3, and with $N = L/H \geq 1.5$, one can calculate for compounds with a high retention factor the following maximum allowable sampling flow rate for straight columns:

$$F_{\text{max}} \approx 4.5 \cdot D_M \cdot L$$

(17)

From this equation one can see that at a sampling flow rate of 1 mL/min quantitative trapping of the analytes can be obtained by using extraction columns of approx. 10 m. However, as both the volume and the time needed for desorption of the analytes from a 10 m extraction column can become unacceptable [6], shorter extraction columns, e.g., 2 m $\times$ 0.50 mm i.d., are often preferred in practice. With this 2 m extraction column the maximum allowable sampling flow rate is some 200 $\mu$L/min.

Recovery versus flow rate in on-line extraction-GC with geometrically deformed columns. Based on the above data on peak dispersion in geometrically deformed extraction columns it should be possible, with 2 m columns, to use sampling flow rates much larger than 200 $\mu$L/min without analyte losses during trapping. This is experimentally verified in Figure 8 by plotting the recovery of pyrene after on-line extraction versus the sampling flow rate for straight, coiled, and stitched open-tubular extraction columns. With coiled columns indeed higher flow rates can be used than with straight columns without analyte losses during extraction. However, the beneficial effect is only about 2-fold, as is to be expected on the basis of the data on peak dispersion in coiled columns. Stitching of the extraction column proves to be much more effective. Quantitative recoveries are obtained even for sampling flow rates of 4 mL/min, in other words, with a stitched open-tubular extraction column it is possible to extract relatively large sample volumes within acceptable sampling times. To demonstrate this, on-line extraction-GC was carried out for a 10 mL drinking water sample spiked with organochlorine pesticides (1 ng/mL) applying a sampling flow rate of 1 mL/min. The recovery, relative to a 2.5 $\mu$L cold splitless injection of a 4 $\mu$g/mL standard, was quantitative (96–102%), with RSD 2.3–4.0%, $n = 3$) for dieldrin, endrin, and methoxychlor (Figure 9). The lower recoveries for p,p'-DDT and especially mirex can be

![Graph](plot.png)

**Figure 8.** Effect of deformation of the extraction column on the maximum allowable sampling flow rate in on-line extraction-GC. Sample: see Figure 7. Column: 200 cm $\times$ 0.50 mm i.d., 13 $\mu$m CP-Sil-5-CB. (▲) straight, (○) coiled with $R_{\text{coil}} = 22$ mm, (+) coiled with $R_{\text{coil}} = 1.13$ mm; (●) stitched, $L = 165$ cm.
attributed to adsorption of these very apolar analytes in the HPLC pump and the transfer lines, which could not be prevented even by adding 20% of methanol to the sample. Obviously, geometrical deformation of open-tubular extraction columns facilitates their practical use in on-line extraction-GC of relatively large volumes of aqueous samples.

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REFERENCES


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