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Rectangular Capillary Electrophoresis: Some Theoretical Considerations

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Key Words

Capillary electrophoresis
Rectangular capillary electrophoresis
Band spreading

Summary

A theoretical study of the use of rectangular columns in capillary electrophoresis (CE) is presented. It was done employing some of the most important parameters that normally define the performance of CE separations, i.e. thermal effect, analysis speed, efficiency and sample capacity. Theoretical results from rectangular and cylindrical capillaries are compared in terms of the aforementioned parameters. Also, an estimate of the additional zone broadening that arises from the non-infinite dimension in the y-direction, in which the channel has its largest dimension, is presented.

Introduction

The use of rectangular columns in electrophoresis was first described by Tiselius in 1937 [1]. Nowadays, their utility has been shown for the separation by isotachopheresis [2–6] and capillary zone electrophoresis (CZE) [7, 8] of different compounds. Recently, a new approach that employs CZE coupled to electrophoresis in rectangular cross sections has been described for continuous electrophoretic separations [9]. Also, the use of micromachined channels on a chip has shown important possibilities for obtaining fast separations, i.e. of a few seconds, with high efficiencies (about 5000 theoretical plates per second) in miniaturized systems [10–14].

Nevertheless, the use of this sort of columns is actually not applied much in capillary electrophoresis because the disadvantages that they present compared with cylindrical columns. These disadvantages can be sum-

marized as: a) several technical problems associated with the practical development of rectangular capillaries [15, 16], b) the necessity of optimizing both the optics and the orientation of the rectangular capillary for efficient radiation throughput [16], c) wall thickness has a greater influence on temperature gradients for rectangular sections than in cylindrical ones [17].

However, rectangular columns also present a large number of advantages that make them very interesting for their use in capillary electrophoresis especially when the separation of larger quantities is required. These advantages are briefly: a) heat dissipation is more efficient in rectangular columns [1, 15] than in circular ones for large width/thickness ratios, b) the width of rectangular capillaries can be increased without altering their heat dissipation, increasing sample capacity [8, 15], c) for path-length-dependent detection systems (UV absorption, fluorescence, etc.) better detection limits can be achieved [8], d) flat walls produce less optical distortion and scatter compared to the walls of circular capillaries [8, 18].

Several authors have theoretically shown that the thermal dissipation achieved employing rectangular capillaries is better than that obtained with circular ones [15, 17, 19, 20], but to our knowledge, there is no theoretical study on other interesting parameters such as efficiency and sample capacity in this kind of column. However, it would be interesting to make a comparative study of the different possibilities, in terms of thermal dissipation, analysis time, efficiency and sample capacity that can be achieved employing different tubing geometries in capillary electrophoresis. The goal of this work is to describe such a theoretical study.

The comparison with circular columns is made here, as usual, by considering the same cross sectional area for both columns. In this work and to make it easier to understand this comparison we employ the parameter $\phi = 2b/2a$ as the width/thickness ratio for rectangular capillaries. Thus, $\phi = 1$ corresponds to a square capillary. A scheme of the different measures is shown in Figure 1 (2a and 2b are the thickness and width respectively in a rectangular column).

Figure 1
Scheme of different magnitudes employed for circular and rectangular capillaries.

Theory

1 Thermal Dissipation

Considering an electrolyte of zero coefficient of resistivity and constant thermal conductivity (mathematical symbols are defined at the end of this paper) in a cylindrical column immersed in a ideal thermostating medium, the difference between the temperature at the wall exterior (T_m) and the temperature at distance x (see Figure 1) from the centre (T_{C2}) is given by [21]

$$T_{C2} = T_m + \frac{W_v}{2} \left[\frac{R_2^2 - x^2}{2k_1} + \frac{R_2^2}{k_2} \ln \frac{R_1}{R_2} \right] \quad (1)$$

The same situation but using rectangular capillaries is defined by the equation [17]

$$T_{R2} = T_m + W_v \left[\frac{a^2 - x^2}{2k_1} + \frac{abd}{(a+b)k_2} \right] \quad (2)$$

where

$$W_v = E^2 \lambda c \quad (3)$$

Note that Eq. (2) is only valid for infinitely large ϕ ratios, that is, when the a parameter entirely controls the heat dissipation. The present study also aims at rectangular columns with $\phi \gg 1$; however, the effect of non-infinite ϕ values will be accounted for.

