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Theory of linear non-equilibrium chromatography with beds of a finite length

Jindřich Stárek

J. Heyrovský Institute of Physical Chemistry and Electrochemistry, Czechoslovak Academy of Sciences, Dolejškova 3, 182 23 Prague 8 (Czechoslovakia)

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ABSTRACT

The phenomenological model of linear non-equilibrium chromatography in an isothermal column (adsorber) with constant cross-section was solved for finite, static and statistically homogeneous and isotropic sorption layers. The model applies the linear adsorption isotherm and accounts for contributions from convection, axial dispersion, external mass transfer and internal diffusion and the adsorption rate. The Laplace inversion of the solutions was obtained and the statistical moments up to the fourth order were calculated on this basis. Analysis of the moments obtained confirmed the negative influence of the dead volume of the column and of boundary effects on the component separation in chromatographic analysis. Comparison of the relationships for the first normal and second central moments, obtained by solving the models of infinite, semi-infinite and finite sorption layers, demonstrated that the choice of the theoretical model for experimental data processing is not critical.

INTRODUCTION

The models and theories of gas chromatography (GC) and of the closely connected dynamics of adsorption have undergone intense development in the last 35 years and have been used to analyse chromatographic processes from various points of view, *e.g.*, the shape of the adsorption isotherm, axial dispersion, external and internal mass transfer and adsorption rate. The solution of these models and theories has been based on a number of different theoretical approaches; most often, the phenomenological model, following from a set of mass balance partial differential equations, has been employed. The largest group of these theories consists of the phenomenological theories of linear non-equilibrium chromatography that, especially after the introduction by Kubín [1] and Kučera [2] of their moment analysis method and its further development [3–10], contributed greatly to progress with the theoretical principles of chromatography and its application in the study of transport processes [11] in adsorption and catalysis [12]. However, the transport of the adsorbate in finite layers and the effects of the boundary conditions at their edges has not yet been systematically analysed. These effects have been stated or assumed with little or no discussion, mainly in applications of chromatographic methods.

Boundary effects have been studied only with respect to the experimental determination of the axial dispersion coefficient for chemical engineering calculations on reactors. Analysis has been carried out for empty tubes with various locations of injection and measurement points inside [13–16] or outside [16] the test section. The effect of various initial and boundary conditions on the dispersion of the tracer in columns with finite and non-adsorbing packing was analysed in refs. 16–18. Brenner [17] studied the dispersion model for non-adsorbing layers of finite length and obtained equations for the dimensionless breakthrough curve and the average adsorbate concentration in the layer. Carleton *et al.* [18] appear to be the only workers to have studied the transport of the adsorbate in a finite sorption layer, obtaining the first normal statistical moment of the eluted peaks for a non-isobaric layer. However, they did not consider dispersion of the adsorbate outside the layer and limited their analysis to the original Danckwerts boundary conditions [19].

This work is an attempt to solve the problem of linear chromatography with a finite sorption layer under the conditions of axial dispersion and with slow establishment of equilibrium between the mobile and stationary phases, utilizing the above-mentioned moment method of Kubín [1] and Kučera [2]. On the basis of the statistical moments obtained, the influence of the dead volume of the column and effects at the packing boundary on the GC separation are discussed.

THEORETICAL

Definition of the problem

Consider an infinite column (adsorber) with constant cross-section S_L, in a section of which, $z \in \langle 0,z_L \rangle$ is located a static, statistically homogeneous and isotropic sorption layer with finite length L and external porosity α (Fig. 1). Hypothetical indication sensors are located at points A and B, while injection takes place at point O. An "incompressible" carrier medium flows along the z-axis with a volumetric flow-rate F_v. The linear flow-rates at intervals $z \in (-\infty,0)$, $z \in \langle 0,z_L \rangle$ and $z \in (z_L, +\infty)$ are denoted as ${}^{A}u$, u and ${}^{B}u$, respectively. It follows from the restriction of constant cross-section of the column, for a linear flow-rate that

$$ {}^{A}u = {}^{B}u = \frac{F_v}{S_L} \tag{1a} $$

and

$$ u = \frac{F_v}{\alpha\, S_L} \tag{1b} $$

and thus also that

$$ {}^{A}D_p({}^{A}u) = {}^{B}D_p({}^{B}u) \tag{2} $$

where the superscripts A and B characterize the quantities related to the entrance and exit sections, respectively.

It is further assumed that:

(1) The column is isothermal and of the fixed-bed type.

(2) The mobile phase flows through the column in the axial direction, is incompressible (and hence has a constant density) and consists of a mixture of inert carrier medium and n adsorbates with low concentrations that do not interact.

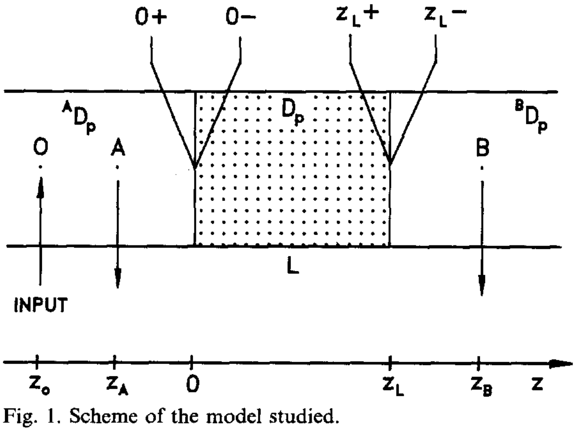

Fig. 1. Scheme of the model studied.

(3) The vector field of the mobile phase velocities is quasi-stationary.

(4) The sorption layer, consisting of porous granules is statistically homogeneous and isotropic and can be considered as a coherent continuum [20–22].

(5) The granules of adsorbent (with uniform size and with statistically homogeneous and isotropic porous structure) have the shape of spheres, "infinite" cylinders or "infinite" plates, and can also be considered as a continuum. Adsorption on the external surface and the contact regions between the grains can be neglected.

(6) The resistance of the phase boundary to mass transfer is zero.

(7) Radial effects can be neglected in the column.

(8) Adsorption is governed by a linear isotherm.

(9) The source of adsorbates is located only in the front of sorption layer.

The transport process of any arbitrary adsorbate in the column can then be represented by the following set of equations:

$$\frac{\partial\, {}^{A}c(z,t)}{\partial t} + {}^{A}u \cdot \frac{\partial\, {}^{A}c}{\partial z} - {}^{A}D_{p} \cdot \frac{\partial^{2}\, {}^{A}c}{\partial z^{2}} = {}^{A}Q_{z}(z,t) \qquad (\text{for } z < 0) \qquad (3)$$

$$\frac{\partial c(z,t)}{\partial t} + u \cdot \frac{\partial c}{\partial z} - D_{p} \cdot \frac{\partial^{2} c}{\partial z^{2}} = Q_{c}(z,t) \qquad (\text{for } 0 \leqslant z \leqslant z_{L}) \qquad (4)$$

$$\frac{\partial\, {}^{B}c(z,t)}{\partial t} + {}^{A}u \cdot \frac{\partial\, {}^{B}c}{\partial z} - {}^{A}D_{p} \cdot \frac{\partial^{2}\, {}^{B}c}{\partial z^{2}} = 0 \qquad (\text{for } z > z_{L}) \qquad (5)$$

$$\frac{\partial C(z,r,t)}{\partial t} - D_{r}\left(\frac{\nu - 1}{r} \cdot \frac{\partial C}{\partial r} + \frac{\partial^{2} C}{\partial r^{2}}\right) = Q_{n}(z,r,t) \qquad (6)$$

$$Q_{c} = -\frac{H\, S_{v}}{\alpha}\left[c - C|_{r=R}\right] \qquad (7)$$

$$Q_{n} = -\frac{\partial n(z,r,t)}{\partial t} = -H_{n}(K_{n}C - n) \qquad (8)$$

with boundary conditions for:

(a) equality of the flows at the adsorbent grain boundary,

$$Q_{c} = -D_{r} \cdot \frac{P_{v}}{\alpha} \cdot \left.\frac{\partial C}{\partial r}\right|_{r=R} \qquad (9)$$

(b) symmetry in the centre of the adsorbent grain,

$$0 = \left.\frac{\partial C}{\partial r}\right|_{r=0} \qquad (10)$$

The Danckwerts conditions [19] in the extended form of Wehner and Wilhelm [23] are considered to be valid at the boundary of the sorption layer; these conditions are based on the intuitive assumptions for:

(a) continuity of the concentrations,

$${}^{A}c(0^{-}) = c(0^{+}) \qquad (11a)$$

$$c(z_{L}^{-}) = {}^{B}c(z_{L}^{+}) \qquad (11b)$$

(b) equality of the flows,

$${}^{A}u(0^{-})\,{}^{A}c(0^{-}) - {}^{A}D_{p} \cdot \frac{\partial\, {}^{A}c(0^{-})}{\partial z} = \alpha\left[u(0^{+})c(0^{+}) - D_{p} \cdot \frac{\partial c(0^{+})}{\partial z}\right] \qquad (12a)$$

$$\alpha\left[u(z_{L}^{-})c(z_{L}^{-}) - D_{p} \cdot \frac{\partial c(z_{L}^{-})}{\partial z}\right] = {}^{B}u(z_{L}^{+})\,{}^{B}c(z_{L}^{+}) - {}^{A}D_{p} \cdot \frac{\partial\, {}^{B}c(z_{L}^{+})}{\partial z} \qquad (12b)$$

Combination of conditions 11 and 12, assuming that ${}^{\mathrm{A}}u(0^-) = \alpha\, u(0^+) = \alpha\, u(z_{\mathrm{L}}^-) = {}^{\mathrm{B}}u(z_{\mathrm{L}}^+)$ (see eqn. 1), permits us to write

$$ {}^{\mathrm{A}}D_{\mathrm{p}} \cdot \frac{\partial\, {}^{\mathrm{A}}c(0^-)}{\partial z} = \alpha\, D_{\mathrm{p}} \cdot \frac{\partial c(0^+)}{\partial z} \tag{13a} $$

$$ {}^{\mathrm{A}}D_{\mathrm{p}} \cdot \frac{\partial\, {}^{\mathrm{B}}c(z_{\mathrm{L}}^+)}{\partial z} = \alpha\, D_{\mathrm{p}} \cdot \frac{\partial c(z_{\mathrm{L}}^-)}{\partial z} \tag{13b} $$

In eqns. 3–13, t is time, z is the axial coordinate in the column, r is the radial coordinate in the adsorbent grain, Q_z is the rate of increase of the adsorbate concentration from the source, K_{n} is the slope of the Henry adsorption isotherm and ν is a shape factor with values of 1, 2 or 3 for prismatic, cylindrical or spherical particles of adsorbent, respectively, with characteristic dimension R.

The local concentration of adsorbate in the fluid phase, c, the linear flow-rate of the fluid phase, u, the axial dispersion coefficient, D_{p}, the rate of change in concentration c through adsorbate transport into the adsorbent grains, Q_{c}, the Shilov *et al.* [24] and Mecklenburg [25] external mass transfer coefficient, H, related to unit intergranular free volume, the external porosity, α, the external specific surface of the adsorbent grains $S_{\mathrm{v}} = \nu(1 - \alpha)/R$, related to unit volume of the layer, and the mean area of the boundary between the pores and the external free volume, $P_{\mathrm{v}} = \beta S_{\mathrm{v}}$ (also related to unit volume of the layer), are all quantities averaged throughout a physically infinitesimal volume element [20–22] of the *sorption layer.*

Similarly, the local adsorbate concentration in the pores, C, the local concentration of the adsorbed compound, n, related to unit pore volume, the effective coefficient of internal diffusion, D_{r}, the rate of change of concentration C through adsorption, Q_{n}, the coefficient of the adsorbate transfer from the volume towards the internal surface of the pores, H_{n}, and the internal porosity of the adsorbent granules, β, are all quantities averaged throughout a physically infinitesimal volume element [20–22] of the *adsorbent grain.*

Various types of chromatography or dynamics of adsorption can be characterized by the following initial and boundary conditions:

Case $t < 0$:

$$ \begin{array}{ll} {}^{\mathrm{A}}c(z,t) = 0 & \text{for } -\infty < z < 0 \\ c(z,t) = 0 & \text{for } 0 \leqslant z \leqslant z_{\mathrm{L}} \\ {}^{\mathrm{B}}c(z,t) = 0 & \text{for } z_{\mathrm{L}} < z < +\infty \\ C(z,r,t) = n(z,r,t) = 0 & \text{for } 0 \leqslant r \leqslant R \quad \text{and} \quad 0 \leqslant z \leqslant z_{\mathrm{L}} \end{array} $$

Case $t = 0$:

$$ \begin{array}{ll} {}^{\mathrm{A}}c(z,t) = {}^{\mathrm{A}}c_{\mathrm{i}}(z) & \text{for } -\infty < z < 0 \\ c(z,t) = c_{\mathrm{i}}(z) & \text{for } 0 \leqslant z \leqslant z_{\mathrm{L}} \\ {}^{\mathrm{B}}c(z,t) = {}^{\mathrm{B}}c_{\mathrm{i}}(z) & \text{for } z_{\mathrm{L}} < z < +\infty \\ \left.\begin{array}{l} C(z,r,t) = C_{\mathrm{i}}(z) \\ n(z,r,t) = n_{\mathrm{i}}(z) \end{array}\right\} & \text{for } 0 \leqslant r \leqslant R \quad \text{and} \quad 0 \leqslant z \leqslant z_{\mathrm{L}} \end{array} \tag{14} $$

Case $t > 0$:

$$ \begin{array}{ll} {}^{\mathrm{A}}c(z,t) = \text{finite} & \text{for } z \to -\infty \\ {}^{\mathrm{B}}c(z,t) = \text{finite} & \text{for } z \to +\infty \end{array} $$

where ${}^{\mathrm{A}}c_{\mathrm{i}}(z)$, $c_{\mathrm{i}}(z)$, ${}^{\mathrm{B}}c(z)$ and $C_{\mathrm{i}}(z)$ are the initial distributions of the corresponding concentrations and z_{L} is the positional coordinate of the end of sorption layer.

