



Statistical theory of linear adsorption capillary chromatography with porous-layer stationary phase

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ABSTRACT

A set of accurate expressions of elution-curve moments are derived from the moments of residence time and displacement in a step based on probability theory. Then the problems about residence time and displacement in a step of a solute molecule in the porous layer of capillary columns and in the moving mobile phase are described by a set of mass-balance equations respectively. The set of equations are solved in Fourier–Laplace domain, and the characteristic functions of residence time of a step, as well as the moments, are obtained by means of computing software Mathematica. At last, using numerical inverse Laplace transform, the elution curves for various conditions are calculated. In the case of large desorption constant the results entirely coincide with those of mass-balance-equation theory and in the case of small desorption constant they are equivalent to those of stochastic theory.

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1. Introduction

Because of the extreme complexity of chromatographic processes, it is difficult to obtain an accurate elution curve by pure theoretical calculation. Giddings and Eyring [1,2] gave an analytical expression of elution curves for pure-rate-controlling adsorption chromatography. However, in most cases, diffusions cannot be ignored. Cavazzini, Felinger and Dondi et al. [3–6] used characteristic function theory (CF theory) to obtain an expression containing axial diffusions in mobile phases in frequency domain, then to give the elution curves in time domain by numerical inversion. In the model of Cavazzini et al., the diffusions in stationary phases and the lateral diffusions in mobile phases are not considered. This is correct for slow-desorption processes, because in these processes diffusions do not play a major role. In most cases, elution curves can be approached by Cram–Charlier series [7] or Edgeworth–Cramer series [8,9], or simply by Gaussian distribution. In this way calculating an elution curve is reduced to calculating its retention time and moments. However, there have not been general moment expressions suitable for various desorption constants. Moreover while the skew of elution curves exceeds 1 much, they are hard to be expanded in Cram–Charlier series or similar series at all.

We have presented a new stochastic theory based on mass balance principle, in which the lateral diffusions are involved [10], and used in linear capillary chromatography with uniform stationary phases and with multiple-site nonporous layer stationary phases [11,12]. But the case of porous layers is much more complex. In this paper we intend to think over all the factors which affect the linear capillary adsorption chromatography with porous layers, including the desorption rates and both the axial and the lateral diffusions in stationary phases and mobile phases, as well as the structure of stationary phases, the pressure drop in mobile phases and so on. Starting from a series of basic parameters such as the column parameters (the column length, the column radius, the thickness of porous layer, the porosity and the specific surface area), the operating conditions (the linear flow rate, the time distribution of sample injection, the gas pressure drop along the column) and the physico-chemical parameters of solutes (the desorption rate constants, the distribution constants, the diffusion coefficients), we calculate the elution curves and their moments, and compare them with those in literature. However, in this paper we will still limit the study only in the capillary columns, not concern the more complex packed columns.

2. General Laplace transform of elution curves

According to the random walk model [13], a solute molecule in a column can be imagined to move in the way of

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moving–adsorbing–moving alternately progressing and to go from the inlet to the outlet step by step. The processes can be expressed by following formula [10–12]:

$$\begin{cases} \tau_c = \sum_{j=1}^n \tau_j \\ \sum_{j=1}^n \eta_j \leq L < \sum_{j=1}^{n+1} \eta_j \end{cases} \quad (1)$$

where n is the number of steps for a molecule to pass through a column, τ_c represents the total time for a molecule to spend in the column, τ_j and η_j are the residence time and displacement in the j th step respectively. Obviously, n , τ_c , τ_j and η_j are all random. The second formula in Eq. (1) represents the condition that a molecule leaves the column. Denote $\sum_{j=1}^n \tau_j$ and $\sum_{j=1}^n \eta_j$ of given n by τ'_n and η'_n respectively, and denote the probability density function (PDF) of (η'_n, τ'_n) by $f_{\eta'_n \tau'_n}(z, t)$ and the PDF of η_{n+1} by $f_n(z)$. Because of independence of η_{n+1} and (η'_n, τ'_n) in linear chromatography, there is

$$\begin{aligned} P_n(\tau'_n \leq t, \eta'_n \leq L < \eta'_n + \eta_{n+1}) \\ = \int_0^t \left(\int_{z' \leq L < z' + z''} f_{\eta'_n \tau'_n}(z', t') f_n(z'') dz' dz'' \right) dt' \\ = \int_0^t \int_{-\infty}^L f_{\eta'_n \tau'_n}(z', t') dz' \int_{L-z'}^{\infty} f_n(z'') dz'' \end{aligned} \quad (2)$$

where $P_n(\tau'_n \leq t, \eta'_n \leq L < \eta'_n + \eta_{n+1})$ represents the probability of $\tau'_n \leq t$, $\eta'_n \leq L$ and $\eta'_n + \eta_{n+1} > L$. Let $f_{\eta\tau}(z, t)$ be the PDF of the displacement and residence time in an arbitrary step and $\tilde{f}_{\eta\tau}(\omega, p)$ be its Fourier–Laplace transform. Generally, we add a random variable to the subscript of a function to indicate that the function is a PDF of the variable and add a wave above the function symbol to represent its Laplace or Fourier–Laplace transform.