Substituting Eq. (3) in Eqs. (1) and (2), we obtain for cylindrical columns

$$T_{C2} = T_m + \frac{E^2 \lambda c}{2} \left[\frac{R_2^2 - x^2}{2k_1} + \frac{R_2^2}{k_2} \ln \frac{R_1}{R_2} \right] \quad (4)$$

and for rectangular capillaries

$$T_{R2} = T_m + E^2 \lambda c \left[\frac{a^2 - x^2}{2k_1} + \frac{abd}{(a+b)k_2} \right] \quad (5)$$

Using these two equations we have plotted the temperature difference (ΔT) within the column ($\Delta T = T_{C2} - T_m$ for circular section and $\Delta T = T_{R2} - T_m$ for rectangular) against the distance from the centre (x) for both capillaries (Figure 2). For the moment the same cross sectional area and wall thickness are employed for both capillaries. A rectangular capillary, $\phi = 8$, is used for

Table I. Values employed in Figure 2

$S_{col} = 3.1416 \times 10^{-8} \text{ m}^2$
$R_2 = 100 \text{ } \mu\text{m}$
$R_1 = 180 \text{ } \mu\text{m}$
$b = 500 \text{ } \mu\text{m}$
$\phi = 8$
$d = 80 \text{ } \mu\text{m}$
$E = 30,000 \text{ V m}^{-1}$
$c = 10 \text{ mol m}^{-3}$
$\lambda = 0.015 \text{ m}^2 \Omega^{-1} \text{ mol}^{-1}$
$k_1 = 0.4 \text{ W m}^{-1} \text{ K}^{-1}$
$k_2 = 1.5 \text{ W m}^{-1} \text{ K}^{-1}$

comparison. The conditions are given in Table I. As can be seen in Figure 2, a parabolic temperature profile appears in both capillaries. However, under these conditions, the temperature difference is almost three-times as great at the center ($x=0$) of the circular capillary as the rectangular. If larger or smaller cross sectional areas for both capillaries are employed, the absolute values of temperature will obviously change. However, the difference between both capillaries remains the same if an identical ϕ value is employed.

In order to test the influence of the capillary geometry on the temperature gradient we have employed Eqs. (4) and (5) and $S_{col} = 4ab$ and $S_{col} = \pi R_2^2$ for showing in Figure 3 the increase in temperature at the capillary centre ($\Delta T_{x=0}$) when different cross sectional areas are used. Considering the same separation conditions as Figure 2, it is shown in Figure 3 that circular columns provide higher temperature rises than rectangular capillaries. For the same cross sectional area the higher the ϕ value the lower the increase in temperature. On the other hand, for a given limit to the temperature rise, the higher the ϕ value the larger the area of the lumen that can be allowed.

2 Analysis Speed

Considering the direct proportionality between the speed of analysis and electric field:

$$E = \frac{L}{t_m \mu} \quad (6)$$

it is important to study the influence of the electric field on heat generation at the centre of columns ($\Delta T_{x=0}$), of the same cross sectional area and different column geometries. As seen in Figure 4, for the same electric field cylindrical tubing provides a higher heating effect than rectangular columns. Also, the electric field needed, for the same increase in temperature is greater when a higher ϕ value is employed (or when the $2b/2a$ ratio is higher).

To study better the influence of the ϕ value and cross sectional area (S) on analysis speed we have represented in Figure 5, employing the same separation conditions as Figure 4 and $\Delta T_{x=0} = 1 \text{ K}$ value, the maximum electric field allowed as a function of the cross sectional

Figure 2

Temperature difference ($\Delta T = T_2 - T_m$) within column for circular and rectangular sections with $\phi = 8$, against distance from capillary centre (x). Same cross-sectional area and wall thickness, d , employed for both capillaries. Other conditions given in Table I. Vertical scale applies to these conditions (see text).

Figure 3

Influence of capillary geometry and cross-sectional area (S) on temperature rise at capillary centre ($\Delta T_{x=0} = T_2 - T_m$). One circular and four rectangular columns of different ϕ ratios were employed. Other conditions as Figure 2.

Figure 4

Influence of electric field on heating generation at centre of column ($\Delta T_{x=0}$). Same cross-sectional area ($S_{col} = \pi \times 10^{-8} \text{ m}^2$) and five different column geometries employed. Conditions: variable electric field, separation distance $L = 1 \text{ m}$ (= total capillary length). Other conditions as Table I.

Figure 5

Effect of ϕ ratio and cross-sectional area (S) on maximum electric field allowed for $\Delta T_{x=0} = 1 \text{ K}$ in circular (surface plotted with more lines) and rectangular (surface plotted with less lines) geometries. Separation conditions as Figure 4.

area for different ϕ values. As can be seen for the same S value, higher electric fields are allowed when ϕ increases. Also, similarly taking $\Delta T_{x=0} = 1 \text{ K}$ constant, the higher ϕ , the higher the S values permitted for the same electric field, giving higher sample capacity.

