

# Interference and heat effects: moment analysis for two-component chromatography

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## ABSTRACT

Moment analysis approach has been developed for two-component non-equilibrium non-isothermal adsorption chromatography. Heat effects and interference between components which may exist through the adsorption equilibrium as well as through rate equations, have been studied for linear perturbation cases. The analytical expressions of the first and second chromatographic moments have been obtained. They are just the vectorization of those obtained for a single-component isothermal system. The influence of interference and heat transfer on the retention times and variances has been displayed. This work leads to a good understanding of competitive adsorption chromatography.

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## INTRODUCTION

Adsorption chromatography has been applied to many industrial processes, which generally involve multicomponent systems. The most important feature of multicomponent chromatography is the interference or coupling between components, which may occur through the adsorption equilibrium isotherms as well as through rate equations (*e.g.* diffusion).

Most simple models of multicomponent chromatography consist of the extension of the single-component analysis for low concentrations within the Henry's law region. Indeed, under such conditions, the system is linear and uncoupled, and the principle of superposition applies. However, at higher concentration, the interference or coupling between components through adsorption isotherms as well as rate equations becomes essential feature of multicomponent

chromatography. As adsorption is always exothermic, adsorption processes are accompanied by heat transfer, which may sometimes be very important [1].

Based on very fast mass transfer (ideal model or equilibrium theory) and its extension (constant-pattern), the interference through the equilibrium isotherms had been studied by many authors [1–6]. Certain linear systems in which interference occurs through both the equilibrium isotherms and diffusion have been studied by spatial moments analysis [7]. Of course, with recourse to numerical computation, more general cases can be resolved.

Adsorption chromatography processes have often been assumed to be isothermal. The first analysis of thermal effects in a pulse chromatography experiment appears to be that of Cerro and Smith [8]. In their work, heat effects were demonstrated by studying the deviation from linear chromatography theory by varying the injection pulse size and concentration. In order to answer the question of whether the linearity of such systems is a sufficient condition to insure

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the absence of thermal effects, Haynes [9] made a study based on temporal moment analysis.

We have recently studied the interference for isothermal non-equilibrium perturbation chromatography by means of the most simple approach: temporal moment analysis widely used in the single-component case [10–12]. In the present paper, an extension of this approach has been performed to non-isothermal system. The analytic expressions of the first and second chromatographic moments have been obtained. They show clearly the influence and heat transfer on the retention times and variances.

#### MODEL

The principle of “perturbation chromatography” or “step and pulse chromatography”, is best illustrated with single-component adsorption isotherms [13]. Consider a chromatographic column packed with spherical adsorbent particles, through which flows a mixture of two adsorbable species (gases or liquids) together with an inert carrier. A small concentration change of pulse type is then performed on the chromatographic column, which is initially at equilibrium and not necessarily clean.

In this paper, following simplifying assumptions are used: (i) The column is initially at equilibrium state. (ii) The equilibrium relationships are linearized as in the single-component chromatographic case. In general, adsorption equilibrium relationships are not linear, however, the linearization is realistic for small sample changes or perturbations, and can give simple characteristic results. (iii) Without loss of generality, the overall rate of adsorption for all the components is represented by the linear driving force (LDF) model. This is due to the well-known equivalence between the LDF model and diffusion model [1]. (iv) The heat transfer resistance in the particle is assumed to be concentrated at the particle surface.

#### Column model

Mass and heat balances in the column void:

$$\frac{\partial \mathbf{c}}{\partial t} + u \cdot \frac{\partial \mathbf{c}}{\partial x} - D_L \cdot \frac{\partial^2 \mathbf{c}}{\partial x^2} + \gamma \cdot \frac{\partial \mathbf{q}}{\partial t} = 0 \quad (1)$$

$$\begin{aligned} \frac{\partial T}{\partial t} + u \cdot \frac{\partial T}{\partial x} - D_L \cdot \frac{\partial^2 T}{\partial x^2} \\ = \gamma \cdot \frac{-\Delta \mathbf{H}^T}{C_f} \frac{\partial \mathbf{q}}{\partial t} - \gamma \cdot \frac{C_e}{C_f} \frac{\partial T_s}{\partial t} \end{aligned} \quad (2)$$

with

$$\mathbf{c} = \begin{pmatrix} c_1 \\ c_2 \end{pmatrix}, \mathbf{q} = \begin{pmatrix} q_1 \\ q_2 \end{pmatrix}$$

