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A new moment analysis method to estimate the characteristic parameters in chromatographic general rate model

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ABSTRACT

In conventional moment analysis, detailed information regarding the retention equilibrium and mass transfer kinetics is derived from the 1st normalized moment and standard deviation of the chromatograms respectively. The moment values are determined from their analytical expressions. In the moment analysis method of this work, the moment values are estimated accurately from the simulated chromatograms by the application of the weighed residual moment method. For parameters estimation, our moment analysis method can be implemented not only on the symmetric chromatograms with linear isotherms as in conventional moment analysis, but also to the analysis of asymmetric chromatograms with nonlinear and competitive isotherms. Also compared to the commonly used parameter estimation method (fitting with experimental concentration points), our moment analysis method approached faster to the optimized values and the final parameters were also better identified.

1. Introduction

Over decades, mathematical modeling has been applied to study phenomenological aspects of the chromatographic processes and to predict chromatographic column performance. Accurate prediction of the chromatograms (effluent curves) requires correct characteristic model parameters. Minimization of the errors between the simulated chromatograms and the discrete measurement concentration data is a common practice in order to accurately estimate the parameters. For example, Wilhelm, Casamatta, Carillon, Rigal, and Gaset (1989) proposed a model for the separation of sugars and determined axial dispersion coefficient by parameter fitting. Li, Gu, and Gu (1998) used mathematical modeling to fit the pore tortuosity and pore diffusivity in a scale up experiment. Felinger, Zhou, and Guiochon (2003) determined the competitive adsorption isotherm by the inverse method.

Another effective strategy for estimation of the chromatographic parameters is the moment analysis method. In 1965, Kubin and Kucera introduced the analytical expressions of the statistical moments of the chromatograms derived from a general rate model (Kubin, 1965; Kucera, 1965). After that, a number of researchers extended the work of Kubin and Kucera for various applications (Haynes & Sarma, 1973; Moulijn, Kolk, & Rijnders, 1977; Suzuki, 1990). Most recently Miyabe (2009) systematically studied the behaviors of different chromatographic processes by moment analysis. The idea behind the moment analysis method is to determine the retention (adsorption) equilibrium and mass transfer kinetics from the moments of the chromatograms. In this conventional moment analysis, only the 1st normalized moment and 2nd central moment are analyzed because it is most difficult to measure experimentally higher order moments with high accuracy (Miyabe & Guiochon, 2003). The conventional method can be applied only with linear isotherms which theoretically result in symmetric chromatograms.

Alopaeus, Laavi, and Aittamaa (2008) developed the weighted residual moment method for dynamic plug-flow reactor models and simple plug flow chromatographic models. Roininen and Alopaeus (2011) presented the weighted residual moment method for solving the models including axial dispersion in reactors in a successive paper. Recently Liu, Roininen, Pulkkinen, Sainio, and Alopaeus (2013) extended the weighted residual moment method to solve the nonlinear multicomponent chromatographic general rate model. The weighted residual moment method is based on minimization of errors in the column profile moments. This suggests that the method predicts the moments of the chromatograms also with minimized errors. Therefore the accurate predictions of retention time (1st normalized moment), physical dispersion (2nd central moment) and skewness (3rd central moment) of the chromatograms can be achieved. This feature indicates that the weighted residual moment method is especially suitable for the chromatograms moment analysis. In the conventional moment analysis, the moment values of the chromatograms are calculated

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with the available analytical expressions (Miyabe, 2009). In this work, the moment values with minimized errors are obtained from the simulated chromatograms. The numerical tool used to solve the model is the weighted residual moment method.

In this paper the 1st normalized moment, 2nd central moment and 3rd central moment are used in the moment analysis for asymmetric chromatograms caused by nonlinear isotherms. The moment values and the discrete concentration points of measured chromatograms are used respectively in the objective functions in order to estimate the model parameters. With the optimized parameters by the two objective functions, simulations are performed and the results are discussed. Finally, the merits of our moment analysis method over the conventional method are discussed.

2. Research methods

2.1. The concepts of moments

The concepts of 1st normalized moment, 2nd and 3rd central moments are first reviewed due to their fundamental nature in this work. The mean, standard deviation and skewness of the chromatograms, closely related to the moments, are used in the moment analysis of this work. A brief review on these definitions is presented below (Guiochon & Golshan-Shirazi, 1994).

The 1st normalized moment (M_1), denoted also as μ, is the mean of the curve. For a chromatographic effluent curve it can be expressed as:

$$\mu = M_1 = \frac{\int_0^\infty C(t,L)t\ dt}{\int_0^\infty C(t,L)\,dt} \tag{1}$$

where $C(t, L)$ is the concentration at the column exit, L is the column length, and t is time. Eq. (1) is the continuous expression of the 1st normalized moment. The measured and simulated chromatograms appear as a number of discrete concentration points. Therefore the moment values of the chromatograms are calculated from the definitions of the discrete forms of the moments in this work. For the 1st normalized moment,

$$\mu = M_1 = \frac{\sum_{i=1}^{k} C(t_i)t_i\Delta t_i}{\sum_{i=1}^{k} C(t_i)\Delta t_i} \tag{1a}$$

k is the total number of the experimental concentration points or the simulated concentration points. The column length L is dropped out from the equation above for simplicity. Δt_i is the time interval between ith and $(i-1)$th sampling points. If the sampling is with constant frequency, then Δt_i drops away.