3 Efficiency

The plate height, H , is given by

$$H = H_d + H_t \quad (7)$$

where H_d and H_t are the plate heights related to molecular diffusion and heating effect respectively. The influence of diffusion on plate height, and therefore on efficiency, is defined in CE by the same equation for circular and rectangular columns

$$H_d = \frac{2D_m}{\mu E} \quad (8)$$

In order to obtain the equations that relate the separation efficiency to the thermal effect for both, cylindrical and rectangular columns, we have employed the equation by Virtanen [22] as also derived by Knox and Grant [23]. For cylindrical capillaries they applied a modification of the Taylor equation for calculating the band dispersion in an open tube

$$\frac{\sigma_{ct}^2}{(\Delta u/u) L} = \frac{R_2^2 \Delta u}{24 D_m} \quad (9)$$

and the thermally induced dispersion term is now given by

$$\sigma_{ct}^2 = \frac{(\Delta u/u)^2 L R_2^2 u}{24 D_m} \quad (10)$$

Employing the expression that relates Δu to the different viscosity that the thermal gradient initiates in the interior of the column [23],

$$\frac{\Delta u}{u} = 0.013 \Delta T = \beta \Delta T \quad (11)$$

with ΔT in K, we can substitute $x = 0$ for Eq. (4), in Eq. (11) and the result in Eq. (10). Knowing that $H = \sigma^2/L$ and $u = \mu E$ we can obtain the final expression for the plate height due to thermal effects in a circular capillary

$$H_{ct} = \frac{4.40 \times 10^{-7} R_2^2 E^5 \lambda^2 c^2 \mu}{D_m} \left(\frac{R_2^2}{k_1} \right)^2 \quad (12)$$

Note that from Eq. (4) we only consider the influence of the heating in the lumen itself on the band dispersion.

A similar approach can be applied to rectangular capillaries. In this case, and although there are indications that the corners of the capillary do not degrade the separation [8], we have employed the relation proposed by Golay [24] who considers the contribution of the "end-effect" to band dispersion, according to the next expression

$$D = D_m + 0.1514 \frac{u^2 a^2}{D_m} \quad (13)$$

In the appendix a discussion of the factor 0.1514 is given. Note that we consider the worst case because the "end-effect" contribution to band dispersion is almost eight times larger than if we consider only the Taylor diffusion coefficient as given by Golay [24] and Aris [25]

$$D = D_m + \frac{2u^2 a^2}{105 D_m} \quad (14)$$

Applying the Einstein equation to the second term on the right hand side of Eq. (13) and using the same approximation as in Eqs. (9) and (10) we obtain

$$H_{rt} = \frac{0.3028 a^2 u}{D_m} \left(\frac{\Delta u}{u} \right)^2 \quad (15)$$

Substituting Eq. (5) in Eq. (11) and the result in Eq. (15) we obtain the final expression for the plate height due to the thermal effect in a rectangular capillary

$$H_{rt} = \frac{1.28 \times 10^{-5} a^2 E^5 \lambda^2 c^2 \mu}{D_m} \left(\frac{a^2}{k_1} \right)^2 \quad (16)$$

provided ϕ is not too small.

The plate height for a cylindrical (H_c) capillary can be obtained substituting Eqs. (8) and (12) in Eq. (7). The final expression is therefore given by

$$H_c = \frac{2D_m}{\mu E} + \frac{4.40 \times 10^{-7} R_2^2 E^5 \lambda^2 c^2 \mu}{D_m} \left(\frac{R_2^2}{k_1} \right)^2 \quad (17)$$

and doing the same for a rectangular (H_r) capillary

$$H_r = \frac{2D_m}{\mu E} + \frac{1.28 \times 10^{-5} a^2 E^5 \lambda^2 c^2 \mu}{D_m} \left(\frac{a^2}{k_1} \right)^2 \quad (18)$$

Using these two equations and $S_{col} = 4ab$ and $S_{col} = \pi R_2^2$, and knowing that $\phi = 2b/2a$ we can study the dependence of H on the ϕ ratio in a rectangular column for a constant electric field, and compare it with a circular column. In this case we have employed a rectangular cross sectional area four times larger than the circular (as shown in Figure 3, the larger the cross sectional area the worse the heat dissipation). As seen in Figure 6, when ϕ increases, the heating dissipation increases (also shown in Figure 3), and as a result it is possible to achieve lower plate heights, or higher efficiencies, than obtained with circular columns. Figure 6 also shows that if the end-effect is not taken into account in a rectangular column, the minimum ϕ value required for obtaining lower ($H_r < H_c$) plate heights is approximately two times smaller than that obtained when the end-effect is considered.

In order to study the relation between efficiency and analysis speed and considering that $N = L/H$, we have represented in Figure 7 the minimum capillary length (L) required for obtaining a value of $N = 200,000$ plates depending on electric field (E) and capillary geometry, i.e. cylindrical and rectangular columns with different ϕ ratios. As seen, for low fields circular and rectangular columns require similar capillary length. Therefore, both columns provide the same analysis time since, under these conditions molecular diffusion is the main dispersive effect. However, for larger electric fields and $\phi \gg 1$, the higher the ϕ value the shorter the length of column required and as a result the analysis speed is considerably increased. For instance, employing a rectangular column with $\phi = 10$ at $E = 45,000$ V/m only a 7.5 cm column is required to obtain $N = 200,000$ plates.

