# DESCRIPTION OF SAMPLE INTRODUCTION IN CHROMATOGRAPHY AS A SEPARATE TERM IN THE MASS-BALANCE EQUATION

PER LÖVKVIST* and JAN ÅKE JÖNSSON

*Department of Analytical Chemistry, University of Lund, P.O. Box 124, S-221 00 Lund (Sweden)*

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## SUMMARY

The process of sample introduction into the chromatographic column is described as a separate term in the mass-balance equation. This approach is applied to non-ideal linear equilibrium chromatography, and a general explicit solution is derived for the case where the sample introduction is independent of the concentration within the column. Concentration and flux profiles are presented for a number of input profiles.

## INTRODUCTION

The physical processes operating in a chromatographic column can be described by a simple differential equation, based on mass-balance considerations, which was originally developed by Lapidus and Amundson[1]. With this defined, it still remains to describe the introduction of the sample into the chromatographic system mathematically. The usual practice is to include this in the initial and boundary conditions.

If the sample introduction process is viewed instead as an addition of sample to the chromatographic bed, it is natural to express it as an additional term of the mass-balance equation. This is a more realistic description, as the sample is in practice added to the system from outside. For non-ideal linear equilibrium chromatography, this approach has special advantages, as it makes it possible to obtain a general explicit solution, provided that the sample introduction process is independent of the concentration within the system.

The use of an additional term in the mass-balance equation was suggested earlier[2]. In this paper, it will be discussed in more detail and applied to the special case of non-ideal linear equilibrium chromatography. Expressions for the concentration and flux profiles in the column will be derived for different types of sample introduction functions.

THEORY

*Mass-balance equation*

For non-ideal linear equilibrium chromatography the mass-balance equation[1] is usually written:

$$D \frac{\partial^2 C}{\partial z^2} - u \frac{\partial C}{\partial z} - (1 + k) \frac{\partial C}{\partial t} = 0 \tag{1}$$

(For explanation of the symbols, see the List of Symbols at the end of the paper). If the sample introduction is viewed as an addition of sample to the column, an injection function should be added[2] to eqn. 1:

$$D \frac{\partial^2 C}{\partial z^2} - u \frac{\partial C}{\partial z} - (1 + k) \frac{\partial C}{\partial t} + I(z, t) = 0 \tag{2}$$

The term $I(z, t)$ describes the change in concentration due to the addition of sample and has the dimensions of mass per time and length. Eqn. 2 is applicable in all cases where sample introduction is independent of the conditions in the column, *i.e.* when the sample is added to the column from an outside source. This is consistent with the common techniques of sample introduction in chromatography.

*Concentration profile*

In order to solve the mass-balance equation (eqn. 2) it is convenient to think of the injection function as composed of an infinite number of infinitely narrow pulse injections. In linear chromatography these can be considered independently of each other, which makes it possible to use a convolution procedure[3].

A unit pulse injected at $(z, t) = (0, 0)$ will result in a Gaussian concentration profile in the column[4,5]:

$$C(z, t) = P(z, t) = \begin{cases} \dfrac{1}{\sqrt{2D_{eff}t}} \cdot \varphi \left( \dfrac{z - u_{eff}t}{\sqrt{2D_{eff}t}} \right), & t > 0 \\ \delta(z) & , \quad t = 0 \\ 0 & , \quad t < 0 \end{cases} \tag{3}$$

Here $\varphi$ is the normalized gaussian function

$$\varphi(x) = \frac{1}{\sqrt{2\pi}} e^{-x^2/2} \tag{4}$$

For mathematical convenience we have also defined $P(z, t)$ for $t < 0$, *i.e.* before the sample is introduced. Eqn. 3 is the solution of the mass-balance equation (2) for $I(z, t) = \delta(z) \cdot \delta(t)$, using the boundary conditions

$$C(z, t) \to 0, \quad z \to \pm \infty$$

$$C(z, t) = 0, \quad t < 0 \tag{5}$$

The concentration profile for a general input profile $I(z, t)$, which is independent of $C$, can now be found from that of a pulse injection using a convolution procedure over both time and space:

$$C(z, t) = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} I(z', t') \cdot P(z - z', t - t') \, dt' \, dz' \tag{6}$$