$\mathbf{c}$  and  $\mathbf{q}$  are the variations of the mobile and adsorbed phase concentrations (differences with respect to the initial state).

$$-\Delta \mathbf{H}^T = (-\Delta H_1, -\Delta H_2)$$

it is adsorption heat vector. The thermal conductivity here considered is given by  $D_T = C_f D_L$  [1].

Initial and boundary conditions:

$$\mathbf{c}(x, 0) = \mathbf{0}, \mathbf{c}(\infty, t) = \mathbf{0}, \mathbf{c}(0, t) = S_c \delta(t) \quad (3)$$

$$T(x, 0) = 0, T(\infty, t) = 0, T(0, t) = S_T \delta(t) \quad (4)$$

where  $\delta(t)$  is the Dirac function.  $S_c$  and  $S_T$  are, respectively, the strengths (peak areas) of the input pulses in the concentrations and temperature of the mobile phase.

#### Particle model

$$\frac{\partial \mathbf{q}}{\partial t} = [k](\mathbf{q}^* - \mathbf{q}) \quad (5)$$

$$\frac{\partial T_s}{\partial t} = \frac{-\Delta \mathbf{H}^T}{C_e} \cdot \frac{\partial \mathbf{q}}{\partial t} + \frac{3h_p}{RC_e} \cdot (T - T_s) \quad (6)$$

where  $[k]$  is  $(2 \times 2)$  square matrix whose elements represent the overall mass transfer rate coefficients in the particle. If only mass diffusion resistance exists in the particle,  $k_{ii}$  ( $i = 1, 2$ ) characterizes the main diffusion of adsorbed species  $i$ , and  $k_{12}$  (or  $k_{21}$ ) characterizes the co- or counter-diffusion due to the presence of the other species. When  $[k] = \infty$ , adsorption is at equilibrium.  $h_p$  is the heat exchange coefficient between the mobile phase and the adsorbent solid phase.

Adsorption equilibrium:

$$\mathbf{q}^* = [K_c]\mathbf{c} + K_T T_s \quad (7)$$

here, the equilibria between the mobile phase and the stationary adsorbed phase have been linearized for small changes in concentrations and the solid temperature.  $[K_c]$  is  $(2 \times 2)$  square matrices whose elements are the linearized equilibrium derivatives  $K_{c_{ij}} = \partial q_i^* / \partial c_j$  with respect to concentrations.  $\mathbf{K}_T$  is the vector composed of the linearized equilibrium derivatives  $K_{T_i} = \partial q_i^* / \partial T_s$  with respect to the solid temperature.

The interferences between components through the equilibrium isotherms and rates are displayed by the cross-terms (non-diagonal elements) of the matrices. For example, the modification of the diffusion of one component by the presence of the other component is represented by the cross-term rate coefficients  $k_{ij} (i \neq j)$  characterizing co- or counter-diffusions. When these coefficients  $k_{ij} (i \neq j)$  are zero, the diffusion of one component is not affected by the other component. If all the cross-terms of these two matrices are zero, or no interference through the equilibrium isotherms or rates, the system is uncoupled, which is split into the single-component one for each component.

MOMENT SOLUTION

As in our isothermal studies [10-12], we will define the moments for the mobile phase concentrations and temperature (which may be just considered as one component). It is convenient to define these moments in matrix form:

$$\mathbf{m}^1 = \begin{pmatrix} m_{c_1}^1 \\ m_{c_2}^1 \\ m_T^1 \end{pmatrix} = \int_0^\infty t \begin{pmatrix} c_1 \\ c_2 \\ T \end{pmatrix} dt = [\mu] \int_0^\infty \begin{pmatrix} c_1 \\ c_2 \\ T \end{pmatrix} dt \tag{8}$$

$$\begin{aligned} \mathbf{m}^2 &= \begin{pmatrix} m_{c_1}^2 \\ m_{c_2}^2 \\ m_T^2 \end{pmatrix} = \int_0^\infty (t[I] - [\mu])^2 \begin{pmatrix} c_1 \\ c_2 \\ T \end{pmatrix} dt \\ &= [\sigma] \int_0^\infty \begin{pmatrix} c_1 \\ c_2 \\ T \end{pmatrix} dt \end{aligned} \tag{9}$$

$[\mu]$  and  $[\sigma]$  are the corresponding average retention times and variances in tensor form.

