



# A method-of-moments formulation for describing hydrodynamic dispersion of analyte streams in free-flow zone electrophoresis



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## ABSTRACT

In this work, a method-of-moments formulation has been presented for estimating the dispersion of analyte streams as they migrate through a free-flow zone electrophoresis (FFZE) channel under laminar flow conditions. The current analysis considers parallel-plate based FFZE systems with an applied pressure-gradient along the channel length for sample and carrier electrolyte transport, and an external electric field in the transverse direction for enabling the electrophoretic separation. A closed-form expression has been derived using this mathematical approach for describing the spatial variance of sample streams as a function of their position in the separation chamber at steady state. This expression predicts that the hydrodynamic dispersion component in an FFZE assay scales as  $Pe_x^2$  where  $Pe_x$  denotes the Péclet number based on the analyte's transverse electrophoretic migration velocity rather than its longitudinal pressure-driven flow speed as expected in transport processes induced by a pressure-gradient. Interestingly however, the coefficient multiplying this dimensionless group, i.e.,  $1/210$ , is identically equal to the constant preceding the square of the relevant Péclet number in the latter case (i.e., Péclet number based on the longitudinal flow speed). It must be noted that while the mathematical analysis reported in this work is only valid for FFZE systems in the absence of any unwanted Joule heating, pressure-driven cross-flow and/or differences in the electrical conductivity between the sample and carrier electrolyte, it can also be applied to numerically estimate the effect of these factors on the separation resolution of the assay.

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## 1. Introduction

Free-flow zone electrophoresis (FFZE) is an important liquid phase separation method that allows for continuous fractionation of charged species based on their electrophoretic mobilities in the system [1,2]. This technique has been successfully applied to a wide variety of samples ranging from small metabolites to large biological cells owing to its high throughput of the analyte species and reliance on relatively gentle operating conditions [3,4]. More recently, the FFZE assay has been integrated to other analytical procedures on the microfluidic platform significantly improving its ability to analyze complex mixtures [5–8]. The miniaturization of FFZE separations to micrometer sized compartments has further enhanced the performance of this assay by reducing Joule heating

effects, allowing the injection of narrow sample streams as well as minimizing the hydrodynamic dispersion of analyte zones [9–11].

The FFZE technique is commonly practiced by continuously introducing a sample mixture into the separation channel along with a co-current flow of a carrier electrolyte using pressure-drive [12–18]. These liquid streams are subjected to a transverse electric field as they travel through the system in order to then deflect the constituent analytes in the sample away from the direction of the pressure-driven transport. Consequently, analyte zones that exit the separation channel at different lateral positions are formed enabling the desired fractionation. As with any other separation method, the widths of these analyte zones broaden during their passage through the FFZE channel [19–22]. Such broadening inherently occurs due to molecular diffusion orthogonal to the flow direction of the analyte zone as well as the parabolic shape of the pressure-driven velocity field across the channel depth [23–27]. In addition, non-idealities such as Joule heating, differences in the electrical conductivity between the sample and carrier electrolyte (electromigration dispersion) and/or pressure-driven cross-flow arising from complete/partial blockage of electroosmotic transport by the channel side-walls (electrodynamic distortion) [28–30]