Eqn. 6 can be explained in the following way: $I(z', t') \, dt' \, dz'$ represents the amount injected at the point $(z', t')$. This will give rise to the concentration distribution $I(z', t') \, P(z - z', t - t') \, dt' \, dz'$ in the column. Here $z - z'$ is the distance from the injection point and $t - t'$ is the time since the injection. Integration over all possible values of $z'$ and $t'$ gives eqn. 6.

By insertion, it is easy to show that $C(z, t)$ from eqn. 6 satisfies the mass-balance equation (eqn. 2). This is a consequence of the fact that it is based on a pulse input that itself is a correct solution.

Lapidus and Amundson[1] obtained a solution to eqn. 1, employing general boundary and initial conditions $C(0, t)$ and $C(z, 0)$. They assumed, however, a semi-infinite column, which contrasts to the infinite column implicit in the treatment above. As $C(0, t)$ in that case must be specified in the boundary condition, it cannot be altered by column processes. For example, sample that is already present in the column is not allowed to diffuse to $z = 0$, which is physically implausible. The consequences of such a boundary condition for a pulse input have previously been discussed[2].

*Elution curve and flux*

It is important to distinguish carefully between the concentration profile in the column and the observed elution curve. This is the flux of solute at the end of the column and thus has the dimensions of mass per time while the concentration is most appropriately given in units of mass per length. The flux profile in the column can be derived from the concentration profile using the general equation[2,6]:

$$J(z, t) = \int_{z}^{\infty} \frac{\partial C(z, t)}{\partial t} \, dz \tag{7}$$

For the special case of non-ideal linear equilibrium chromatography the following relation can be derived[6]:

$$J(z, t) = u_{eff} C(z, t) - D_{eff} \frac{\partial C(z, t)}{\partial z} \tag{8}$$

Inserting the column profile from eqn. 6 into eqn. 7 or eqn. 8 one obtains:

$$J(z, t) = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} I(z', t') \cdot P_1(z - z', t - t') \, dt' \, dz' \tag{9}$$

where

$$P_1(z, t) = \left( \frac{u_{\text{eff}}}{2} + \frac{z}{2t} \right) P(z, t) \tag{10}$$

$P_1$ is the flux profile obtained from a unit pulse injection[6,7], and eqn. 9 is thus obtained through a convolution procedure analogous to that in eqn. 6.

Usually when convolution procedures are applied to chromatography, the column process is treated from the viewpoint of system theory, *i.e.* as a Gaussian operator modifying a time-dependent input signal[3]. The resulting elution curve contains no information on the distribution of the sample in space. Moreover, the assumption that a pulse injection will produce a peak that is Gaussian in the time dimension is only valid for large plate numbers[7]. Solutions obtained in this manner are not compatible with the mass-balance equations (eqns. 1 and 2).

*Special cases*

The equations above were derived for a general input function $I(z, t)$ describing an injection that might vary over both time and place. In practice, however, one rarely encounters such a complicated situation. Rather, injection is made at a given position or at a given time, and the function is zero elsewhere. Below, a few such cases are discussed.

*Injection at z = 0 only*. This is the way the sample is usually introduced in column chromatography. The injection function is then:

$$I(z, t) = I_1(t) \cdot \delta(z) \tag{11}$$

The equations describing concentration and flux simplify to:

$$C(z, t) = \int_{-\infty}^{\infty} I_1(t') \cdot P(z, t - t') \, dt' \tag{12}$$

$$J(z, t) = \int_{-\infty}^{\infty} I_1(t') \cdot P_1(z, t - t') \, dt' \tag{13}$$