By similar way, these moments can easily be obtained by means of matrix diagonalization and the Laplace transform.

$$[\mu] = \begin{bmatrix} \mu_{11} & \mu_{12} & \mu_{13} \\ \mu_{21} & \mu_{22} & \mu_{23} \\ \mu_{31} & \mu_{32} & \mu_{33} \end{bmatrix} = \frac{L}{u} \left( [I] + \gamma \begin{bmatrix} [K_c] & \mathbf{K}_T \\ -\alpha_s \mathbf{H}^T [K_c] & \alpha_s (1 - \mathbf{H}^T \mathbf{K}_T) \end{bmatrix} \right) \tag{10}$$

$$\begin{aligned} [\sigma] &= \begin{bmatrix} \sigma_{11} & \sigma_{12} & \sigma_{13} \\ \sigma_{21} & \sigma_{22} & \sigma_{23} \\ \sigma_{31} & \sigma_{32} & \sigma_{33} \end{bmatrix} = \frac{2D_L L}{u^3} \left( [I] + \gamma \begin{bmatrix} [K_c] & \mathbf{K}_T \\ -\alpha_s \mathbf{H}^T [K_c] & \alpha_s (1 - \mathbf{H}^T \mathbf{K}_T) \end{bmatrix} \right)^2 \\ &+ \frac{2L}{u} \gamma \left\{ \frac{\alpha_s}{\alpha_p} \begin{bmatrix} [0] & 0 \\ -\mathbf{H}^T [K_c] & (1 - \mathbf{H}^T \mathbf{K}_T) \end{bmatrix} \right. \\ &+ \left. \left( \frac{[I]}{-\alpha_s \mathbf{H}^T} \right) \left[ ([k]^{-1} - \frac{1}{\alpha_p} \mathbf{K}_T \mathbf{H}^T) \right. \right. \\ &\left. \left. \times [K_c], \left( [k]^{-1} - \frac{1}{\alpha_p} (\mathbf{K}_T \mathbf{H}^T - [I]) \right) \mathbf{K}_T \right] \right\} \end{aligned} \tag{11}$$

with

$$\mathbf{H}^T = \frac{1}{C_e} \cdot (-\Delta H_1, -\Delta H_2)$$

$$\mathbf{K}_T = \begin{pmatrix} K_{T_1} \\ K_{T_2} \end{pmatrix}$$

Where  $\mu_{ij}$  and  $\sigma_{ij}$  indicate the retention time and variance of component  $i$  due to the input variation of only one component  $j$ .

DISCUSSION

*Isothermal case and interference*

In this case, adsorption equilibrium is independent of temperature and there is no heat of adsorption, we obtain then  $\mathbf{K}_T = \mathbf{H} = \mathbf{0}$ ,  $\alpha_p = \infty$ . Consequently, all the elements associated with temperature in the retention time and variance

matrices ( $\mu_{3j}$ ,  $\mu_{i3}$ ,  $\sigma_{3j}$ ,  $\sigma_{i3}$ ) become zero. So, we obtain the reduced retention time and variance matrices as follows:

$$[\mu]_{2 \times 2} = \begin{bmatrix} \mu_{11} & \mu_{12} \\ \mu_{21} & \mu_{22} \end{bmatrix} = \frac{L}{u} \cdot ([I] + \gamma[K_c]) \quad (12)$$

$$[\sigma]_{2 \times 2} = \begin{bmatrix} \sigma_{11} & \sigma_{12} \\ \sigma_{21} & \sigma_{22} \end{bmatrix} = \frac{2D_1 L}{u^3} \times ([I] + \gamma[K_c])^2 + \frac{2L}{u} \cdot \gamma[k]^{-1}[K_c] \quad (13)$$

which are identical to those obtained in our isothermal study [11].