$$\tilde{f}_{\eta\tau}(\omega, p) = \int_0^{\infty} \int_{-\infty}^{\infty} f_{\eta\tau}(z, t) e^{i\omega z - pt} dz dt \quad (3)$$

where i is the imaginary unit. Then we have

$$\tilde{f}_{\eta'_n \tau'_n}(\omega, p) = (\tilde{f}_{\eta\tau}(\omega, p))^n \quad (4)$$

The PDF of τ'_n is given by

$$\begin{aligned} f_{\tau'_n}(t) &= \frac{d}{dt} P_n(\tau'_n \leq t, \eta'_n \leq L < \eta'_n + \eta_{n+1}) \\ &= \int_{-\infty}^L f_{\eta'_n \tau'_n}(z', t) dz' \int_{L-z'}^{\infty} f_n(z'') dz'' \end{aligned} \quad (5)$$

Making Fourier–Laplace transform of $f_{\tau'_n}(t)$ with respect to L and t , we have

$$\tilde{f}_{\tau'_n}(\omega, p) = \int_0^{\infty} \int_{-\infty}^{\infty} f_{\tau'_n}(t) e^{i\omega L - pt} dL dt = g(\omega) (\tilde{f}_{\eta}(\omega, p))^n \quad (6)$$

where

$$g(\omega) = \frac{1}{i\omega} \int_0^{\infty} f_n(z'') (e^{i\omega z''} - 1) dz'' \quad (7)$$

The practical residence time should include all possible steps, so its PDF should be

$$f_{\tau_c}(t) = \sum_{n=0}^{\infty} f_{\tau'_n}(t) \quad (8)$$

The function of $f_{\tau_c}(t)$ contains the variable of L . Its Fourier–Laplace transform with respect to L and t is

$$\tilde{f}_{\tau_c}(\omega, p) = \int_0^{\infty} \int_{-\infty}^{\infty} f_{\tau_c}(t) e^{i\omega z - pt} dz dt = \sum_{n=0}^{\infty} \tilde{f}_{\tau'_n}(\omega, p) = \frac{g(\omega)}{1 - \tilde{f}_{\eta\tau}(\omega, p)} \quad (9)$$

The Laplace transform of $f_{\tau_c}(t)$ with respect to t can be given by inverse transform of $\tilde{f}_{\tau_c}(\omega, p)$ with respect to ω :

$$\tilde{f}_{\tau_c}(p) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \frac{g(\omega)}{1 - \tilde{f}_{\eta\tau}(\omega, p)} e^{-i\omega L} d\omega \quad (10)$$

The integrand of Eq. (10) has a first pole at

$$\omega = \omega(p) \quad (11)$$

which is determined by

$$\tilde{f}_{\eta\tau}(\omega, p) = 1 \quad (12)$$

Using the residue theorem, the integral of Eq. (10) is calculated approximately to be

$$\tilde{f}_{\tau_c}(p) = e^{-i\omega(p)L} \quad (13)$$

Here we omit a factor related to the residue of $g(\omega)/(1 - \tilde{f}_{\eta\tau}(\omega, p))$ at $\omega = \omega(p)$, for not too short columns the factor has no influence on results. So far, we obtain the Laplace transform of elution curves without any additional conditions.

3. Residence time and displacement in a step

A step defined in this paper contains two parts: corresponding to the static zone and to the moving zone respectively. Let (η_s, τ_s) be the displacement and the residence time in the static zone per step, (η_m, τ_m) be the corresponding ones in the mobile zone, we have

$$\begin{cases} \tau = \tau_s + \tau_m \\ \eta = \eta_s + \eta_m \end{cases} \quad (14)$$

Movement of solute molecules in static zones includes two parts: diffusion in porous layers and adsorption–desorption on solid surfaces. The corresponding displacements and residence times are denoted by (η_{s1}, τ_{s1}) and (η_{s2}, τ_{s2}) respectively. Obviously all the (η_{s1}, τ_{s1}) , (η_{s2}, τ_{s2}) and (η_m, τ_m) are random and characterized by their PDFs. In our model the general diffusion–drift equations are used to determine the PDFs [11,12]. In the case of porous layers, the diffusion in pores can be approached by the diffusion in homogeneous media, see appendix A. Thus taking into account the adsorption–desorption on solid surfaces, the mass balance equations of solute molecules in static zones can be simplified as

$$\begin{cases} \frac{\partial C}{\partial t} = D_{sr} \left(\frac{\partial^2 C}{\partial r^2} + \frac{1}{r} \frac{\partial C}{\partial r} \right) + D_{sa} \frac{\partial^2 C}{\partial z^2} + \varepsilon_s \sum_j (k_{dj} C_{sj} - k'_{aj} C) \\ \frac{\partial C_{sj}}{\partial t} = -k_{dj} C_{sj} + k'_{aj} C \\ C(r, z, t) \Big|_{t=0} = C_{sj}(r, z, t) \Big|_{t=0} = 0 \\ \frac{\partial C}{\partial r} \Big|_{r=R+d_i} = 0 \\ -D_{sr} \frac{\partial C(r, z, t)}{\partial r} \Big|_{r=R} = \frac{\delta(t)\delta(z)}{2\pi R} - \frac{\nu}{2} C(R, z, t) \end{cases} \quad (15)$$

where $C(r, z, t)$ represents the concentration of solute molecules in pores, $C_{sj}(r, z, t)$ the amount adsorbed by the site of type j per area of solid surfaces, C and C_{sj} are their abbreviation respectively,

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