Flow injection analysis simulations and diffusion coefficient determination by stochastic and deterministic optimization methods

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HIGHLIGHTS

• Former random walk approach for FIA simulations has been improved.
• Random walk and uniform dispersion models have been used for FIA simulations.
• Diffusivities have been optimized by genetic and the Levenberg–Marquardt methods.
• Both approaches have given similar results in agreement with experimental ones.

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GRAPHICAL ABSTRACT

ABSTRACT

Stochastic and deterministic simulations of dispersion in cylindrical channels on the Poiseuille flow have been presented. The random walk (stochastic) and the uniform dispersion (deterministic) models have been used for computations of flow injection analysis responses. These methods coupled with the genetic algorithm and the Levenberg–Marquardt optimization methods, respectively, have been applied for determination of diffusion coefficients. The diffusion coefficients of fluorescein sodium, potassium hexacyanoferrate and potassium dichromate have been determined by means of the presented methods and FIA responses that are available in literature. The best-fit results agree with each other and with experimental data thus validating both presented approaches.

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1. Introduction

Flow injection analysis (FIA) is used for a quantitative determination of solutions composition [1–3]. The method is based on an injection of a sample solution into a flowing carrier, where controllable dispersion and generation of a reproducible signal at a detector occur [1–3]. The method is known for its accuracy, reproducibility and sample throughput. According to Kolev [4], modeling of FIA can be classified as “black box” and analytical–experimental models. The main drawbacks of the first group are narrow applicability area, trial-and-error method used for their development and inability to allow deeper insight into physics and chemistry of the process [4]. The second group is free from the above restrictions, however requires more complex mathematical treatment. There are two parameters that can be used for characterizing of the Poiseuille (steady-state laminar) flow in the cylindrical channels: the Fourier number \( \tau = D t_m/r_0^2 \) and the Peclet number \( Pe = 2r_0/D \) (\( D \) denotes the diffusion coefficient, \( t_m \) – the mean residence time, \( r_0 \) – the channel radius and \( \tau \) – the mean fluid velocity). Among the deterministic models, the analytical solutions of the convection–diffusion problem [5,6] are the most attractive, however these are applicable to terminal
situations: (i) the negligible molecular diffusion, for \( \tau < 0.002 \) or (ii) the molecular diffusion dominating overall dispersion, for \( \tau > 0.8 \). According to Vanderslice et al. [7], in the region of an experimental interest (defined by the numbers: \( \text{Pe} > 1000 \) and \( 0.002 < \tau < 0.8 \)) only numerical solutions of the diffusion–convection equation are valid. The most advanced approach for describing FIA systems is the general dispersion model, in which the Navier–Stokes equations are applied for fluid dynamics simulations. The approach was used by Akker et al. to model \( \mu \)-FIA systems [8,9] and exploited later by Sokalski et al. [10]. The uniform dispersion model is a special case of the general model, in which the Navier–Stokes equations are approximated using the computational fluid dynamics (CFD) method for the numerical solution. The Navier–Stokes equations stated above were solved using commercial CFD software.

Regarding the dispersion processes, for \( \tau > 0.8 \) the advantage of this approach is the existence of the Taylor's analytical solution of the diffusion–convection equation. The methods of determination of diffusion coefficients that are based on these three methods possess different advantages and limitations. By using the analytical solution two approaches were proposed: the statistical moments method by Reijn et al. [12] and curve fitting by Kolev et al. [13,14]. In the first method the means and variances of the concentration at different distances are determined by assuming the following assumptions: (i) the transient period is much shorter than the mean residence time [4,10]. For a determination of diffusion coefficients from FIA responses two different optimization methods are used: the genetic algorithm for random walk model and the Levenberg–Marquardt method in the case of the uniform dispersion model. There are no papers in literature presenting such approaches. The versatility of these methods is demonstrated for the determination of diffusion coefficients on the grounds of the experimental FIA responses obtained by Vanderslice et al. [7], Wentzell et al. [18] and Parab et al. [19].

2. Theory

Dispersion of a sample solution is controlled by the molecular diffusion and convection. It depends on a flow rate of a carrier solution, channel dimensions and a diffusion coefficient. The following conditions are assumed to simplify the convection–diffusion problem: (i) a solution of low concentration is injected into a flowing carrier stream in (ii) a cylindrical channel of constant cross-section width where (iii) a steady-state laminar flow occurs. Regarding the last assumption, investigations show that the transient period before the steady-state flow is reached much faster than the mean residence time [4]. The numerical results obtained by Sokalski et al. also confirm this assumption [10]. The first condition allows assuming a constant (independent of concentration) diffusion coefficient, whilst assumptions (ii) and (iii) result in the parabolic velocity profile:

\[
v = 2\bar{v} \left( 1 - \left( \frac{r}{r_0} \right)^2 \right)
\]

where \( \bar{v} \) is the average carrier velocity, \( r \) is the distance from the center of the channel and \( r_0 \) is the channel radius.

