Mathematical modeling of micro-extraction mechanism

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Abstract

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1. Mathematical Model and Numerical Method

In this section we will describe a slight modification of the diffusion model proposed by Zhang and Pawliszyn [1] in order to build a numerical model that is adequate for variable discontinuous diffusion processes, such as those encountered in micro-extraction techniques. We first explain in details a general diffusion model, that is actually very well known in the literature (see details LeVeque [2]).

We will assume the full device in which the diffusion process will happen has two uniform dimensions, say y and z, and one dimension (x) for which we have compartments of different sizes.

The main assumption made about the process is that the dominant/relevant diffusion process occurs only in one direction (x), therefore being uniform in the other dimensions (y, z). As a result, we will obtain a model that is independent of the device size in y and z direction.

1.1. Compartmental model

Consider a single compartment of the device to have dimensions (L_x, L_y, L_z). Fick's law assumes that the diffusion flux (J), providing the mass per area unit and per time unit, crossing a section area at a certain position in the x-coordinate and time t, is given by

$$J(x,t) = -D(x)\frac{\partial C(x,t)}{\partial x}, \tag{1}$$

where $C(x,t)$ denotes the concentration of the material (amount of substance per volume) undergoing a diffusion process, at a certain place and time; $D(x)$ denotes the diffusion coefficient (cross section area per time units), which depends on the environment that contains the substance, therefore may be different in different x positions.

We will subdivide the compartment into a set of discrete points. If we define the compartment to be positioned in the interval $[0, L_x]$, we can subdivide it into N sub-intervals of size dx, such that $x_i = i\,dx$, $i = 0, 1, ..., n$ with $dx = L_x/n$. The mass $M_{i+1/2}$ on a sub-interval $[x_i, x_{i+1}]$ of the domain depends only on the lateral fluxes, therefore,

$$\frac{dM_{i+1/2}(t)}{dt} = L_y\,L_z(J(x_i,t) - J(x_{i+1})), \tag{2}$$

where

$$M_{i+1/2}(t) = L_y L_z \int_{x_i}^{x_{i+1}} C(x, t) \, dx, \tag{3}$$

and we have used the notation of $i + 1/2$ so that it is clear that this mass is defined between i and $i + 1$ positions. Also note that the flux in the position x_i has positive sign, as it is indicating inward flow into the compartment, and the flux in the position x_{i+1} has negative sign, since the flow at this point indicates outward flow.

Equation 2 may be re-written, assuming sufficient regularity of the functions, as

$$\int_{x_i}^{x_{i+1}} \frac{\partial C(x, t)}{\partial t} \, dx = - \int_{x_i}^{x_{i+1}} \frac{\partial J(x, t)}{\partial x} \tag{4}$$

where we note that the problem is therefore independent of L_y and L_z. Also, in order to be valid for any interval of the form $[x_i, x_{i+1}]$, it requires that

$$\frac{\partial C(x, t)}{\partial t} = \frac{\partial}{\partial x} \left(D(x) \frac{\partial C(x, t)}{\partial x} \right). \tag{5}$$

If $D(x)$ is independent of x, we arrive at the same familiar equation used in Zhang and Pawliszyn [1]. However, we will assume the media is anisotropic, so that the diffusivity is not constant, as actually happens in the microextraction devices at interfaces of compartments. By using the model proposed in Zhang and Pawliszyn [1], compactly written as $C_t = DC_{xx}$, we can't, in general, expect local mass conservation of the system. However, with the slight change in the model, by considering the divergence of a flux term, as in equation (5), the mass conservation is readily obtained in the interior of the compartment for non constant diffusion processes and we will also insure it at the compartment interfaces.

Without loss of generality, we may assume $L_y = 1$ and $L_z = 1$, as the solution of the problem is independent on these values. Now, the mass variation at an interval $[x_i, x_{i+1}]$ can be written as

$$\frac{dM_{i+1/2}(t)}{dt} = J(x_i, t) - J(x_{i+1}). \tag{6}$$

The diffusion fluxes may be obtained via centred differencing (second order accurate with respect to dx) formula as,

$$J(x_i, t) = -D(x_i) \frac{C_{i+1/2}(t) - C_{i-1/2}(t)}{dx} + O(dx^2). \tag{7}$$

Using the mean concentration instead of the pointwise concentration (a second order approximation in dx),

$$C_{i+1/2}(t) = \frac{1}{dx} \int_{x_i}^{x_{i+1}} C(x, t) \, dx = \frac{1}{dx} M_{i+1/2}(t) + O(dx^2), \tag{8}$$

we may write the approximate diffusion flux as,

$$J(x_i, t) = -D(x_i) \frac{M_{i+1/2}(t) - M_{i-1/2}(t)}{dx^2} + O(dx^2), \tag{9}$$

where the first order $O(dx)$ terms cancel due to the symmetry of the differences (midpoint), resulting in a second order accurate scheme. Therefore, the evolution of the mass in this approximate system is given by

$$\frac{dM_{i+1/2}(t)}{dt} = \frac{D(x_{i+1})M_{i+3/2}(t) - (D(x_{i+1}) + D(x_i))M_{i+1/2}(t) + D(x_i)M_{i-1/2}(t)}{dx^2}, \tag{10}$$

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which is valid in the interior of the domain $i = 1, ..., n - 1$.