Figure 6

Dependence of plate height (H) on ϕ value for rectangular column of constant cross-sectional area ($S_{\text{col}} = \pi \times 10^{-8} \text{ m}^2$) with and without "end-effect". Circular column, cross-sectional area: ($S_{\text{col}} = \frac{\pi}{4} \times 10^{-8} \text{ m}^2$) used as reference. Separation conditions: $E = 30,000 \text{ Vm}^{-1}$, electrophoretic mobility $\mu = 5 \times 10^{-8} \text{ m}^2 \text{ s}^{-1} \text{ V}^{-1}$, $D_m = 4 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$. Other conditions as Figure 4.

Figure 7

Minimum capillary length (L) to obtain efficiency $N = 200,000$ plates against electric field (E) and capillary geometry for circular (surface plotted with more lines) and rectangular (surface plotted less lines) columns. Constant cross-sectional area considered for both columns varying $\phi = 2b/2a$ for rectangular capillary. Other conditions as Figure 6.

The analysis time in this case is equal to 30 s ($\mu = 5 \times 10^{-8} \text{ m}^2/\text{sV}$ has been employed), almost five times smaller than the time for a cylindrical column under the same conditions.

4 Sample Capacity

With Eqs. (17) and (18) we can represent (Figure 8) the maximum cross sectional area allowed for a given plate height and electric field depending on the column geometry. In Figure 8 we have used a maximum value for H of $6 \times 10^{-7} \text{ m}$ and $E = 30,000 \text{ V/m}$, the remaining conditions are as Figure 7. In Figure 8 we observe that when the ϕ ratio increases, the available cross sectional area increases too, leading to a larger sample capacity. For instance, if we compare the circular column with the $\phi = 10$ rectangular capillary, we observe that a four times larger cross-sectional area is available employing the latter.

In Figure 8 we have represented the maximum surface area of the lumen allowed for fixed E and H values, but independent of the injected quantity. In order to consider the influence of injection on the efficiency, we can define the "apparent plate height" ($\langle H \rangle$) under given separation conditions in which extra-column effects are included. In our case we only estimate the effect of injection on band broadening neglecting other effects such as; detection, solute adsorption on the capillary wall, conductivity difference between the sample zone and the surrounding buffer.

The plate height due to injection for circular and rectangular capillaries is:

$$H_{\text{inj}} = \frac{V_{\text{inj}}^2}{12LS_{\text{col}}^2} \quad (19)$$

For a clindrical capillary $\langle H_c \rangle$ is now given by

$$\langle H_c \rangle = \frac{V_{\text{inj}}^2}{12LS_{\text{col}}^2} + \frac{2D_m}{\mu E} + \frac{4.40 \times 10^{-7} R_2^2 E^5 \lambda^2 c^2 \mu}{D_m} \left(\frac{R_2^2}{k_1} \right)^2 \quad (20)$$

and doing the same for a rectangular capillary

$$\langle H_r \rangle = \frac{V_{\text{inj}}^2}{12LS_{\text{col}}^2} + \frac{2D_m}{\mu E} + \frac{1.28 \times 10^{-5} a^2 E^5 \lambda^2 c^2 \mu}{D_m} \left(\frac{a^2}{k_1} \right)^2 \quad (21)$$

To study the relation between plate height and sample capacity for the different columns, we have plotted in Figure 9, $\langle H \rangle$ against the injected volume employing Eqs. (20) and (21). We have considered the same conditions as Figure 6 but employing a variable injection volume and five different column geometries with identical cross sectional area. As can be seen, the higher the injected volume the lower the efficiency.

Figure 8

Available cross-sectional area against column geometry for same electric field ($E = 30,000 \text{ Vm}^{-1}$) and plate height ($H = 6 \times 10^{-7} \text{ m}$). Conditions as Figure 6.

Figure 9

Apparent plate height ($\langle H \rangle$) against injected volume (V_{inj}) for five column geometries with identical cross-sectional area. Conditions as Figure 6.

Figure 10

Maximum available injected volume (V_{inj}) against analysis time (t) for five different capillary geometries with equal cross-sectional area. Conditions: representation made considering constant value of $\langle H \rangle = 10^{-5}$ m for all columns and $L = 1$ m, other conditions as Figure 7.

Also, when rectangular columns with large ϕ values are employed, better efficiencies and larger injected volumes are achieved, obtaining almost identical results for rectangular columns where $\phi = 6, 8$ and 16 .

Similar results were obtained when we calculated the maximum injected volume that can be achieved, for constant efficiency and varying speed of separation (Figure 10). In this case we have considered a constant

value of $\langle N \rangle = 10^5$ (including injection effects) and $L = 1$ m (corresponding to $\langle H \rangle = 10^{-5}$ m) for different capillary geometries maintaining the same cross sectional area. As seen the minimum analysis time for a fixed injected volume is almost fivetimes lower when employing the rectangular column with $\phi = 16$ than that obtained with the circular one. Also, if we consider in Figure 10 the x-direction and for the same efficiency $\langle N \rangle = 10^5$, the shorter the analysis time, the smaller the injected volume allowed. This decrease is more critical for a circular than for a rectangular column with $\phi = 16$, because at these short analysis times the heating effect becomes the parameter controlling efficiency of separation. On the other hand, unlike Figure 9, a clear difference between rectangular capillaries $\phi = 6, 8$ and 16 appears at Figure 10. This difference is easily explained because, while in Figure 9 the electric field was considered constant, in this case it is variable. Again, under these conditions and for the same cross sectional area, the larger the ϕ ratio, the better the heating dissipation achieved.