2.1. Random walk model

The random walk model presented by Betteridge et al. [20] and exploited later by Wentzell et al. [18] considers a sample solution as a number of individual molecules that take random steps (dependent on the diffusion coefficient) and are translated downstream due to convection, with velocity given by Eq. (1). According to Kolev [4], the main drawbacks of this approach are the discrepancy with the experimental results in quantitative aspect and the statistical noise in the simulated FIA responses. Two assumptions made in previous works are improved in this paper. Instead of a uniform distribution for distance steps in \( x, y \) and \( z \) directions (between \( -2\sqrt{\Delta t} \) and \( 2\sqrt{\Delta t} \)), the normal distribution with the standard deviation \( \sqrt{2\Delta t} \) is presented, that conforms to the diffusion equation solution. The second modification concerns determination of concentrations. Formerly the FIA responses were determined by counting molecules passing through the detector, however in this way a flux-related quantity is determined. Now this is replaced by determination of concentrations in agreement with the equation \( c = f/v \) (\( v \) is a molecule velocity in the moment of passing through the detector). Presently applied smoothing minimizes the statistical noise that is inherent in random walk model. A critical issue in random walk approach is the diffusion in the neighborhood of walls, here, when new coordinates would place a molecule outside the channel, the transverse coordinates would remain unchanged. The fixed time between iterations is \( r_0^2/2000 \), resulting in a standard deviation of 0.1 \( r_0 \) irrespectively of the diffusion coefficient (this value appeared to be the upper limit when simulated results are independent on time intervals). In all simulations the number of molecules is \( 10^8 \) and a superposition of three lognormal distribution functions is used for smoothing the simulated FIA responses. The illustration of the present modifications in comparison to the original assumptions made by former authors is presented in Fig. 1. For the original assumptions [18,20] the random walk model results deviate quantitatively from the numerical dependence obtained by Vanderslice et al. as well as from the present ones. This confirms the Kolev's reservations [4] regarding the previous random walk model version. The present one gives almost the same results as the uniform dispersion model.

2.2. Uniform dispersion model

The second approach used in this work is similar to the previously applied by Bate et al. [11] and Vanderslice et al. [7]. Under the assumptions (i–iii) the diffusion–convection equation can be written in cylindrical coordinates as:

\[
\frac{\partial c}{\partial t} = \frac{D}{r} \frac{\partial}{\partial r} \left( r \frac{\partial c}{\partial r} \right) + D \frac{\partial^2 c}{\partial r^2} - \nu \frac{\partial c}{\partial \theta}
\]

where \( c \) is the component concentration and \( D \) is its diffusion coefficient.
The Peclet number is a measure of contribution of the convective flow to the total dispersion. According to Koley [4], the axial diffusion can be neglected for $Pe > 1000$, resulting in the following equation:

$$\frac{\partial c}{\partial t} = D \frac{\partial}{\partial r} \left( r \frac{\partial c}{\partial r} \right) - 2D \left( 1 - \frac{r}{r_0} \right)^2 \frac{\partial c}{\partial r} \quad (3)$$

In order to make the present numerical method as efficient as possible, the dispersion process is divided into steps during which the following actions occur: (1) computations of concentration accumulation in the radial direction, (2) translation of nodes in the axial direction according to the flow velocity profile (expressed by Eq. (1)), and (3) determination of the concentration at new nodes by interpolation using cubic-spline (allowing for subsequent integration in the radial direction). Such partitioning speeds up calculations, lowers memory use and allows for adapting a grid to a plug position. The radial diffusion equation is solved numerically using the method of lines (where spatial derivatives are approximated by finite differences according to the central three-point scheme) and the Radau 5 solver. Accumulations in the first and last radial nodes are conformed to the Neumann boundary condition (zero flux at $r = 0$ and $r = r_0$). For the total number of time steps of 200 and 2000 spatial nodes, grid-independent solutions are obtained.