Solution of the model

The solution of the set of eqns. 3–8 with initial and boundary conditions 9–11, 13 and 14 can be considerably simplified using the Laplace integral transformation:

$$L\{f(t)\} \equiv \tilde{f}(s) = \int_{0}^{+\infty} f(t)\,\mathrm{e}^{-st}\,\mathrm{d}t \tag{15}$$

where s is a complex parameter. Solution [26] of the new set of transformed equations then leads to the following relationships for the transformed adsorbate concentrations in the different parts of the column (adsorber):

(A) The region in front of the sorption layer [$z \in (-\infty,0)$]:

$$\begin{aligned}{}^{\mathrm{A}}\tilde{c}(z,s) = {} & \frac{1-\dfrac{{}^{\mathrm{A}}\lambda_2}{{}^{\mathrm{A}}\lambda_1}}{W_{11}(s)}\cdot \mathrm{e}^{{}^{\mathrm{A}}\lambda_1 z}\int_{-\infty}^{0} {}^{\mathrm{A}}X(\xi,s)\,\mathrm{e}^{-{}^{\mathrm{A}}\lambda_2\xi}\,\mathrm{d}\xi - \mathrm{e}^{{}^{\mathrm{A}}\lambda_1 z}\int_{-\infty}^{0} {}^{\mathrm{A}}X(\xi,s)(\mathrm{e}^{-{}^{\mathrm{A}}\lambda_2\xi} - \mathrm{e}^{-{}^{\mathrm{A}}\lambda_1\xi})\,\mathrm{d}\xi \, + \\ & \int_{-\infty}^{z} {}^{\mathrm{A}}X(\xi,s)[\mathrm{e}^{{}^{\mathrm{A}}\lambda_2(z-\xi)} - \mathrm{e}^{{}^{\mathrm{A}}\lambda_1(z-\xi)}]\,\mathrm{d}\xi - \frac{\lambda_2-\lambda_1}{{}^{\mathrm{A}}\lambda_1}\cdot\frac{\alpha\,D_{\mathrm{p}}}{{}^{\mathrm{A}}D_{\mathrm{p}}}\cdot\frac{U(s)}{T(s)}\cdot \mathrm{e}^{{}^{\mathrm{A}}\lambda_1 z}\end{aligned} \tag{16a}$$

(B) The section of the sorption layer ($z \in \langle 0,z_{\mathrm{L}}\rangle$):

$$\begin{aligned}\tilde{c}(z,s) = {} & \frac{1-\dfrac{{}^{\mathrm{A}}\lambda_2}{{}^{\mathrm{A}}\lambda_1}}{W_{11}(s)}\cdot \mathrm{e}^{{}^{\mathrm{A}}\lambda_1 z}\int_{-\infty}^{0} {}^{\mathrm{A}}X(\xi,s)\,\mathrm{e}^{-{}^{\mathrm{A}}\lambda_2\xi}\,\mathrm{d}\xi + \int_{0}^{z} X(\xi,s)[\mathrm{e}^{\lambda_2(z-\xi)} - \mathrm{e}^{\lambda_1(z-\xi)}]\,\mathrm{d}\xi \, - \\ & [W_{11}(s)\,\mathrm{e}^{\lambda_2 z} - W_{21}(s)\,\mathrm{e}^{\lambda_1 z}]\,\frac{U(s)}{T(s)}\end{aligned} \tag{16b}$$

(C) The region after the sorption layer [$z \in (z_{\mathrm{L}},+\infty)$]:

$$\begin{aligned}{}^{\mathrm{B}}\tilde{c}(z,s) = {} & \frac{1-\dfrac{{}^{\mathrm{A}}\lambda_2}{{}^{\mathrm{A}}\lambda_1}}{W_{11}(s)}\cdot \mathrm{e}^{(\lambda_1-{}^{\mathrm{A}}\lambda_2)z_{\mathrm{L}}}\int_{-\infty}^{0} {}^{\mathrm{A}}X(\xi,s)\,\mathrm{e}^{{}^{\mathrm{A}}\lambda_2(z-\xi)}\,\mathrm{d}\xi + \mathrm{e}^{{}^{\mathrm{A}}\lambda_2(z-z_{\mathrm{L}})}\int_{0}^{z_{\mathrm{L}}} X(\xi,s)[\mathrm{e}^{\lambda_2(z_{\mathrm{L}}-\xi)} - \mathrm{e}^{\lambda_1(z_{\mathrm{L}}-\xi)}]\,\mathrm{d}\xi \, - \\ & \mathrm{e}^{{}^{\mathrm{A}}\lambda_2(z-z_{\mathrm{L}})}\int_{z_{\mathrm{L}}}^{+\infty} {}^{\mathrm{B}}X(\xi,s)\,\mathrm{e}^{{}^{\mathrm{A}}\lambda_1(z_{\mathrm{L}}-\xi)}\,\mathrm{d}\xi + \int_{z_{\mathrm{L}}}^{z} {}^{\mathrm{B}}X(\xi,s)\,\mathrm{e}^{{}^{\mathrm{A}}\lambda_2(z-\xi)}\,\mathrm{d}\xi + \int_{z}^{+\infty} {}^{\mathrm{B}}X(\xi,s)\,\mathrm{e}^{{}^{\mathrm{A}}\lambda_1(z-\xi)}\,\mathrm{d}\xi \, - \\ & \{W_{11}(s)\,\mathrm{e}^{[(\lambda_2-{}^{\mathrm{A}}\lambda_2)z_{\mathrm{L}}+{}^{\mathrm{A}}\lambda_2 z]} - W_{21}(s)\,\mathrm{e}^{[(\lambda_1-{}^{\mathrm{A}}\lambda_2)z_{\mathrm{L}}+{}^{\mathrm{A}}\lambda_2 z]}\}\,\frac{U(s)}{T(s)}\end{aligned} \tag{16c}$$

It holds for the auxiliary functions that

$$\lambda_{1,2} = \frac{u}{2D_{\mathrm{p}}} \pm \sqrt{\left(\frac{u}{2D_{\mathrm{p}}}\right)^2 + \frac{\sigma_{\mathrm{v}}}{D_{\mathrm{p}}}} \tag{17a}$$

$${}^{\mathrm{A}}\lambda_{1,2} = \frac{{}^{\mathrm{A}}u}{2\,{}^{\mathrm{A}}D_{\mathrm{p}}} \pm \sqrt{\left(\frac{{}^{\mathrm{A}}u}{2\,{}^{\mathrm{A}}D_{\mathrm{p}}}\right)^2 + \frac{s}{{}^{\mathrm{A}}D_{\mathrm{p}}}} \tag{17b}$$

$${}^{(\mathrm{A,B})}X(z,s) = \frac{{}^{(\mathrm{A,B})}\gamma_{\mathrm{v}}(z,s)}{{}^{(\mathrm{A})}D_{\mathrm{p}}[{}^{(\mathrm{A})}\lambda_1 - {}^{(\mathrm{A})}\lambda_2]} \tag{17c}$$

$$W_{ij}(s) = 1 - \frac{\alpha\,D_{\mathrm{p}}}{{}^{\mathrm{A}}D_{\mathrm{p}}}\cdot\frac{\lambda_i}{{}^{\mathrm{A}}\lambda_j} \qquad (\text{for } i = 1,2 \quad \text{and} \quad j = 1,2) \tag{17d}$$

$$T(s) = W_{11}W_{22}\,\mathrm{e}^{\lambda_2 z_{\mathrm{L}}} - W_{12}W_{21}\,\mathrm{e}^{\lambda_1 z_{\mathrm{L}}} \tag{17e}$$