At the boundaries of the compartment ($x_0 = 0$ and $x_n = L_x$) we may enforce one of two boundary conditions of interest:

(i) A flux condition, defining an exact value of $J(x_0, t)$ or $J(x_n, t)$ for all times, also known as Neumann boundary condition. The interesting value for our problem is to set a no flux boundary conditions, which may be imposed by simply forcing $J(x_0, t) = 0$ or $J(x_N, t) = 0$, or, equivalently, that

$$\frac{\partial C(x_0, t)}{\partial x} = 0, \quad \frac{\partial C(x_N, t)}{\partial x} = 0. \tag{11}$$

This condition is useful for if the compartment if the first ($J(x_0, t) = 0$) or last compartment ($J(x_n, t) = 0$), so that the system is closed (conserves mass globally).

(ii) An interface boundary condition, defined when the boundary meets another compartment. At these interfaces we will impose that the concentrations always respect a certain proportion ratio, that is, the limits from left and right of the transition point are such that, for example in case of an interface at point x_n,

$$\lim_{x \to x_n^-} C(x, t) = K \lim_{x \to x_n^+} C(x, t), \tag{12}$$

where K defines the proportionality gap. Additionally, the interface boundary conditions require that $J(x_0^-, t) = J(x_0^+, t)$ or $J(x_n^-, t) = J(x_n^+, t)$, which mean, for example for the point x_n,

$$D(x_n^-)\frac{\partial C(x_n^-, t)}{\partial x} = D(x_n^+)\frac{\partial C(x_n^+, t)}{\partial x}, \tag{13}$$

which basically states that, in the limit, the outward flow of the compartment (x_n^-) matches the inward flow in the adjacent compartment (x_n^+), ensuring mass conservation.

Numerically, these boundary conditions can be enforced with the following approximations:

(i') The no flow condition can be imposed by simply considering either $J(x_0, t) = 0$ or $J(x_n, t) = 0$, so that

$$\frac{dM_{1/2}(t)}{dt} = D(x_1)\frac{M_{3/2}(t) - M_{1/2}(t)}{dx^2}, \tag{14}$$

or

$$\frac{dM_{n-1/2}(t)}{dt} = D(x_{n-1})\frac{M_{n-3/2}(t) - M_{n-1/2}(t)}{dx^2}. \tag{15}$$

(ii') In order to ensure mass conservation in discrete level for the interface boundary condition, we need to have a single diffusion coefficient at the point $D(x_n)$. A usual choice in this case is to have

$$D(x_n) = \frac{D(x_{n-1/2}) + D(x_{n+1/2})}{2}, \tag{16}$$

where $D(x_{n-1/2})$ is the diffusion coefficient at the cell control volume of the compartment and $D(x_{n+1/2})$ will be the diffusion at the fist control volume of the neighbor compartment. At the interface points, we also need to impose the concentration proportion ratio. This implies in a mass proportionality, that may be written, for x_n, as

$$M_{n-1/2} = KM_{n+1/2}. \tag{17}$$

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This means that, when we are at the closest control volume from the left to the transition point, we have

$$\frac{dM_{n-1/2}}{dt} = \frac{D(x_n)M_{n-1/2}/K - (D(x_n) + D(x_{n-1}))M_{n-1/2} + D(x_{n-1})M_{n-3/2}}{dx^2}, \qquad (18)$$

An analogous construction may be built when the interface is at point x_0.

If the diffusion coefficient is known for all points defining the devide, we now can solve the system independently for each compartment. For example, considering a compartment with no flow condition at x_0 and interface at x_n, we have

$$\frac{dM_{1/2}}{dt} = D_1 \frac{M_{3/2} - M_{1/2}}{dx^2},$$

$$\frac{dM_{i+1/2}}{dt} = \frac{D_{i+1}M_{i+3/2} - (D_{i+1} + D_i)M_{i+1/2} + D_iM_{i-1/2}}{dx^2}, \quad i = 1, ..., n-2,$$

$$\frac{dM_{n-1/2}}{dt} = \frac{D_nM_{n-1/2}/K - (D_n + D_{n-1})M_{n-1/2} + D_{n-1}M_{n-3/2}}{dx^2},$$

where $D_i = D(x_i)$. Note that, if $K = 1$, the interface condition recovers the no flow condition, isolating this compartment from the adjacent one.