2.3. Optimization

In order to present the usefulness of both approaches, the determination of diffusion coefficients on the grounds of the experimental results [7,18,19] by means of optimization methods is carried out. Simulated responses represent average concentrations in the cross-section at the detector position. The FIA responses computed in the random walk model still have stochastic characteristics; therefore a genetic algorithm [21] is applied that is capable of finding optimal parameters in this case. The initial population consists of 30 individuals with diffusion coefficients distributed uniformly in the logarithmic scale in the range $10^{-10}$–$10^{-8.5}$ m$^2$ s$^{-1}$. Subsequent populations consist of 20 individuals stochastically generated from the ten exhibiting the best fit (least square error). In the case of the uniform dispersion model, the Levenberg–Marquardt method of residuals minimization is used, for which the estimation starts at $10^{-10}$ m$^2$ s$^{-1}$ (an initial value of the diffusion coefficient where optimization starts) for all considered cases. Because the experimental responses published by different authors are expressed in different ways (as concentration, normalized concentrations or absorbance) simulated results are normalized similarly as in the Akker et al. works [8,9]: (numerical response) × (average experimental response)/(average numerical response).

<table>
<thead>
<tr>
<th>Table 1</th>
<th>The experimental FIA conditions [7,18,19] used in simulations and diffusion coefficients determined by the uniform dispersion model coupled with the Levenberg–Marquardt method (UD-LM) and the random walk model coupled with the genetic algorithm (RW–GA) along with respective optimization times.</th>
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<td>Data source</td>
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<td>Vanderslice et al. [7]</td>
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<td>Wentzell et al. [18]</td>
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Fig. 2. The experimental (a, c) and the numerical (b, d) FIA responses obtained by Vanderslice et al. [7] (open circles) and the best fit dependences obtained by the uniform dispersion model (UD-LM) and the random walk model (RW–GA). The FI conditions and the determined values of diffusion coefficient are collected in Table 1 (rows 3–6).

Fig. 3. The experimental FIA responses measured by Wentzell et al. [18] (open circles) and the best-fit dependences obtained by the uniform dispersion model (UD-LM) and the random walk model (RW–GA). The FI conditions and the determined values of diffusion coefficient are collected in Table 1 (rows 7–12).
Stochastic and deterministic simulations as well as optimizations are carried out using programming tools and built-in functions in Mathcad 14 by PTC on a computer with a 2.53 GHz Core 2 Duo processor and 4 GB RAM. The Mathcad files allowing for optimization using both approaches can be obtained free from the author via e-mail.

3. Results and discussion

The determination of diffusion coefficients on the grounds of the experimental results by Vanderslice et al. [7], Wentzell et al. [18] and Parab et al. [19] is carried out. The experimental FI conditions that are used in simulations are collected in Table 1. The determined...
values of diffusion coefficients obtained by the uniform dispersion model and the Levenberg–Marquardt optimization (UD-LM) as well as the random walk model and the genetic algorithm (RW–GA) are presented in columns 7 and 8, respectively, along with optimization times in columns 9 and 10. The experimental FIA responses and the best-fit dependences are presented in Figs. 2–4. For high diffusion coefficient and high residence time, almost symmetrical, Gaussian-like peaks are modeled (e.g. Fig. 4c and d). On the other hand, for low diffusion coefficient and low residence time, non-symmetrical, double-humped peaks are predicted (Fig. 2b and d). This effect is not fully evident in the experimental curves (in Fig. 2a and c) that is probably caused by turbulences generated by pump pulsation or mismatch between tubing and the detector [7].

The optimization results for the experimental and numerical responses obtained by Vanderslice et al. [7] are presented in Table 1 and Fig. 2. The experimental results and the best-fit dependences are presented in Fig. 2a and c, showing a reasonably good agreement. The determined diffusion coefficient (average from Table 1 for cases 2a and c) of fluorescein sodium \((2.6 \times 10^{-10} \text{m}^2 \text{s}^{-1})\) is close to the value determined by Vanderslice et al. \((2.5 \times 10^{-10} \text{m}^2 \text{s}^{-1})\). The numerical results calculated by Vanderslice et al. [7] and the best-fit dependences are presented in Fig. 2b and d. Now, the determined value of diffusion coefficient \((2.3 \times 10^{-10} \text{m}^2 \text{s}^{-1})\) is slightly lower than the one used by Vanderslice et al., which can be attributed to a different numerical procedure (explicit one) used in their calculations [7]. Present numerical results are in very good agreement with the previous ones pointing out the validity of the present methods. The double-humped peaks that are presented in Fig. 2d are caused by high flow rates. The determined Peclet numbers, \(5100 < Pe < 7700\), confirm the negligence of the axial diffusion in the uniform dispersion model. The Fourier numbers determined for these cases, \(0.17 < \tau < 0.26\), exclude use of methods that are based on the Taylor's analytical solutions.