The 2nd central moment (M_2) about the mean μ is the variance. It describes the “width” of the curve.

$$M_2 = \frac{\int_0^\infty C(t,L)(t-\mu)^2\,dt}{\int_0^\infty C(t,L)\,dt} \tag{2}$$

The discrete form of 2nd central moment (M_2) is:

$$M_2 = \frac{\sum_{i=1}^{k} C(t_i)(t_i-\mu)^2\Delta t_i}{\sum_{i=1}^{k} C(t_i)\Delta t_i} \tag{2a}$$

Its square root is the standard deviation σ, which is:

$$\sigma = \sqrt{M_2} \tag{3}$$

The 3rd central moment (M_3) is a measure of the deviation from symmetry of the curve. Any symmetric distribution will have a 3rd central moment of zero. The skewness, γ, closely related to the 3rd central moment is often used to describe the lopsidedness of the curve. A distribution that is skewed to the right (the tail of the distribution is longer on the right) will have a positive skewness. A distribution that is skewed to the left (the tail of the distribution is longer on the left) will have a negative skewness. The expressions of M_3 and γ are:

$$M_3 = \frac{\int_0^\infty C(t,L)(t-\mu)^3\,dt}{\int_0^\infty C(t,L)\,dt} \tag{4}$$

The discrete form of 3rd central moment (M_3) is:

$$M_3 = \frac{\sum_{i=1}^{k} C(t_i)(t_i-\mu)^3\Delta t_i}{\sum_{i=1}^{k} C(t_i)\Delta t_i} \tag{4a}$$

$$\gamma = \frac{M_3}{\sigma^3} \tag{5}$$

The effluent curve could also be characterized based on higher order moments, such as kurtosis calculated by using the fourth moment. However, this would need extremely accurate effluent curve data which is not typically available. As kurtosis and higher moments do not generally correspond to typical visually analyzed effluent curve characteristics, contrary to the three first moments, they are left out from the present study.

2.2. Experimental

The separation was carried out in a pilot scale batch column (inner diameter 0.225 m, resin bed length 5.3 m, bed porosity $\varepsilon_b = 0.34$) at 60 °C and with 30 l/h flow rate. The resin used in chromatographic separation test was a strong acid cation exchange resin (Finex CS 11 GC) in sodium form (particle porosity $\varepsilon_p = 0.4$). Total feed volume was 11.5 l. Concentrations of glucose and galactose were 10.61 g/100 ml and 10.04 g/100 ml, respectively. The experimental setup was reported in more detail in Saari, Häkkä, Jumppanen, Heikkilä, and Hurme (2010, p. 33). The distribution coefficients were 1.08 and 1.24 for glucose and galactose respectively from equilibrium measurement data (Saari, Heikkilä, & Hurme, 2010, p. 55).

2.3. Mathematical model

Separation of monosaccharides is often based on ligand exchange, i.e. formation of weak complexes with metal cations, such as Ca^{2+}, in the ion exchange resin. In the present work, however, the ion exchange resin was used in Na^+ form, and the separation is mostly due to size exclusion and to a smaller extent to interactions with the functional groups of the resin. In order to include such weak adsorptive interactions, the Langmuir isotherm model was used instead of a linear exclusion model. The general rate model applied in this work is introduced in Wilhelm et al. (1989) and Li et al. (1998). The dimensionless models for the bulk-fluid phase and the particle phase are:

$$\frac{\partial \psi_b}{\partial \theta} = -\frac{\partial \psi_b}{\partial \zeta} + \frac{1}{Pe}\frac{\partial^2 \psi_b}{\partial \zeta^2} - \xi(\psi_b - \psi_{p,r=1}) \tag{6}$$

$$\frac{\partial \psi_p}{\partial \theta} = \frac{\eta}{\varepsilon_p}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial \psi_p}{\partial r}\right) \tag{7}$$

with the dimensionless initial and boundary conditions

$$\text{I.C.}\quad \theta = 0;\quad \psi_b = \psi_b(0,\zeta);\quad \psi_p = \psi_p(0,r,\zeta) \tag{8}$$

$$\text{B.C.}\quad \zeta = 0,\ \frac{\partial \psi_b}{\partial \zeta} = Pe\left(\psi_b - \frac{C_f(\theta)}{C_{ref}}\right);\quad \zeta = 1,\ \frac{\partial \psi_b}{\partial \zeta} = 0 \tag{9}$$