Conclusions

In this paper we have examined the effect of capillary geometry, i.e. rectangular and cylindrical columns, on heating effect, analysis speed, efficiency and sample capacity. It has been shown that if the same cross sectional area is employed for both type of columns, and always considering $\phi \gg 1$, the main advantage of using rectangular capillaries is their higher analysis speed as result of their better heat dissipation. If both geometries are compared in terms of sample capacity it has been demonstrated that, for the same electric field and efficiency, larger cross-sectional areas can be used with rectangular geometries, providing higher sample capacities than cylindrical one. Additionally the advantages of employing rectangular columns increase when the ϕ ratio increases. However, in this case the limitation derived for the construction of too-narrow rectangular capillaries has to be taken into account. Finally, in both cases the relation between injected volume and analysis speed is better when employing rectangular geometries which makes this type of column a very useful tool for CE micropreparative purposes.

We are currently carrying out different investigations employing cylindrical and rectangular capillaries in order to study the influence and relation of these parameters.

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Appendix

An estimate of the additional zone broadening that arises from the non-infinite dimension in the y-direction (direction in which the channel has its largest dimension) can be obtained as follows:

As derived i.a. by Taylor [26] and Aris [25, 27], the flow-induced dispersion can be expressed as

$$D_t = \frac{\kappa_{\text{Aris}} \bar{u}^2 d^2}{D_m} \quad (22)$$

where D_t is the dispersion coefficient, d is some convenient characteristic length in the cross-section of the channel, e.g. the radius or diameter for a cylindrical channel, D_m is the diffusion coefficient and, $\bar{u}$ is the average velocity in the channel. κ_{Aris} is a numerical constant, the value of which depends on the geometry and the flow profile in the channel, and on the choice of the characteristic length. E.g. for cylindrical channels with the radius as d , κ equals $1/48$ [26]; for infinitely wide slits taking $2a$ as the height, κ equals $2/105$ [24, 25].

In our case we have a channel of height $2a$ and width $2b$, as defined in the main text. We choose a as the characteristic length. Without loss of generality one can make D_m equal to one and a equal to one. We define $\phi = b/a = b$. The coordinates used are x ($-1 \dots 1$) in the "a" direction, y ($-\phi \dots \phi$) in the "b" direction and z in the direction of migration.

The migration velocity profile developed in CE due to thermal non-uniformity in the lumen is similar to that in pressure driven laminar flow. The derivations given below therefore apply to both cases. However, the form of Eq. (22) is somewhat inconvenient for the CE case, as the value of $\bar{u}$ (the migration velocity increase averaged over the lumen) is not directly accessible, experimentally, as is the average velocity a tube. It is therefore more convenient to express the velocity $u(x, y)$ and $\bar{u}$ in the "force" that brings it about, being the pressure gradient in the flow case and the thermal dissipation in the CE case. One has:

$$\frac{d^2 u}{dx^2} + \frac{d^2 u}{dy^2} = C = \text{"Force"}, \text{ as DE,} \quad (23)$$

differential equation with $u(\text{wall}) = 0$, as BC, boundary condition

for both cases, the difference being that:

$$C = \frac{1}{\eta} \frac{dP}{dz} \quad \text{for the flow case} \quad (24)$$

$$C = \frac{W \beta \mu E}{k_1} \quad \text{for the CE case}$$

where u is the velocity of the liquid in the case of pressure induced flow, the migration velocity in the case of thermally disturbed CE, P is the pressure, z is the coordinate in the direction of migration, W is power dissipated in CE per unit volume, k_1 is the thermal conductivity of the running buffer, E is the electric field strength, β is the relative thermal coefficient of the electrophoretic mobility, $\beta = (d\mu/dT)/\mu$, and μ is the mobility of the ion considered.

Eq. (23) determines $\bar{u}$, by:

$$\bar{u} = \gamma C d^2 \quad (25)$$

γ being another numerical factor, describing the permeability in the case of pressure driven flow, e.g. 1/8 for a cylinder. Instead of using Eq. (22), normalizing on the average migration velocity, $\bar{u}$, one can also normalize the dispersion on the "driving force", C , and write instead of Eq. (22):

$$D_f = \frac{C^2 d^6 \kappa_{\text{Virtanen}}}{D_m} \quad (26)$$

with

$$\kappa_{\text{Aris}} = \frac{\kappa_{\text{Virtanen}}}{\gamma^2} \quad (27)$$

The purpose of this appendix is therefore to calculate or estimate the values of γ , κ_{Aris} , and κ_{Virtanen} . One has to start with the velocity profile to obtain γ .