$$U(s) = \frac{W_{12}}{W_{11}}\left(1 - \frac{{}^{\mathrm{A}}\lambda_2}{{}^{\mathrm{A}}\lambda_1}\right) \mathrm{e}^{\lambda_1 z_{\mathrm{L}}} \int_{-\infty}^{0} {}^{\mathrm{A}}X(\xi,s)\, \mathrm{e}^{-{}^{\mathrm{A}}\lambda_2 \xi}\, \mathrm{d}\xi - W_{12} \int_{0}^{z_{\mathrm{L}}} X(\xi,s)\, \mathrm{e}^{\lambda_1(z_{\mathrm{L}}-\xi)}\, \mathrm{d}\xi +$$

$$W_{22} \int_{0}^{z_{\mathrm{L}}} X(\xi,s)\, \mathrm{e}^{\lambda_2(z_{\mathrm{L}}-\xi)}\, \mathrm{d}\xi - \left(1 - \frac{{}^{\mathrm{A}}\lambda_1}{{}^{\mathrm{A}}\lambda_2}\right) \int_{z_{\mathrm{L}}}^{+\infty} {}^{\mathrm{B}}X(\xi,s)\, \mathrm{e}^{{}^{\mathrm{A}}\lambda_1(z_{\mathrm{L}}-\xi)}\, \mathrm{d}\xi . \qquad (17\mathrm{f})$$

where

$$\sigma_v(s) = s + \frac{H\, S_v}{\alpha\, A(s)} \qquad (18\mathrm{a})$$

$$A(s) = 1 + \frac{H}{\beta} \cdot \frac{R}{D_{\mathrm{r}}} \cdot \frac{\psi_v(\rho)}{\rho\, \psi'_v(\rho)} \qquad (18\mathrm{b})$$

$${}^{\mathrm{A}}\gamma_v(z,s) = \tilde{Q}_z(z,s) + {}^{\mathrm{A}}c_{\mathrm{i}}\,(z) \qquad (18\mathrm{c})$$

$$\gamma_v(z,s) = c_{\mathrm{i}}\,(z) + \frac{H\, S_v\, \gamma(z,s)}{\alpha\, A(s)\, \sigma(s)} \qquad (18\mathrm{d})$$

$${}^{\mathrm{B}}\gamma_v(z,s) = {}^{\mathrm{B}}c_{\mathrm{i}}\,(z) \qquad (18\mathrm{e})$$

The functions $\gamma(z,s)$, $\sigma(s)$, $\psi_v(\rho)$ and ρ are defined by the expression

$$\gamma(z,s) = c_{\mathrm{i}}\,(z) + \frac{n_{\mathrm{i}}\,(z)\, H_{\mathrm{n}}}{s + H_{\mathrm{n}}} \qquad (19\mathrm{a})$$

$$\sigma(s) = s\left(1 + \frac{K_{\mathrm{n}}\, H_{\mathrm{n}}}{s + H_{\mathrm{n}}}\right) \qquad (19\mathrm{b})$$

$$\psi_v(\rho) = \sum_{k=0}^{+\infty} \frac{\rho^{2k}}{2^k\, k!\, v(v+2) \ldots [v + 2(k-1)]} = \begin{cases} ch(\rho) & (v = 1) \\ I_0\,(\rho) & (v = 2) \\ \dfrac{sh(\rho)}{\rho} & (v = 3) \end{cases} \qquad (19\mathrm{c})$$

$$\rho = R\sqrt{(\sigma/D_{\mathrm{r}})} \qquad (19\mathrm{d})$$

Solution for basic types of sampling

Inversion 16c describes an arbitrary type of dynamic adsorption or desorption from the point of view both the initial distributions of concentrations in the layer and the course of the input adsorbate concentration. Consequently, both common special cases, elution and frontal, can be obtained.

First consider general sampling of the adsorbate at point $z_0 \in (-\infty, 0)$ prior to the sorption layer determined by the function $c_0\,(t)$. For the usual assumption of zero initial ($t = 0$) distributions of the adsorbate concentrations ${}^{\mathrm{A}}c_{\mathrm{i}}\,(z) = c_{\mathrm{i}}\,(z) = {}^{\mathrm{B}}c_{\mathrm{i}}\,(z) = C_{\mathrm{i}}\,(z) = n_{\mathrm{i}}\,(z) = 0$, it follows from eqns. 18d and 18e that

$$\gamma_v(z,s) = {}^{\mathrm{B}}\gamma_v(z,s) = 0 \qquad (20)$$

The adsorbate sampling can be described by the source function:

$$Q_z(z,t) = u\, c_0\,(t)\, \delta(z,z_0) \qquad (21)$$

and it therefore holds according to eqn. 18c that

$${}^{\mathrm{A}}\gamma_v(z,s) = \tilde{Q}_z(z,s) = u\, \tilde{c}_0\,(s)\, \delta(z,z_0) \qquad (22)$$

Substitution and rearrangement of inversion 16c yields the following relationship for the transformed elution curve:

$$^{\mathrm{B}}\tilde{c}(z,s) = \tilde{c}_0\,(s) \cdot \frac{u}{\alpha\, D_{\mathrm{p}}} \cdot \frac{\lambda\, \mathrm{e}^{-(z - z_{\mathrm{L}} - z_0)\tau}}{\left(\lambda + \frac{^{\mathrm{A}}D_{\mathrm{p}}}{\alpha\, D_{\mathrm{p}}} \cdot \tau\right)^2 \mathrm{e}^{\lambda z_{\mathrm{L}}} - \left(\lambda - \frac{^{\mathrm{A}}D_{\mathrm{p}}}{\alpha\, D_{\mathrm{p}}} \cdot \tau\right)^2 \mathrm{e}^{-\lambda z_{\mathrm{L}}}} \tag{23}$$

where it holds for the auxiliary functions λ and τ that

$$\tau(s) = \sqrt{\left(\frac{^{\mathrm{A}}u}{2\,^{\mathrm{A}}D_{\mathrm{p}}}\right)^2 + \frac{s}{^{\mathrm{A}}D_{\mathrm{p}}}} \tag{24a}$$

$$\lambda[\sigma_{\mathrm{v}}(s)] = \sqrt{\left(\frac{^{\mathrm{A}}u}{2\alpha D_{\mathrm{p}}}\right)^2 + \frac{\sigma_{\mathrm{v}}(s)}{D_{\mathrm{p}}}} \tag{24b}$$

It follows from the definition of the Dirac δ-function that [27]

$$\int_a^b f(\tau)\, \delta(\tau,\tau_0)\, \mathrm{d}\tau = \begin{cases} 0 & \text{for } \tau_0 \notin (a,b) \\ f(\tau_0) & \text{for } \tau_0 \in (a,b) \end{cases} \tag{25}$$

Laplace inversion of the solution for general sampling of the adsorbate readily yields the inversion for both basic types of sampling.

The elution case, the most common approach to chromatographic analysis, usually carried out by injection with a syringe, can be successfully modelled by the impulse Dirac δ-function. Then

$$c_0\,(t) = \frac{M_{\mathrm{A}}}{u\, S_{\mathrm{L}}} \cdot \delta(t,t_0) \tag{26}$$

where M_{A} is the total injected amount of the adsorbate. Supposing that the start of time measurement is given by the moment of the sampling ($t_0 = 0$), then $L\{\delta(t,0)\} = 1$, and the term $\tilde{c}_0\,(s)$ in eqn. 23 describing the inversion of the elution curve in this case is given by

$$\tilde{c}_0\,(s) = \frac{M_{\mathrm{A}}}{u\, S_{\mathrm{L}}} \tag{27}$$

The frontal case, employed primarily in separation processes, utilizes a second basic type of sampling, where a constant concentration, $c_0\,(t) = c_0 =$ constant, is maintained at the injection point during the separation. The initial adsorbate concentration in the adsorber is zero. This type can be described by the step function. Subsequently, eqn. 23 with the term

$$\tilde{c}_0\,(s) = c_0/s \tag{28}$$

describes the inversion of the breakthrough curve.