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further aggravate this process deteriorating the resolving power of the assay [2,31]. While the contribution to stream broadening due to molecular diffusion orthogonal to the flow direction is relatively simple to estimate, the hydrodynamic dispersion component and those arising from the non-idealities in the system rely on a complex interplay between the local streamline velocity and analyte diffusion across these streamlines [23–27]. Unfortunately, no rigorous theoretical approaches currently exist in the literature that can quantitatively describe the latter kinds of dispersion phenomena, although some simplified analyses of these processes have been reported previously based on the moving boundary theory [32–34]. In this article, we attempt to fill such a gap in knowledge by presenting a mathematical formulation of the stream dispersion problem in FFZE assays based on the method-of-moments approach. The reported formulation has been later applied to derive a closed-form expression for the steady state spatial variance of analyte zones as a function of their location in an FFZE channel in the absence of any non-idealities in the system. This expression predicts that the hydrodynamic dispersion component in an FFZE assay scales as  $Pe_x^2$  where  $Pe_x$  denotes the Péclet number based on the analyte's transverse electrophoretic migration velocity rather than its longitudinal pressure-driven flow speed as expected in transport processes induced by a pressure-gradient. Interestingly however, the coefficient multiplying this dimensionless group, i.e.,  $1/210$ , is identically equal to the constant preceding the square of the relevant Péclet number in the latter case (i.e., Péclet number based on the longitudinal flow speed) [35]. It is important to point out that while the current analysis ignores the effects of various non-idealities such as Joule heating, pressure-driven flow across the channel width and/or differences in the electrical conductivity between the sample and carrier electrolyte, the method-of-moments approach outlined in this work can also be applied to numerically estimate the influence of these unwanted factors on the separation performance of the assay.

## 2. Mathematical formulation

To evaluate sample dispersion in an FFZE system, we consider the flow of an analyte stream between two parallel plates separated by a distance  $d$  (see Fig. 1) under the influence of a pressure-driven flow in the axial direction (along the  $z$ -coordinate) and an electric field ( $E$ ) applied across the width of the separation chamber (along the  $x$ -coordinate). In order to simplify our mathematical analysis, we assume the locations of the parallel plates to be  $y = \pm d/2$  yielding a pressure-driven velocity profile  $u_p = (3\bar{U}/2)(1 - (4y^2/d^2))$  with  $\bar{U}$  being the spatially averaged value of  $u_p$ . The advection–diffusion equation governing the concentration of the sample species ( $C$ ) in this situation may be written as

$$\mu E \frac{\partial C}{\partial x} + \frac{3\bar{U}}{2} \left(1 - \frac{4y^2}{d^2}\right) \frac{\partial C}{\partial z} = D \left( \frac{\partial^2 C}{\partial x^2} + \frac{\partial^2 C}{\partial y^2} + \frac{\partial^2 C}{\partial z^2} \right) \quad (1)$$

where  $\mu$  and  $D$  refer to the net electrokinetic mobility (algebraic sum of the electrophoretic and electroosmotic mobilities) and diffusion coefficient of the analyte molecules, respectively. Upon normalizing all length scales with respect to  $d$ , i.e.,  $x^*, y^*, z^* = x/d, y/d, z/d$ , and the sample concentration by its inlet value ( $C_0$ ), i.e.,  $C^* = C/C_0$ , Eq. (1) may be reduced to the dimensionless form

$$Pe_x \frac{\partial C^*}{\partial x^*} + \frac{3}{2} Pe_z (1 - 4y^{*2}) \frac{\partial C^*}{\partial z^*} = \frac{\partial^2 C^*}{\partial x^{*2}} + \frac{\partial^2 C^*}{\partial y^{*2}} + \frac{\partial^2 C^*}{\partial z^{*2}} \quad (2)$$

The quantities  $Pe_x = \mu Ed/D$  and  $Pe_z = \bar{U}d/D$  here denote the Péclet numbers in the  $x$  and  $z$ -directions, respectively, yielding measures of advective transport relative to diffusion along the width and length of the separation compartment. The analyte concentration in this system is subjected to the boundary conditions