The migration velocity profile in the rectangular channel can be calculated to be (leaving out the constant (C in Eq. (23)) which is to be inserted later):

$$u(x, y) = \frac{1 - x^2}{2} - 16 \sum_{j=1,3,5,\dots}^{\infty} \frac{(-1)^{\frac{j-1}{2}} \cos\left(\frac{j\pi x}{2}\right) \cosh\left(\frac{j\pi y}{2}\right) \operatorname{sech}\left(\frac{j\pi \phi}{2}\right)}{(j\pi)^3} \quad (28)$$

This expansion is different from that applied by Golay [24]; he used a sum of products of cosines, which in itself is a particular solution of the DE (Eq. (23)), satisfying the BC (Eq. (23)). In Eq. (28) on the contrary, we start with the particular solution $1/2(1 - x^2)$, that does satisfy the BC at the edge $x = \pm 1$, but not the BC at the edge $y = \pm \phi$. The latter is taken care of by the general solution term consisting of the infinite sum. The present approach leads to a faster convergence of the series sum. Discussing the BC in Eq. (23) in more detail: they are fulfilled by Eq. (28); for $x = \pm 1$ the cos-terms are zero; for $y = \pm \phi$ the cosh sech product is 1. The resulting simple sum of cos-terms converges to the quadratic expression in the first part of Eq. (28), with an end result zero, so that the BC at $y = \pm \phi$ is also satisfied.

Some profiles calculated with Eq. (28) are shown in Figure 11. For values of $\phi > 5$ it is clearly seen that the

Figure 11
Migration velocity profiles in rectangular channel calculated with equation 28 for $x = \pm 1$ and $y = \pm \phi$. In (A) $\phi = 6$ employed, and $\phi = 1$ in (B).

Figure 12

Velocity profiles in y-direction calculated with equation 30 ("one-term") and employing extended 10-term expression ("10-terms"). In both cases $\phi = 6$ used. "one-term" line drawn with shift of 0.03 to improve visibility of figure.

migration rate is virtually constant over most of the y-range; only close to the borders $y = \pm \phi$ one finds a decreased velocity. In the mid-range the infinite sum of Eq. (28) can be neglected, one finds the parabolic profile as would be found for an infinitely wide channel, with infinite ϕ .

We now find a general estimate of the thickness of the disturbed region by considering the infinite sum: Inspection of the numerical results make clear that the first term in the expansion in Eq. (28), $\cosh(\pi/2x)$ is predominant; for $y = \pm \phi$ it constitutes approximately 90 % of the sum; for other y values even more. The thickness of the disturbance thus is described with good accuracy by the first cosh sech product ($j = 1$) in Eq. (28):

$$u(x, y) \approx \frac{1 - x^2}{2} - 16 \frac{\cos\left(\frac{\pi x}{2}\right) \cosh\left(\frac{\pi y}{2}\right) \operatorname{sech}\left(\frac{\pi \phi}{2}\right)}{\pi^3} \quad (29)$$

Next, the problem is approximated as one-dimensional instead of two-dimensional by declaring the variation of migration with x unimportant for dispersion. Although the migration velocity in itself varies from zero to about 1.5 times the average velocity, the effect of this non-uniformity on dispersion is small at large values of ϕ because of the relatively fast equilibration in the x-direction. Thus, a one-dimensional channel cross-section is treated with a velocity profile $\langle u \rangle(y)$ (follow-

ing from the integration to x of Eq. (29) and division by 2 to take the average):

$$\langle u \rangle(y) = \frac{1}{3} - 32 \frac{\cosh\left(\frac{\pi y}{2}\right) \operatorname{sech}\left(\frac{\pi \phi}{2}\right)}{\pi^4} \quad (30)$$

Figure 12 shows the $\langle u \rangle(y)$ -profile according to Eq. (30) and the one calculated for a 10-term expression. It is seen that there is hardly any difference (the one-term expression has been plotted with a shift of 0.03, to improve visibility of the lines).

With this approximation of the velocity profile the elegant treatment by Aris [25], can be applied. Readers interested in all details should consult this paper. Briefly, the treatment consist of finding the numerical factor, κ_{Aris} , for the flow-induced dispersion (Eq. (22)), by means of the following steps:

1. A velocity $u_r(y)$ relative to $\bar{u}$ is defined:
 $u_r(y) = u(y) - \bar{u}$.

2. $u_r(y)$ is used, via

$$\frac{d^2 c^{(1)}(y)}{dy^2} = u_r(y) \quad (31)$$

to find the change of $c^{(1)}$, the first position moment at position y, with y, taking into account for $c^{(1)}$ the same boundary conditions (derivative zero at $y = \pm \phi$) must hold as for the concentration itself.