Comparison of the Laplace images of the solutions for the elution and frontal cases of adsorbate sampling with $uc_0 = M_{\mathrm{A}}/S_{\mathrm{L}}$ yields the following relationship between the eluted peaks and breakthrough curves:

$$[^{\mathrm{B}}c(z,t)]_{\mathrm{elution}} = \left[\frac{\partial\, ^{\mathrm{B}}c(z,t)}{\partial\, t}\right]_{\mathrm{frontal}} \tag{29}$$

It holds in general that

$$L\left\{\frac{\partial\, ^{\mathrm{B}}c(z,t)}{\partial\, t}\right\} = s\, ^{\mathrm{B}}\tilde{c}(z,s) - {}^{\mathrm{B}}c_{\mathrm{i}}\,(z) = s\, ^{\mathrm{B}}\tilde{c}(z,s) \tag{30}$$

as it is assumed that $^{\mathrm{B}}c_{\mathrm{i}}\,(z) = 0$.

Statistical moments of the elution curves

An attempt to carry out the inverse transformation of the obtained Laplace images was not successful. Consequently, the statistical moments of the elution curves will be employed to characterize adsorbate transport in a column with a finite sorption layer. The normal statistical moments μ'_k and the central moments μ_k can be derived [1,2] from the relationships

$$\mu'_k = (-1)^k \lim_{s \to 0+} \frac{\dfrac{\mathrm{d}^k \tilde{f}(s)}{\mathrm{d}s^k}}{\tilde{f}(s)} \tag{31a}$$

and

$$\mu_k = \sum_{i=0}^{k} \binom{k}{i} (-\mu'_k)^i \mu'_{k-i} \tag{31b}$$

where $\tilde{f}(s)$ is the known Laplace inversion.

As the breakthrough curve resulting in the frontal case of adsorbate injection, in contrast to the eluted peak, does not have the character of a frequency function [it does not fulfil the condition $\lim_{t \to +\infty} {}^{\mathrm{B}}c(z,t) = 0$], there are no statistical moments of this curve. However, there are the moments of the derivative $\partial^{\mathrm{B}}c(z,t)/\partial t$ that, with respect to eqns. 29 and 31, will correspond with the moments of the eluted peak, independently of the amount of adsorbate injected.

After tedious calculations, the following equations for the normal and central statistical moments of the elution curves are obtained from the respective inversions (eqns. 23 and 27, or 23, 28 and 30) with respect to eqn. 31:

$$\mu'_0(z) = 1 \tag{32a}$$

$$\mu'_1(z) = \frac{z_\mathrm{L}}{u}\left[(\chi_\mathrm{v})_1 + \left(x_\mathrm{E} + 2 \cdot \frac{x_\mathrm{D}}{Pe}\right)\right] \tag{32b}$$

$$\mu_0(z) = 1 \tag{33a}$$

$$\mu_1(z) = 0 \tag{33b}$$

$$\begin{aligned}\mu_2(z) = 2 \cdot \frac{z_\mathrm{L}^2}{u^2}\Bigg\{&\frac{1}{Pe^2}[Pe - (1 - \mathrm{e}^{-Pe})](\chi_\mathrm{v})_1^2 + 2 \cdot \frac{x_\mathrm{D}}{Pe^2}(1 - \mathrm{e}^{-Pe})(\chi_\mathrm{v})_1 + \\ &\varepsilon(x_\mathrm{v})_2 + \frac{x_\mathrm{D}}{Pe}\left[x_\mathrm{E} + \frac{x_\mathrm{D}}{Pe}(3 + \mathrm{e}^{-Pe})\right]\Bigg\}\end{aligned} \tag{33c}$$

$$\begin{aligned}\mu_3(z) = 2 \cdot \frac{z_\mathrm{L}^3}{u^3}\Bigg\{&\frac{6}{Pe^3}[Pe(1 + \mathrm{e}^{-Pe}) - 2(1 - \mathrm{e}^{-Pe})](\chi_\mathrm{v})_1^3 - 12 \cdot \frac{x_\mathrm{D}}{Pe^3}[Pe\,\mathrm{e}^{-Pe} - (1 - \mathrm{e}^{-Pe})](\chi_\mathrm{v})_1^2 + \\ &6 \cdot \frac{x_\mathrm{D}^2}{Pe^3}[Pe\,\mathrm{e}^{-Pe} + 2(1 - \mathrm{e}^{-Pe})](\chi_\mathrm{v})_1 + 6 \cdot \frac{1}{Pe^2}\varepsilon[Pe - (1 - \mathrm{e}^{-Pe})](\chi_\mathrm{v})_1(x_\mathrm{v})_2 + \\ &6 \cdot \frac{x_\mathrm{D}}{Pe^2}\varepsilon(1 - \mathrm{e}^{-Pe})(\mathrm{x}_\mathrm{v})_2 + 3\varepsilon(x_\mathrm{v})_3 + 2 \cdot \frac{x_\mathrm{D}^2}{Pe^2}\left[3x_\mathrm{E} + 2 \cdot \frac{x_\mathrm{D}}{Pe}(5 + 3\mathrm{e}^{-Pe})\right]\Bigg\}\end{aligned} \tag{33d}$$

$$\begin{aligned}\mu_4(z) = 4 \cdot \frac{z_\mathrm{L}^4}{u^4}\Bigg\{&\frac{3}{Pe^4}[Pe^2(1 + 4\mathrm{e}^{-Pe}) + 2Pe(4 + 11\mathrm{e}^{-Pe}) - 2(1 - \mathrm{e}^{-Pe})(14 + \mathrm{e}^{-Pe})](\chi_\mathrm{v})_1^4 - \\ &12 \cdot \frac{x_\mathrm{D}}{Pe^4}[2Pe^2\,\mathrm{e}^{-Pe} - Pe(1 - 7\mathrm{e}^{-Pe}) - 2(1 - \mathrm{e}^{-Pe})(2 + \mathrm{e}^{-Pe})](\chi_\mathrm{v})_1^3 + 6 \cdot \frac{x_\mathrm{D}^2}{Pe^4}[2Pe^2\,\mathrm{e}^{-Pe} +\end{aligned}$$

$$Pe(3 - 5\mathrm{e}^{-Pe}) + 2(4 - 7\mathrm{e}^{-Pe} + 3\mathrm{e}^{-2Pe})](\chi_v)_1^2 + 24 \cdot \frac{x_D^3}{Pe^4}[2Pe\,\mathrm{e}^{-Pe} + (1 - \mathrm{e}^{-Pe})(4 + \mathrm{e}^{-Pe})](\chi_v)_1 +$$

$$6 \cdot \frac{x_D}{Pe^3} \cdot x_E[Pe - (1 - \mathrm{e}^{-Pe})](\chi_v)_1^2 + 12 \cdot \frac{x_D^2}{Pe^3} \cdot x_E(1 - \mathrm{e}^{-Pe})(\chi_v)_1 + 6 \cdot \frac{1}{Pe^3}\varepsilon[Pe^2 + Pe(5 + 7\mathrm{e}^{-Pe}) -$$