The results obtained by Wentzell et al. [18] and the best-fit dependences are presented in Fig. 3a–f showing a good agreement. The predicted responses show slightly lower residence time and a higher dispersion than the experimental ones. The determined diffusion coefficient (average from Table 1) of potassium hexacyanoferrate \((1.1 \times 10^{-9} \text{m}^2 \text{s}^{-1})\) is higher than that determined by von Stackelberg et al. [22] \((7.6 \times 10^{-10} \text{m}^2 \text{s}^{-1})\). The determined values of diffusion coefficient are independent of tubing material (PTFE for cases presented in Fig. 3a–c and stainless-steel in Fig. 3d–f), however they depend on the flow rate. The reason of this could be the too idealistic assumptions when compared with the experimental conditions. Among them, the assumption of the constant (independent on concentration) diffusion coefficient seems too rough for this multicomponent system (consisting of potassium hexacyanoferrate, potassium chloride and water). The calculated Peclet numbers for these cases, \(7200 < Pe < 14000\), allow neglecting the axial diffusion in the uniform dispersion model. The calculated Fourier numbers, \(0.32 < \tau < 0.72\), once again exclude application of the moments method or curve fitting that base on the axially dispersed plug flow model.

The experimental FIA responses obtained by Parab et al. [19] and the best-fit dependences are presented in Fig. 4a–j. The predicted dependences show slightly higher residence time and a higher dispersion than the experimental ones. The agreement between the actual and the present responses is better than that obtained by Parab et al. [19] using the axial dispersion plug flow model. Discrepancies between experimental and previous theoretical results were attributed by these authors to ‘both transverse mixing and velocity variation effects’ contributing to the total dispersion for the Fourier numbers less than 0.8. Kolev and Pugor [15] shown that in this case experimental dispersion coefficients are lower than those calculated in the axially dispersed plug flow model. The average of diffusion coefficients of potassium dichromate determined presently \((1.9 \times 10^{-9} \text{m}^2 \text{s}^{-1})\) is very close to the values determined by Vacek et al. [23] \((1.5 \times 10^{-9} \text{m}^2 \text{s}^{-1})\) and \((1.8 \times 10^{-9} \text{m}^2 \text{s}^{-1})\). The Peclet numbers for these cases are \(890 < Pe < 4600\). Only in one among the presented cases the Peclet number is lower than 1000: 890 for the case 4i. In this case the diffusion coefficient is redetermined by using Eq. (2) (the uniform dispersion model including the axial diffusion). In this case an additional step (4) is added to the numerical procedure described in Section 2.2: (1) computations of concentration accumulation in the radial direction, (2) translation of nodes in the axial direction according to the flow velocity profile (expressed by Eq. (1)), (3) determination of the concentration at new nodes by interpolation using cubic-spline (allowing for a subsequent integration in the axial and radial directions) and (4) computations of concentration accumulation in the axial direction. Thus the obtained value for the case 4i, \(2.07870 \times 10^{-9} \text{m}^2 \text{s}^{-1}\), is slightly higher than that determined for the neglected axial diffusion, \(2.07858 \times 10^{-9} \text{m}^2 \text{s}^{-1}\). The additional numerical calculations those are required on using, Eq. (2) result in much higher optimization time \(7.8 \times 10^3 \text{s}\). The comparison of the above values shows that the Peclet number range where axial diffusion can be neglected is wider than that suggested by Kolev [4], supporting Bate et al. [11] findings: \(Pe > 100\).

4. Conclusions

Present stochastic and deterministic approaches give almost the same results of the derived diffusion coefficients and the simulated FIA responses that are in good agreement with the experimental ones. Here, it is worth to note that the axial diffusion was neglected only in the case of the uniform dispersion model deterministic one, whilst the random walk model involved diffusion in three directions (also in the axial one). The obtained results confirm the applied assumptions: the negligible axial diffusion for the numerical dispersion model and the normal distribution and the concentration determination for the random walk model. Following other authors [4,11,18], differences between the experimental and the present results can be credited to: changes in channel geometry and cross section area at the detector, coiling and mixing effects giving rise to radial dispersion, non-ideality of solutions, mixing at the tube entrance creating the diffuse and curved interface rather than the sharp plane assumed in simulations. The present methods are general and can be used for the determination of diffusion coefficients in cases where analytical solutions are invalid, offering relatively low computational time and flexibility. The deterministic method presented here can be extended to the binary and multicomponent solutions involving reactions and/or concentrated solutions where the chemical–potential-driven diffusion (chemical diffusion) occurs.

References