3. The product $c^{(1)}(y) \cdot u_r(y)$ is averaged over the cross-section, i.e. integrated (to give I) and divided by the cross sectional area:

$$\kappa_{\text{Virtanen}} = \frac{\int_{-\phi}^{+\phi} c^{(1)}(y) u_r(y) dy}{2\phi} = \frac{I}{2\phi} \quad (32)$$

For one-dimensional cross-sections we used a convenient short-cut for steps 2 and 3: The integral:

$$I = \int_{-\phi}^{+\phi} c^{(1)}(y) u_r(y) dy \quad (33)$$

can be converted by partial integration, and using the fact that $dc^{(1)}/dy$ has to be zero at the boundaries into:

$$I = \int_{-\phi}^{+\phi} [Pv(y)]^2 dy \quad (34)$$

where $Pv(y)$ equals

$$Pv(y) = \int_{-\phi}^y u_r(y') dy' \quad (35)$$

so that the computation of $c^{(1)}(y)$ is not actually needed.

Table II. Average velocity ($\bar{u}$), κ_{Virtanen} und κ_{Aris} for various values of ϕ .

ϕ	$\bar{u}$	κ_{Virtanen}	κ_{Aris}
1.00000	0.141523	0.00030543	0.0152496
1.41421	0.188890	0.000968935	0.0271568
2.00000	0.229155	0.00229981	0.0437959
2.82843	0.259413	0.00422565	0.0627929
4.00000	0.281049	0.00635302	0.0804293
5.65685	0.296363	0.00830389	0.094544
8.00000	0.307191	0.00991249	0.105043
11.3137	0.314848	0.0111647	0.112627
16.0000	0.320262	0.0120175	0.118043
22.6274	0.324091	0.0128028	0.121891
32.0000	0.326798	0.0133088	0.124618
45.2548	0.327712	0.0136738	0.126549
64.0000	0.330066	0.0139355	0.127915
90.5097	0.331023	0.0141223	0.128881
128.000	0.331699	0.0142553	0.129564
181.019	0.332178	0.0143498	0.130048
256.000	0.332516	0.0144168	0.13039
362.039	0.332756	0.0144643	0.130631
512.000	0.332925	0.014498	0.130802
724.077	0.333045	0.0145218	0.130923
1024.000	0.333129	0.0145387	0.131008
1448.15	0.333189	0.0145506	0.131069
2048.00	0.333231	0.014559	0.131112
2896.31	0.333261	0.014565	0.131142
4096.00	0.333282	0.0145692	0.131163
5792.62	0.333297	0.0145722	0.131178
8192.00	0.333308	0.0145743	0.131189

For our particular case, described by Eq. (29), one gets:

$$\bar{u} = \frac{\int_{-\phi}^{+\phi} \langle u \rangle(y) dy}{2\phi} = \frac{1}{3} - \frac{64 \tanh\left(\frac{\pi\phi}{2}\right)}{\phi\pi^5} \quad (36)$$

and for our choice $C = 1$, $d = a = 1$, $\gamma = \bar{u}$.

It remains to carry out the procedure described under 1), 2) and 3) above. Without going into the details we will only state that the numerical evaluation had to be applied only after an explicit expression for the integral I mentioned under 3) above was found.

The results are given in Table II, for various values of ϕ . The numbers in Table II do not include the dispersion caused by the non-uniformity in the x-direction. For an infinitely wide slit this is equal to $\Delta\kappa_{\text{Aris}} = 2/105 = 0.019$. An amount of this order of magnitude (but not precisely that, because the effects are not independent; the solution of the various DE's

Table III. Virtanen values and velocity factors depending on number of terms used for Eq. (26).

Virtanen values				
ϕ	1 Term	2 Terms	3 Terms	5 Terms
1.00000	0.00030543	0.000315176	0.000316144	0.000316397
1.41421	0.00096893	0.000989712	0.000991586	0.000992057
2.00000	0.00229981	0.00233572	0.00233878	0.00233953
2.82843	0.00422565	0.00427826	0.00428258	0.00428363
4.00000	0.00635302	0.00642127	0.00642676	0.00642809
5.65685	0.00830389	0.00838527	0.00839175	0.00839331
8.00000	0.00991249	0.0100042	0.0100115	0.0100132
11.3137	0.0111647	0.0112642	0.0112721	0.0112739
16.0000	0.0121075	0.0122128	0.0122211	0.0122231
22.6274	0.0128028	0.0129124	0.012921	0.012923
32.0000	0.0133088	0.0134215	0.0134303	0.0134324
45.2548	0.0136738	0.0137886	0.0137976	0.0137997
64.0000	0.0139355	0.0140519	0.0140609	0.0140631
90.5097	0.0141223	0.0142398	0.014249	0.0142512
128.000	0.0142553	0.0143736	0.0143828	0.014385
181.019	0.0143498	0.0144686	0.0144779	0.0144801
Velocity factor γ				
ϕ	1 Term	2 Terms	3 Terms	5 Terms
1.00000	0.141523	0.140662	0.14056	0.14058
1.41421	0.18889	0.188281	0.188234	0.188222
2.00000	0.229155	0.228724	0.228691	0.228683
2.82843	0.259413	0.259108	0.259085	0.259079
4.00000	0.281049	0.280834	0.280818	0.280814
5.65685	0.296363	0.296211	0.296199	0.296196
8.00000	0.307191	0.307084	0.307075	0.307073
11.3137	0.314848	0.314772	0.314766	0.314765
16.0000	0.320262	0.320208	0.320204	0.320203
22.6274	0.324091	0.324053	0.32405	0.324049
32.0000	0.326798	0.326771	0.326769	0.326768
45.2548	0.328712	0.328693	0.328692	0.328691
64.0000	0.330066	0.330052	0.330051	0.330051
90.5097	0.331023	0.331013	0.331012	0.331012
128.000	0.331699	0.331693	0.331692	0.331692
181.019	0.332178	0.332173	0.332173	0.332173