**No interference.** If, furthermore, the adsorption of one component is assumed to be unaffected by the presence of the other component (through neither the equilibrium nor rates), then no interference between components takes place. In this case, the system reduces to that of the well known single-component case. The equilibrium matrix  $[K_c]$  and rate matrix  $[k]$  are diagonal ( $K_{c_{12}} = K_{c_{21}} = k_{12} = k_{21} = 0$ ). The retention time and variance for each component, given by the diagonal terms of eqns. 12 and 13, are identical to those of the single-component case.

**Interference.** However, for a two-component system, the adsorption of one component may generally be affected by other component through the equilibrium and rate equations. This affectation (or interference) between components is characterized by the cross-terms (non-diagonal elements) of the matrices  $[K_c]$  and  $[k]$ . The influence of this affectation on the retention time and variance is clearly shown by eqns. 12 and 13 through the cross-terms. For example, if we assume that the equilibrium constant  $K_{c_{11}}$  is the same for the mixture of the two-components as it was for the single-component case, and  $K_{c_{12}}$  is (generally) negative, then the retention time for component 1 of the two-component system is smaller than that of the single-component system [10]. On an average, the component 1 of the mixture moves faster.

As in the single-component case, the adsorption equilibria may influence not only the retention times, but also the variances. However, the adsorption rate modifies only the variances.

Consequently, the interference between components through the equilibria may affect both the retention times and variances, the interference through the adsorption rates plays only a second role, affects only the variances.

It is obvious that moment expressions obtained here, eqns. 12 and 13, are just the vectorization of those for the single-component system. The diagonal elements of these equilibrium and rate matrices of the multicomponent system are formally identical to those of the single-component system. However, the multicomponent system not only has the diagonal elements, but also non-zero non-diagonal elements, which displays more clearly the interferences between components.

#### Heat effects

It is well known that adsorption is always exothermic. Adsorption processes are accompanied by heat transfer, which may sometimes be important. From the mathematical model, eqns. 1–7, it can be seen that heat transfer may affect the adsorption equilibria as well as rates, which is also shown by the moment expressions, eqns. 10–11. So, if temperature is considered as the third component, heat effects become one more interference between the species components (component 1, 2) and the third component.

**Haynes' case.** Haynes [9] studied heat effects in a chromatographic system with a single-component (e.g. component 1) equilibrium adsorption.

Consider now Haynes' case: instantaneous adsorption ( $k_{11} = \infty$ ), no temperature difference between the injection and the initial state ( $S_T = 0$ ). Under these conditions, we have obtained the reduced retention time and variance of the mobile phase concentration as follows:

$$\frac{m_{c_1}^1}{S_{c_1}} = \mu_{11} = \frac{L}{u} \cdot (1 + \gamma K_{c_1}) \quad (14)$$

$$\frac{m_{c_1}^2}{S_{c_1}} = \sigma_{11} = -\frac{2\gamma L}{u} \cdot \frac{H_1 K_{T_1}}{\alpha_p} \cdot K_{c_1} + \frac{2D_1 L}{u^3} \cdot (1 + \gamma K_{c_1})^2 \quad (15)$$

These results are identical to those of Haynes [9]. If, moreover,  $K_{T_1} = 0$  as supposed by Haynes for pulse chromatography, the second last term in eqn. 15 becomes zero, and we get the same conclusion as Haynes no heat effects and system linearity being a sufficient condition. However, in general,  $K_{T_1} \neq 0$ , e.g. for some systems such as water vapor–zeolite NaX ( $K_{T_1} = -1.0 \text{ kg m}^{-3} \text{ K}^{-1}$ , for pressure step: 0–200 Pa) [14], or for perturbation chromatography (the initial state is preadsorbed under a certain concentration),  $K_T$  is not always negligible. Then, the system linearity is not a sufficient condition to insure the absence of heat effects.

So, Haynes' study [9] is concerned with a special case. For more general cases, heat effects should be taken into account. The expressions obtained in eqns. 10 and 11 can be used to estimate these effects.