This is tridiagonal linear differential system. Let $\vec{M}$ denote the vector of masses in the compartment, that is, $\vec{M}(t) = [M_{1/2}(t), M_{3/2}(t), M_{5/2}(t), ..., M_{n-1/2}(t)]$, containing n values. Then the system maybe simply written as

$$\frac{d\vec{M}(t)}{dt} = A\vec{M}(t), \qquad (19)$$

where A is an $n \times n$ matrix given by the diffusion coefficients as

$$A = \frac{1}{dx^2} \begin{pmatrix} -D_1 & D_1 & 0 & 0 & \cdots & \cdots & 0 \\ D_1 & -(D_1 + D_2) & D_2 & 0 & \cdots & \cdots & 0 \\ 0 & D_2 & -(D_2 + D_3) & D_3 & \cdots & \cdots & 0 \\ \vdots & \vdots & \vdots & \vdots & \ddots & \vdots & \\ 0 & \cdots & \cdots & 0 & D_{n-2} & -(D_{n-2} + D_{n-1}) & D_{n-1} \\ 0 & \cdots & \cdots & 0 & 0 & D_{n-1} & -D_{n-1} + (1/K - 1)D_n \end{pmatrix} \qquad (20)$$

For a compartment with interface on the left (K_l) and right (K_r) the system would be defined via the following matrix,

$$A = \frac{1}{dx^2} \begin{pmatrix} -(D_0 + D_1) + K_lD_0 & D_1 & 0 & \cdots & \cdots & 0 \\ D_1 & -(D_1 + D_2) & D_2 & \cdots & \cdots & 0 \\ 0 & D_2 & -(D_2 + D_3) & \cdots & \cdots & 0 \\ \vdots & \vdots & \vdots & \ddots & \vdots & \\ 0 & \cdots & \cdots & D_{n-2} & -(D_{n-2} + D_{n-1}) & D_{n-1} \\ 0 & \cdots & \cdots & 0 & D_{n-1} & -(D_{n-1} + D_n) + D_n/K_r \end{pmatrix}. \qquad (21)$$

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It is easy to see that by setting $K = 1$ recovers the no flux condition. Therefore, in the implementation, the interfaces at the boundary of the device will have a partition constant equal to 1, to ensure no flux condition.

The numerical solution of the time evolution maybe obtained also via finite differences formulas. Given a time span we wish to simulate, say $[0, T]$, we may partition this interval into K time steps, $t_k = k\,dt$, where $dt = T/K$. Let $\vec{M}^k \approx \vec{M}(t_k)$ be an approximate solution of $\vec{M}(t_k)$ at time t_k. An explicit solution of the problem, with first order accuracy with respect to time-step-size (dt), is

$$\vec{M}^{k+1} = \vec{M}^k + dt\,A\vec{M}^k \tag{22}$$

which is the well-known explicit Euler scheme. While this scheme is attractive and easy to implement, it imposes serious stability conditions on the time-step-size,

$$D\frac{dt}{dx^2} < \frac{1}{2}, \tag{23}$$

where D is the maximum diffusion coefficient in the compartment. For small dx, the required dt for the method to work (stably) is usually prohibitive. Therefore, implicit schemes are usually adopted. Here we will a Crank-Nicholson scheme, which is second order accurate with respect to dt and unconditionally stable, may be written as

$$\vec{M}^{k+1} = \vec{M}^k + \frac{dt}{2}A\left(\vec{M}^k + \vec{M}^{k+1}\right). \tag{24}$$

In this implicit scheme we cannot obtain the approximation for time t_{k+1} directly from values at time t_k, as we need to solve a linear system of equation at each time-step. The system is defined as follows

$$(I - \frac{dt}{2}A)\vec{M}^{k+1} = (I + \frac{dt}{2}A)\vec{M}^k, \tag{25}$$

where I is the $n \times n$ identity matrix. Since A is tridiagonal, this system is very simple to solve with Gaussian Elimination.

It is convenient to work the theory in terms of mass, due to the conservation properties of the system. However, since the system is linear, assuming concentrations are piece-wise constant and the grid is uniform (dx is the same for each compartment), then one may multiply all equations by dx and obtain the same continuous equation for the concentrations,

$$\frac{d\vec{C}(t)}{dt} = A\vec{C}(t), \tag{26}$$

where $\vec{C}(t) = [C_{1/2}(t), C_{3/2}(t), C_{5/2}(t), ..., C_{n-1/2}(t)]$. Therefore the same numerical method hold the concentrations.

References

[1] Z. Zhang, J. Pawliszyn, Headspace solid-phase microextraction, Analytical chemistry 65 (1993) 1843–1852.
[2] R. J. LeVeque, Numerical methods for conservation laws, volume 3, Springer, 1992.