$$12(1 - \mathrm{e}^{-Pe})](\chi_v)_1^2(x_v)_2 + 12 \cdot \frac{x_D}{Pe^3}\varepsilon[Pe(1 - 5\mathrm{e}^{-Pe}) + 4(1 - \mathrm{e}^{-Pe})](\chi_v)_1(x_v)_2 +$$

$$6 \cdot \frac{x_D^2}{Pe^3}\varepsilon[3Pe(1 + \mathrm{e}^{-Pe}) + 4(1 - \mathrm{e}^{-Pe})](x_v)_2 + 3 \cdot \frac{1}{Pe^2}\varepsilon^2[Pe^2 + 2Pe - 2(1 - \mathrm{e}^{-Pe})](x_v)_2^2 +$$

$$6 \cdot \frac{x_D}{Pe} \cdot x_E\varepsilon(x_v)_2 + 12 \cdot \frac{1}{Pe^2}\varepsilon[Pe - (1 - \mathrm{e}^{-Pe})](\chi_v)_1(x_v)_3 + 12 \cdot \frac{x_D}{Pe^2}\varepsilon(1 - \mathrm{e}^{-Pe})(x_v)_3 +$$

$$6\varepsilon(x_v)_4 + 3 \cdot \frac{x_D^2}{Pe^2}\left[x_E^2 + 2 \cdot \frac{x_D}{Pe} \cdot x_E(8 + \mathrm{e}^{-Pe}) + 2 \cdot \frac{x_D^2}{Pe^2}(22 + 17\mathrm{e}^{-Pe} + \mathrm{e}^{-2Pe})\right]\Big]\Big\} \qquad (33e)$$

where the dimensionless complexes Pe, x_E, x_D and $(x_v)_k$ are defined by the relationships

$$Pe = z_L \cdot \frac{u}{D_p} \qquad (34)$$

$$x_E = \frac{z - z_L - z_0}{\alpha\, z_L} \qquad (35a)$$

$$x_D = \frac{{}^{A}D_p}{\alpha^2 D_p} \qquad (35b)$$

$$(x_v)_k = \left(\frac{u}{z_L}\right)^{k-1}(\chi_v)_k \quad (\text{for } k = 2,3,4) \qquad (36)$$

For the parameters $(\chi_v)_k$, characterizing transport of the adsorbate into the adsorbent grain, we have

$$(\chi_v)_1 = 1 + \varepsilon(1 + K_n) \qquad (37a)$$

$$(\chi_v)_2 = \frac{R^2}{D_r} \cdot \frac{(1 + K_n)^2}{v(v + 2)} + \frac{\beta R(1 + K_n)^2}{vH} + \frac{K_n}{H_n} \qquad (37b)$$

$$(\chi_v)_3 = \left(\frac{R^2}{D_r}\right)^2 \cdot \frac{2(1 + K_n)^3}{v^2(v + 2)(v + 4)} + \frac{R^2}{D_r} \cdot \frac{2(1 + K_n)}{v(v + 2)}\left[\frac{\beta R(1 + K_n)^2}{vH} + \frac{K_n}{H_n}\right] + \frac{\beta^2 R^2(1 + K_n)^3}{v^2 H^2} + \frac{2\beta R(1 + K_n)K_n}{vH_nH} + \frac{K_n}{H_n^2} \qquad (37c)$$

$$(\chi_v)_4 = \left(\frac{R^2}{D_r}\right)^3 \cdot \frac{(5v + 12)(1 + K_n)^4}{v^3(v + 2)^2(v + 4)(v + 6)} + \left(\frac{R^2}{D_r}\right)^2 \cdot \frac{(1 + K_n)^2}{v^2(v + 2)^2(v + 4)} \cdot \left[\frac{\beta R(5v + 12)(1 + K_n)^2}{vH} + \frac{(6v + 12)K_n}{H_n}\right] + \frac{R^2}{D_r} \cdot \frac{1}{v(v + 2)}\left[\frac{3\beta^2 R^2(1 + K_n)^4}{v^2H^2} + \frac{6\beta R(1 + K_n)^2 K_n}{vH_nH} + \frac{(2 + 3K_n)K_n}{H_n^2}\right] + \frac{\beta^3 R^3(1 + K_n)^4}{v^3H^3} + \frac{3\beta^2 R^2(1 + K_n)^2 K_n}{v^2H^2H_n} + \frac{\beta R(2 + 3K_n)K_n}{vH_n^2H} + \frac{K_n}{H_n^3} \qquad (37d)$$

where ε is the porosity function defined by

$$\varepsilon = \beta(1 - \alpha)/\alpha \qquad (38)$$

DISCUSSION

The terms in the relationships for the moments containing parameters x_E or x_D describe the contribution of the dead section of the column or effects on the boundaries of the sorption layer on adsorbate transport. The moments are independent of the absolute position of the injection and detection points, and are determined only by the total of their distances from the boundaries of the layer.

Let us analyse the influence of the dead volume and of the boundary effects on the separation of two components a and b in a chromatographic analysis. Its efficiency is usually characterized by the resolution:

$$R_s = 2d/(W_a + W_b) \qquad (39)$$

where d is the distance between the peak maxima and W_a and W_b are the individual base peak widths. The peaks are "perfectly" separated for $R_s \geqslant 1$. It holds for a Gaussian shape of the peaks that $d = (\mu_1')_b - (\mu_1')_a$ and $W_{a,b} = 4(\mu_2)^{\frac{1}{2}}_{a,b}$. The new resolution, defined by the following expression, will be utilized as a test criterion:

$$R_s^* = \frac{(\mu_1')_b - (\mu_1')_a}{2[(\mu_2)_a^{\frac{1}{2}} + (\mu_2)_b^{\frac{1}{2}}]} \qquad (40)$$

Let us assume that the axial dispersion coefficients of these components are not well distinguished. After substitution of eqns. 32a and 33c and their limiting cases for $x_E \rightarrow 0$ (neglecting the dead volume) and $x_D \rightarrow 0$ (neglecting the boundary effects) in eqn. 40, we obtain the following relationships:

$$R_s^* < (R_s^*)_{x_E \rightarrow 0} \text{ and } R_s^* < (R_s^*)_{x_D \rightarrow 0} \qquad (41a,b)$$

Consequently, the dead volume and the effects at the boundaries of the sorption layer decrease the separation efficiency, in agreement with experimental results.

For the semi-quantitative determination of these dependences, numerical analysis was applied. The results of the computer simulation are given in Figs. 2 and 3. As the starting point of computation, the retention times of methane (3 min) and carbon dioxide (5 min), found in GC tables [28] for isothermal GC separation on a 35 cm × 0.4 cm I.D. column of activated charcoal (75–100 mesh; 40°C; nitrogen carrier gas at 20 ml/min; thermal conductivity detector), and results of the dynamic adsorption of methane on activated carbon [26] (250–315 μm; 40°C; nitrogen carrier gas; Henry constant of methane $K_n = 28$) was used. In a first approximation, identity of diffusivities was assumed for both separated components; $D_r = 8 \cdot 10^{-2}$ mm^2/s, $H = 1.8$ mm/s and $H_n = 10^3$ s^{-1}. The values of the axial

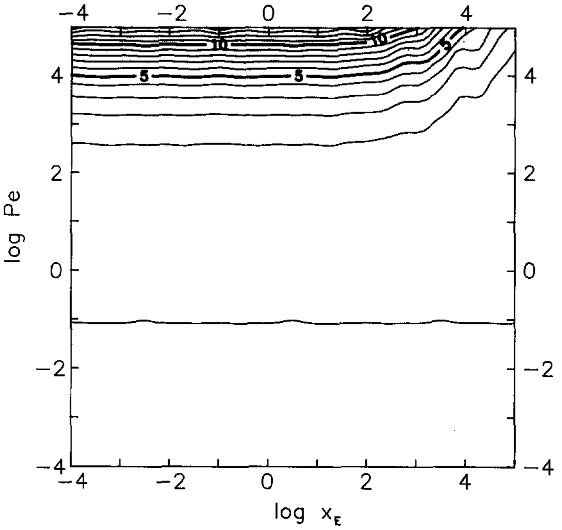

Fig. 2. Contour map of the computer-simulated dependence of resolution, R_s^*, on x_E and Pe (for methane) for the GC separation of methane and carbon dioxide.