If $I_1(t)$ is a step function or a rectangular function, concentration and flux profiles can conveniently be expressed in terms of the functions:

$$F(z, t) = \Phi \left( - \frac{z - u_{\text{eff}}t}{\sqrt{2D_{\text{eff}}t}} \right) \tag{14}$$

$$G(z, t) = \exp \left( \frac{u_{\text{eff}}z}{D_{\text{eff}}} \right) \Phi \left( - \frac{z + u_{\text{eff}}t}{\sqrt{2D_{\text{eff}}t}} \right) \tag{15}$$

Here $\Phi$ is the normal probability integral:

$$\Phi(x) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{x} e^{-x^2/2} \, dx \tag{16}$$

With this notation the integrals of $P$ and $P_1$ can be written

$$\int P(z, t - t') \, dt' = -\frac{1}{u_{\text{eff}}} [F(z, t - t') - G(z, t - t')] + a \tag{17}$$

$$\int P_1(z, t - t') \, dt' = -F(z, t - t') + a \tag{18}$$

Using these relations, it is easy to derive concentration and flux profiles for various important shapes of $I_1(t)$. These are presented in Table I. The concentration profile resulting from a step input was found by several authors, as cited in ref. 6.

TABLE I

CONCENTRATION AND FLUX PROFILES FOR VARIOUS INJECTION PROFILES WHEN INJECTION IS MADE AT $z = 0$ ONLY

The functions $P$, $F$ and $G$ are explained in the text.

| Shape of the injection | Injection function $I_1(t)$ | Concentration profile $C(z, t)$ | Flux profile $J(z, t)$ |
|---|---|---|---|
| Pulse | $m \cdot \delta(t)$ | $m \cdot P(z, t)$ | $m \cdot u_{\text{eff}} \cdot \left(\dfrac{1}{2} + \dfrac{z}{2u_{\text{eff}}t}\right) \cdot P(z, t)$ |
| Step | $0, t < 0$ <br> $J_0, t > 0$ | $\dfrac{J_0}{u_{\text{eff}}} \cdot [F(z, t) - G(z, t)]$ | $J_0 \cdot F(z, t)$ |
| Negative step | $J_0, t < 0$ <br> $0, t > 0$ | $\dfrac{J_0}{u_{\text{eff}}} \cdot [1 - F(z, t) + G(z, t)]$ | $J_0 \cdot [1 - F(z, t)]$ |
| Rectangular | $J_0, t_1 < t < t_2$ <br> $0,$ else | $\dfrac{J_0}{u_{\text{eff}}} \cdot \{[F(z, t - t_1) - F(z, t - t_2)] - [G(z, t - t_1) - G(z, t - t_2)]\}$ | $J_0 \cdot [F(z, t - t_1) - F(z, t - t_2)]$ |

*Injection at $t = 0$ only.* This approximates the mode of sample introduction in thin-layer chromatography. It is also applicable to the elution step of several pre-concentration techniques, where $I(z, t)$ then is the sample profile resulting from the concentration step. The injection function is

$$I(z, t) = I_2(z) \cdot \delta(t) \tag{19}$$

This results in the concentration profile

$$C(z, t) = \int_{-\infty}^{\infty} I_2(z') \cdot P(z - z', t)\, dz' \tag{20}$$

Eqn. 20 was found by Houghton[8], who derived it using eqn. 1 with $C(z, 0) = I_2(z)$ as an initial condition. The flux is similarly found to be

$$J(z, t) = \int_{-\infty}^{\infty} I_2(z') \cdot P_1(z - z', t)\, dz' \tag{21}$$

For a step or rectangular shape of the input function $I_2(z)$, concentration and flux profiles can be further simplified. The integrals of $P$ and $P_1$ are found to be

$$\int P(z - z', t)\, dz' = F(z - z', t) + a \tag{22}$$

and

$$\int P_1(z - z', t)\, dz' = u_{eff} F(z - z', t) + D_{eff} P(z - z', t) + a \tag{23}$$

In Table II, concentration and flux profiles are given for some important cases. Some of these equations were previously found by other authors: the equation given

TABLE II

CONCENTRATION AND FLUX PROFILES FOR VARIOUS INJECTION PROFILES WHEN INJECTION IS MADE AT $t = 0$ ONLY

The functions $P$ and $F$ are explained in the text.