*Heat transfer resistance at the particle surface.* Shown by the formulae 10, the heat transfer resistance at the particle surface does not modify the first moments for the concentrations and temperature. However, it contributes to the variances as adsorption kinetics. So, it is important to distinguish the heat effects from those of kinetics, particularly for the determination of kinetic coefficient  $k$  by chromatographic technique. Taking again the example of water vapor–zeolite, for particle (crystal) diameter  $R = 10^{-4} \text{ m}$ , we have:  $1/k_{11} = 13.3 \text{ s}^{-1}$ , and  $H_1 K_{T_1} / \alpha_p = -25 \text{ s}^{-1}$ . From eqn. 11, the neglect of heat effects would lead to a relative error at least of 200% in the calculation of  $k$ . So the heat effects are, in this case, dominant with respect to kinetics.

## CONCLUSIONS

The moment analysis approach, developed in our previous works to study chromatography interference between components has now been extended to the non-isothermal case. Using the same technique (matrix diagonalization), the analytical expressions for the first and second moments of species components and temperature have been obtained. In these expressions, the interference between species components through both the adsorption equilibria and rates

has clearly been shown by the non-diagonal matrices  $[K_c]$  and  $[k]$ . The influence of heat effects may be considered as one more interference between species component and temperature. This influence may sometimes be important. It shows that the behaviour of any particular component (species or temperature) is affected by the presence of the other components.

## SYMBOLS

$c$	fluid concentration (difference from initial state), $\text{kg m}^{-3}$
$\mathbf{c}$	concentration vector
$C_e$	heat capacity of particle, $\text{J K}^{-1} \text{ m}^{-3}$
$C_f$	heat capacity of mobile phase, $\text{J K}^{-1} \text{ m}^{-3}$
$D_L$	dispersion coefficient, $\text{m}^2 \text{ s}^{-1}$
$h_p$	heat transfer coefficient at the particle surface, $\text{W m}^{-2} \text{ K}^{-1}$
$H$	$= -\Delta H / C_e$ , $\text{K m}^3 \text{ kg}^{-1}$
$\mathbf{H}$	vector composed of $H_i$ ( $i = 1, 2$ )
$-\Delta H$	heat of adsorption, $\text{J kg}^{-1}$
$-\Delta \mathbf{H}$	vector composed of $-\Delta H_i$ ( $i = 1, 2$ )
$[I]$	identity matrix
$K_c$	equilibrium first-order derivative with respect to concentration
$[K_c]$	matrix composed of $K_{c_{ij}}$ ( $i, j = 1, 2$ )
$K_T$	equilibrium first-order derivative with respect to temperature, $\text{kg K}^{-1} \text{ m}^{-3}$
$\mathbf{K}_T$	vector composed of $K_{T_i}$ ( $i = 1, 2$ )
$[k]$	adsorption rate first-order derivative matrix, $\text{s}^{-1}$
$L$	length of column, m
$q$	adsorbed mass (difference), $\text{kg m}^{-3}$
$\mathbf{q}$	adsorbate concentration vector
$q^*$	equilibrium adsorbate concentration, $\text{kg m}^{-3}$
$\mathbf{q}^*$	equilibrium adsorbate concentration vector
$R$	particle radius
$S_c$	strength of concentration input, $\text{kg s m}^{-3}$
$\mathbf{S}_c$	vector composed of $S_{c_i}$ ( $i = 1, 2$ )
$S_T$	strength of temperature input, $\text{K s}$
$T$	fluid temperature, $\text{K}$
$T_s$	adsorbent particle temperature, $\text{K}$
$t$	time, s
$u$	velocity, $\text{m s}^{-1}$
$x$	column axial coordinate, m

*Greek symbols*

$$\alpha_p = 3h_p / RC_e, \text{ s}^{-1}$$

$$\alpha_s = C_e / C_f$$

$$\gamma = (1 - \varepsilon) / \varepsilon$$

$\mu$  first moment, s

$\sigma$  second central moment, s<sup>2</sup>

$\varepsilon$  porosity of the column

*Superscripts*

T transposition

*Subscripts*

$i, j$  component  $i, j$  ( $i, j = 1, 2, 3$ ) (1, 2 indicates concentration, 3 indicates temperature)

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