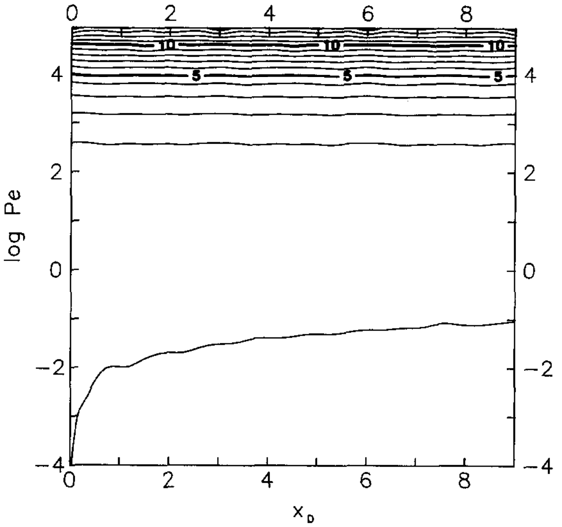

Fig. 3. Contour map of the computer-simulated dependence of resolution, R_s^*, on x_D and Pe (for methane) at a constant level $x_E = 0$ for the GC separation of methane and carbon dioxide.

dispersion coefficients of carbon dioxide ($^{A}D_p$ = 0.216 cm^2/s; D_p = 0.264 cm^2/s) and methane ($^{A}D_p$ = 0.26 cm^2/s; D_p = 0.297 cm^2/s) were calculated from Aris's [29] theoretical expression for these coefficients in a straight empty tube with laminar flow and a parabolic distribution of fluid phase velocities in its cross-section:

$$D_p = D_g + \frac{r_t^2\, u_m^2}{48\, D_g} \tag{42}$$

where D_g is the coefficient of molecular diffusion, r_t is the radius of tube and u_m is the mean linear flow velocity. The tabulated values [30] 0.184 and 0.235 cm^2/s (after conversion to 40°C) were used for the coefficients of molecular diffusion, D_g, of carbon dioxide and methane, respectively. On the basis of these results and estimates, the other parameters (Henry constant of carbon dioxide $K_n = 48.5$, u = 66 mm/s, $\alpha = 0.4$, $\beta = 0.7$, $\varepsilon = 1.0$, $R = 9 \cdot 10^{-2}$ mm, $R^2/D_r = 10^{-1}$ s, $R/H = 5 \cdot 10^{-2}$ s, $D_p/u^2 = 6.006 \cdot 10^{-3}$ and $6.757 \cdot 10^{-3}$ s, $x_D = 5.114$ and 5.471 and Pe = 879 and 781 for carbon dioxide and methane, respectively) were calculated.

Fig. 2 shows the contour map of the dependence of resolution, R_s^*, on the dimensionless parameters x_E and Pe (for methane) for the above-mentioned model example. From the plot it is evident that the peaks are perfectly separated ($R_s^* \geqslant 1$) for $\log x_E < 1.3$ and $\log Pe > 2.6$, *i.e.*, *ca.* $x_E < 20$ and $Pe > 400$. In other words, the length of the dead part of column can be up to eight times greater (2.8 m) than the length of sorption layer without a more substantial change in the separation. For the topical value of $Pe = 781$ in the sorption layer, $R_s^* \geqslant 1$ even for $\log x_E < 3.2$. Generally, the influence of dead volume, characterized by the parameter x_E, decreases with increasing Pe. In agreement with eqn. 41a, for a given value of the Pe, the resolution increases with decreasing dead volume (x_E).

Fig. 3 shows the contour map of the dependence of resolution, R_s^*, on the dimensionless parameters x_D and Pe (for methane) for a constant level $x_E = 0$. The dependence has the same shape as this plot, with minimal difference, also for non-zero values of x_E (verified up to $x_E = 200$). The resolution $R_s^* \geqslant 1$ for $\log Pe > 2.6$ (*ca.* $Pe > 400$) in the whole analysed interval $x_D \in \langle 0,9 \rangle$. The increase in resolution with decreasing boundary effects (see eqn. 42b) at a given Pe is very small, and this is evident only from numerical values.

Further, we restrict ourselves only to the first two non-trivial statistical moments having the fundamental meaning in chromatography: the first normal moment μ'_1, characterizing the time coordinate of the centre (of gravity) of the eluted peak (retention time), and the second central moment μ_2, connected with its width. Table I summarizes expressions for moments μ'_1 and μ_2, calculated on the basis of models of infinite [2,26,31,32], semi-infinite [26,33] and finite sorption layers.

It is evident from comparison of the expressions in Table I that the choice of a theoretical model can essentially affect the treatment and interpretation of chromatographic and dynamic sorption measure-

TABLE I

STATISTICAL MOMENTS FOR MODELS OF AN (A) INFINITE, (B) SEMI-INFINITE AND (C) FINITE SORPTION LAYER

Model	μ'_1	μ_2
A	$\frac{z_L}{u} \cdot \frac{1}{Pe}(2 + Pe)(\chi_v)_1$	$2 \cdot \frac{z_L^2}{u^2} \cdot \frac{1}{Pe}\left[\frac{1}{Pe}(4 + Pe)(\chi_v)_1^2 + \varepsilon(2 + Pe)(x_v)_2\right]$
B	$\frac{z_L}{u}(\chi_v)_1$	$2 \cdot \frac{z_L^2}{u^2}\left[\frac{1}{Pe}(\chi_v)_1^2 + \varepsilon(x_v)_2\right]$
C	$\frac{z_L}{u}\left[(\chi_v)_1 + \left(x_E + 2 \cdot \frac{x_D}{Pe}\right)\right]$	$2 \cdot \frac{z_L^2}{u^2}\left\{\frac{1}{Pe^2}[Pe - (1 - e^{-Pe})](\chi_v)_1^2 + 2 \cdot \frac{x_D}{Pe^2}(1 - e^{-Pe})(\chi_v)_1 + \varepsilon(x_v)_2 + \frac{x_D}{Pe}\left[x_E + \frac{x_D}{Pe}(3 + e^{-Pe})\right]\right\}$

TABLE II

LIMITING EXPRESSIONS OF THE STATISTICAL MOMENTS FOR MODELS OF AN (A) INFINITE, (B) SEMI-INFINITE AND (C) FINITE SORPTION LAYER