leads to coupling between x and y) is to be added to the numbers in column 4 of Table II. Thus for large ϕ the value of $\kappa_{\text{Aris}} = 0.1311 + 0.019 = 0.151$; a value nearly coincident with the result found by Golay [24] and as used in equation 13 of the main text.

For smaller values of ϕ the addition of the value, 0.019, to the values of Table II becomes increasingly problematic. This is the case in the first place since the relative importance of this value increases, e.g. for $\phi = 1$ the original (y -)term, 0.0152, is smaller than the correction. In the second place, when ϕ becomes small there is an increasingly large inaccuracy in treating the transport in the x and y direction as being independent. Unfortunately we did not succeed in applying the Aris approach for finding κ values in two dimensions, so that there is still uncertainty about the κ values at low ϕ .

Fortunately, the most interesting and important cases involve just the large ϕ values, e.g. preparative CE in rectangular "tubes", as considered in this paper, or in the use of rectangular slits in micromachined silicon, glass or quartz. In all these cases large ϕ values appear to promise the best performance and the values of $\kappa = 0.151$ may be used with confidence in these cases.

Another point of uncertainty in the figures in Table II is in the accuracy loss resulting from neglecting the higher terms in the series expansion of Eq. (28). This problem is fortunately within our capabilities. We carried out the scheme 1) ... 3) mentioned above, but starting from the expression Eq. (28), truncating the series at various values of j . Again, only in the last part of this calculation was it necessary to resort to numerical methods. Some typical results are given in Table III. As can be seen, neglecting the second and higher terms on the trigonometric expansion of Eq. (28) does not lead to any significant inaccuracies.

Glossary of Symbols

- a = half rectangular column thickness, (m)
- b = half width of rectangular column, (m)
- c = concentration of electrolyte, (mol m^{-3})
- d = wall thickness of rectangular column, (m)
- D_m = diffusion coefficient, ($\text{m}^2 \text{s}^{-1}$)
- E = electric field strength, (V m^{-1})
- H = plate height, (m)
- $\langle H \rangle$ = apparent plate height, (m)
- H_d = plate height related to molecular diffusion, (m)
- H_{inj} = plate height related to injection, (m)
- H_l = plate height related to Joule heat, (m)
- H_{ct} = plate height into circular column related to Joule heat, (m)
- H_{rt} = plate height into rectangular column related to Joule heat, (m)
- k_1 = thermal conductivity of electrolyte, ($\text{W m}^{-1} \text{K}^{-1}$)
- k_2 = thermal conductivity of wall material, ($\text{W m}^{-1} \text{K}^{-1}$)

- L = column length (in this study is equal to separation length), (m)
- R_1 = external radius, (m)
- R_2 = internal radius, (m)
- S_{col} = internal cross sectional area of column, (m^2)
- t_m = analysis time, (s)
- T_{C2} = temperature of circular column at a distance x ($R_2 \geq x \geq 0$) from centre, (K)
- T_m = temperature of rectangular and circular columns at wall exterior, (K)
- T_{R2} = temperature of rectangular column at a distance x ($a \geq x \geq 0$) from centre, (K)
- ΔT = difference of temperature between wall exterior and the centre of column, (K)
- u = velocity of eluent, (m s^{-1})
- Δu = mean velocity excess in column when self-heating present, (m s^{-1})
- V_{inj} = injected volume, (m^3)
- W_v = power dissipation per unit volume of column, (W m^{-3})
- β = relative thermal coefficient of the electrophoretic mobility, ($d\mu/dT)/\mu$, (K^{-1})
- ϕ = $2b/2a$
- λ = molar conductivity, ($\text{m}^2 \Omega^{-1} \text{mol}^{-1}$)
- μ = global electrophoretic mobility of solute, ($\text{m}^2 \text{s}^{-1} \text{V}^{-1}$)
- σ_{ct}^2 = electrophoretic band dispersion into circular column related to Joule heat, (m^2)

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