| Shape of the injection | Injection function $I_2(z)$ | Concentration profile $C(z, t)$ | Flux profile $J(z, t)$ |
|---|---|---|---|
| Pulse | $m \cdot \delta(z)$ | $m \cdot P(z, t)$ | $m \cdot u_{eff} \cdot \left( \dfrac{1}{2} + \dfrac{z}{2 u_{eff} t} \right) \cdot P(z, t)$ |
| Step | $0, z < 0$ <br> $C_0, z > 0$ | $C_0 \cdot [1 - F(z, t)]$ | $C_0 u_{eff} \cdot \left[ 1 - F(z, t) - \dfrac{D_{eff}}{u_{eff}} P(z, t) \right]$ |
| Negative step | $C_0, z < 0$ <br> $0, z > 0$ | $C_0 \cdot F(z, t)$ | $C_0 u_{eff} \cdot \left[ F(z, t) + \dfrac{D_{eff}}{u_{eff}} P(z, t) \right]$ |
| Rectangular | $C_0, z_1 < z < z_2$ <br> $0,$ else | $C_0[F(z - z_2, t) -$ <br> $F(z - z_1, t)]$ | $C_0 u_{eff} \cdot \Big\{ [F(z - z_2, t) - F(z - z_1, t)] +$ <br> $\dfrac{D_{eff}}{u_{eff}} [P(z - z_2, t) - P(z - z_1, t)] \Big\}$ |

for the flux profile resulting from a negative step input is identical with a solution found by Kreft and Zuber[6], and the corresponding concentration profile is given by several authors (see ref. 6). The concentration profile resulting from a rectangular input was found by Houghton[8].

## DISCUSSION

The general equations (eqns. 6 and 9) permit the accurate calculation of chromatographic curves from any type of sample introduction function, provided that the assumptions of non-ideal linear equilibrium chromatography are valid.

For a large number of theoretical plates, the special cases given in Tables I and II tend towards the corresponding Gaussian frequency or distribution functions. However, for systems with a small number of plates, this approximation is inaccurate. Such conditions are found for example in the treatment of air-sampling by adsorption cartridges, where a high efficiency is not needed. The equations developed in this work will be valuable for the description of such and similar systems.

The use of a separate sample introduction term in the mass-balance equation is not restricted to non-ideal linear equilibrium chromatography. For linear chromatography in general, convolution procedures can be applied and equations analogous to eqns. 6 and 9 could be derived if the concentration profile resulting from a pulse injection were known. For non-linear chromatography, on the other hand, convolution is not allowed, but the application of a separate sample introduction term is still valid.

## LIST OF SYMBOLS

| | |
|---|---|
| $a$ | Arbitrary constant |
| $C$ | Linear concentration (mol/m) |
| $D$ | Diffusion coefficient in mobile phase (m²/s) |
| $D_{eff}$ | $D/(1 + k)$ (m²/s) |
| $F(z, t)$ | Defined in eqn. 14 |
| $G(z, t)$ | Defined in eqn. 15 |
| $I$ | Injection concentration function (mol/m/s) |
| $I_1$ | Injection concentration function (mol/s) |
| $I_2$ | Injection concentration function (mol/m) |
| $J$ | Solute flux (mol/s) |
| $k$ | Capacity factor |
| $m$ | Amount of solute (mol) |
| $P(z, t)$ | Concentration profile resulting from a unit pulse (eqn. 3) (1/m) |
| $P_1(z, t)$ | Flux profile resulting from a unit pulse (eqn. 10) (1/s) |
| $t$ | Time (s) |
| $u$ | Linear flow-rate (m/s) |
| $u_{eff}$ | $u/(1 + k)$ (m/s) |
| $z$ | Column coordinate (m) |
| $\delta$ | Dirac's delta function |
| $\varphi(x)$ | Normalized Gaussian frequency function |
| $\Phi(x)$ | Normal probability integral |

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