Pe	Model	μ'_1	μ_2
$<10^{-2}$	A	$\frac{z_L}{u} \cdot \frac{2}{Pe} (\chi_v)_1$	$4 \cdot \frac{z_L^2}{u^2} \cdot \frac{1}{Pe} \left[\frac{2}{Pe} (\chi_v)_1^2 + \varepsilon(x_v)_2 \right]$
	B	$\frac{z_L}{u} (\chi_v)_1$	$2 \cdot \frac{z_L^2}{u^2} \left[\frac{1}{Pe} (\chi_v)_1^2 + \varepsilon(x_v)_2 \right]$
	C	$\frac{z_L}{u} \left[(\chi_v)_1 + \left(x_E + 2 \cdot \frac{x_D}{Pe} \right) \right]$	$2 \cdot \frac{z_L^2}{u^2} \left[\frac{1}{Pe} (\chi_v)_1^2 + \varepsilon(x_v)_2 + \frac{x_D}{Pe} \left(x_E + 4 \cdot \frac{x_D}{Pe} \right) \right]$
>400	A	$\frac{z_L}{u} (\chi_v)_1$	$2 \cdot \frac{z_L^2}{u^2} \left[\frac{1}{Pe} (\chi_v)_1^2 + \varepsilon(x_v)_2 \right]$
	B	$\frac{z_L}{u} (\chi_v)_1$	$2 \cdot \frac{z_L^2}{u^2} \left[\frac{1}{Pe} (\chi_v)_1^2 + \varepsilon(x_v)_2 \right]$
	C	$\frac{z_L}{u} \left[(\chi_v)_1 + \left(x_E + 2 \cdot \frac{x_D}{Pe} \right) \right]$	$2 \cdot \frac{z_L^2}{u^2} \left[\frac{1}{Pe} (\chi_v)_1^2 + 2 \cdot \frac{x_D}{Pe^2} (\chi_v)_1 + \varepsilon(x_v)_2 + \frac{x_D}{Pe} \left(x_E + 3 \cdot \frac{x_D}{Pe} \right) \right]$

ments. In the methodological basis used, the model of a finite layer is probably the most exact from a physical point of view.

Let us consider the limiting cases for very small or very large values of *Pe*, defined by eqn. 34. For $Pe \to 0$, adsorbate is transported through the column almost exclusively by diffusion. In the second limiting case, $Pe \to +\infty$, on the other hand, transport is controlled by convection. The simpler limiting expressions given in Table II, valid with an error of less than 1%, can be obtained for the moments in these limiting cases. Namely, the term $\exp(-Pe) \approx 1$ (for $Pe < 10^{-2}$) or $\exp(-Pe) \approx 0$ (for $Pe > 5$), and also terms $(n + Pe) \approx Pe$ ($n = 1, \ldots, 4$, see Table I) for $Pe > 100n$, are valid with the same error. The resultant condition $Pe > 400$ is usually achieved for normal chromatographic conditions.

It follows from Table II for very small values of *Pe* that there is a fundamental difference among the statistical moments for various models of the sorption layer. In the more frequent case of large *Pe* values, the corresponding moments reduce to the same expressions, and this process is faster for the model of a finite sorption layer (neglecting the dead volume of the column, *i.e.*, $x_E \to 0$) as the influence of boundary effects (and axial dispersion outside the sorption layer) decreases and as the value of *Pe* increases. These qualitative conclusions have following practical consequences: (i) it is preferable to work in the region of small Peclet numbers for experimental verification of various theoretical models; (ii) otherwise, the largest possible *Pe* values should be used, which can be attained by a suitable choice of experimental conditions. This limits the influence of boundary effects, decreases the dependence on the choice of the theoretical model and simultaneously simplifies the numerical treatment of the experimental data.

CONCLUSIONS

The solution of the phenomenological model of linear non-equilibrium chromatography for beds of a finite length in Laplace domain has been obtained. The statistical moments of the elution peak up to the fourth order have been calculated. By the theoretical and numerical analysis of moments, the negative influence of the dead volume and boundary effects on GC separations has been confirmed. However, these dependences are not excessively important for the usual experimental conditions. The selection of the expressions for the first normal and second central moment, calculated on the basis of the models of an infinite, semi-infinite or finite sorption layer, is not decisive for data analysis of current chromatographic measurements.

SYMBOLS

$A(s)$	function defined by eqn. 18b
c	local concentration of adsorbate in the fluid phase
c_0	input adsorbate concentration
C	local adsorbate concentration in the pores of adsorbent particles
d	distance between two peak maxima
D_g	coefficient of molecular diffusion
D_p	axial dispersion coefficient
D_r	effective coefficient of internal diffusion
F_v	volumetric flow-rate of the fluid phase
H	external mass transfer coefficient
H_n	coefficient of the adsorbate transfer from the volume towards the internal surface of the pores
K_n	slope of the Henry adsorption isotherm
L	length of the sorption layer
$L\{f(t)\}$	operator of the Laplace transform
M_A	total injected amount of the adsorbate
n	local concentration of the adsorbed compound
Pe	Peclet number defined by eqn. 34 (dimensionless)
P_v	mean area of the boundary between the pores and the external free volume, βS_v
Q_c	rate of change in adsorbate concentration through transport into the adsorbent grains
Q_n	rate of change of concentration C through adsorption
Q_z	rate of increase of the adsorbate concentration from the source
r	radial coordinate in the adsorbent grain
r_t	radius of the straight empty tube
R	characteristic dimension of the adsorbent particle
R_s	resolution between two consecutive peaks defined by eqn. 39
R_s^*	resolution defined by means of statistical moments; eqn. 40
s	complex parameter of the Laplace transform
S_L	total cross-sectional area of the column
S_v	external specific surface of the adsorbent grains, $v(1 - \alpha)/R$
t	time
$T(s)$	function defined by eqn. 17e
u	linear flow-rate of the fluid phase
u_m	mean linear flow velocity
$U(s)$	function defined by eqn. 17f
W	base peak width
$W_{ij}(s)$	functions defined by eqn. 17d
x_D	dimensionless parameter defined by eqn. 35b
x_E	dimensionless parameter defined by eqn. 35a
$(x_v)_k$	dimensionless complexes defined by eqn. 36
$X(z,s)$	functions defined by eqn. 17c
z	axial coordinate in the column
z_0	positional coordinate of the adsorbate sampling
z_L	positional coordinate of the end of sorption layer

Greek symbols

α	external porosity of the sorption layer
β	internal porosity of the adsorbent granules
$\gamma(z,s)$	function defined by eqn. 19a
$\gamma_v(z,s)$	functions defined by eqn. 18
δ	Dirac delta function
ε	porosity function, $\beta(1 - \alpha)/\alpha$
$\lambda[\sigma_v(s)]$	function defined by eqn. 24b
$\lambda_{1,2}$	roots of the characteristic equation, defined by eqn. 17a
${}^A\lambda_{1,2}$	roots of the characteristic equation, defined by eqn. 17b
μ_k	kth normal statistical moment
μ_k'	kth central statistical moment
v	shape factor of the adsorbent grain
ρ	function defined by eqn. 19d
$\sigma(s)$	function defined by eqn. 19b
$\sigma_v(s)$	function defined by eqn. 18a
$\tau(s)$	function defined by eqn. 24a
$\psi_v(\rho)$	function defined by eqn. 19c
$(\chi_v)_k$	parameters defined by eqn. 37

Subscripts

i	refers to the initial distribution of the adsorbate concentration
k	refers to the moment order

v	refers to the shape factor of the adsorbent grain

Superscripts

A	pertaining to entrance section of the column
B	pertaining to exit section of the column
$\sim$	refers to the Laplace transform

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