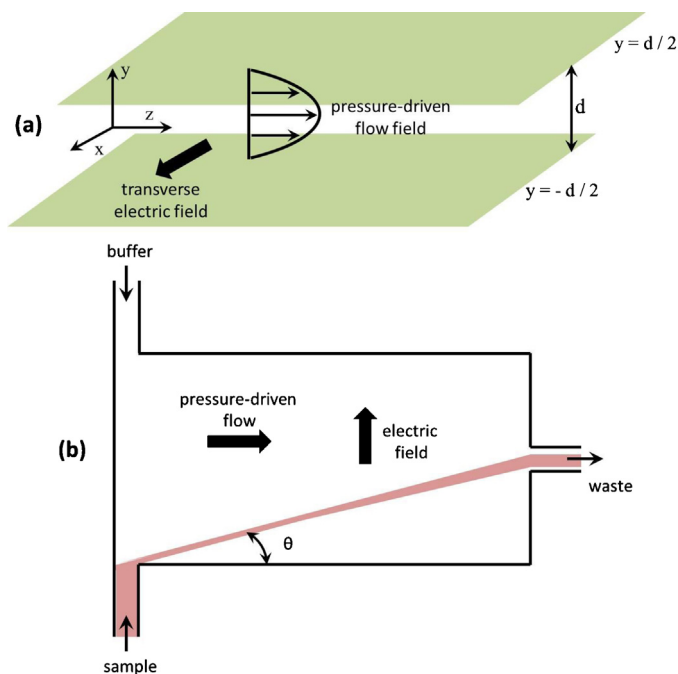


Fig. 1. (a) Schematic of the FFZE fractionation process between two parallel-plates as described in this article. (b) Top view of a microfluidic FFZE device relevant to the mathematical analysis presented in this work.

$\partial C^*/\partial y^* = 0$  at  $y^* = \pm 1/2$ ,  $C^*, \partial C^*/\partial x^* = 0$  as  $x^* \rightarrow \pm \infty$  and  $C^* = 1$  at  $z^* = 0$ ,  $-b/2d \leq x^* \leq b/2d$  where  $b$  denotes the width of the sample stream at the inlet location ( $z^* = 0$ ). In addition to these constraints, the amount of analyte flowing per unit time through any  $x - y$  plane is a constant in the system and equals its value at the inlet of the separation chamber. Mathematically, this condition may be expressed as  $\int_{-1/2}^{1/2} \int_{-\infty}^{\infty} (1 - 4y^{*2}) C^* dx^* dy^* = 2b/3d = 2\delta/3$ . Now multiplying Eq. (2) with  $x^{*p}$  followed by integrating it along the  $x^*$ -coordinate from  $-\infty$  to  $\infty$ , it is possible to show that [35]

$$\frac{3}{2} Pe_z (1 - 4y^{*2}) \frac{\partial \phi_p}{\partial z^*} - p Pe_x \phi_{p-1} = p(p-1) \phi_{p-2} + \frac{\partial^2 \phi_p}{\partial y^{*2}} + \frac{\partial^2 \phi_p}{\partial z^{*2}} \quad (3)$$

Boundary conditions :  $\left. \frac{\partial \phi_p}{\partial y^*} \right|_{y^* = \pm 1/2} = 0$ ;  $\phi_0|_{z^*=0} = \delta$ ;

$$\int_{-1/2}^{1/2} (1 - 4y^{*2}) \phi_0 dy^* = \frac{2\delta}{3}$$

where  $\phi_p = \int_{-\infty}^{\infty} x^{*p} C^* dx^*$ . Further integrating Eq. (3) along the  $y^*$ -coordinate over the region between the parallel plates and defining  $m_p = \int_{-1/2}^{1/2} \phi_p dy^*$  one can obtain

$$\frac{3}{2} Pe_z \int_{-1/2}^{1/2} \left[ (1 - 4y^{*2}) \frac{\partial \phi_p}{\partial z^*} \right] dy^* - p Pe_x m_{p-1} = p(p-1) m_{p-2} + \frac{d^2 m_p}{dz^{*2}} \quad (4)$$

with  $m_0|_{z^*=0} = \delta$ ,  $m_1|_{z^*=0} = 0$  and  $m_2|_{z^*=0} = \delta^3/12$ . Notice that the quantity  $m_p$  in this formulation represents the  $p$ th moment of  $C^*$  in any  $x - y$  plane with  $m_1$  representing the normalized  $x^*$ -position of the center of mass for the analyte stream and the quantity  $m_2/m_0 - m_1^2/m_0^2$  equaling its normalized spatial variance along the  $x$ -axis.

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