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Extending the potential of moment analysis in chromatography

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ABSTRACT

Essential goal of modeling chromatographic processes is to describe the dynamics of concentration fronts traveling through chromatographic columns. Most of the models developed originate from differential mass balances for the fluid and solid phases. Model reduction based on evaluating just a limited number of moments of the profiles is known to be a powerful tool to simplify the description of band profiles. This review article first describes the well-established method of moments for different standard models. Then the method is extended to evaluate more complex and realistic column models. The cases of applying columns packed with core-shell particles and the quantitative description of radial concentration profiles are analyzed.

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1. Introduction

Most of the mathematical models for chromatographic columns originate from differential mass balances for the fluid and solid phases [1–4]. Information about the column effluent profiles is the key for a rational process design and optimization. However, often the original differential mass balances models require the application of time consuming numerical solution techniques and it is often sufficient to condense the information of the complete concentration profile into a few characteristic features. Moment analysis (MA) is well-established method that provides condense information in the form of relatively small number of temporal moments. It can be applied a) to describe in a simpler manner essential feature of the chromatograms, b) to estimate efficiently free model parameters by matching measured and predicted moments, c) to predict performance parameters of the separations and, thus, d) to optimize more easily the process [2,5–10]. In this study, we address essentially just the aspect a). Regarding the importance of these moments there is a clear hierarchy about the quality of representing chromatograms. It is more crucial that there is an agreement between predicted and measured values for lower order moments than for higher order moments. This is due to the fact that the zeroth moment describes the sample mass or peak area, the first moment corresponds to the mean retention time, the second moment quantifies the peak width or column efficiency, and the third moment represents the peak asymmetry (skewness). The fourth order moment still has a physical meaning (kurtosis) but is already difficult to measure precisely and because of that reason is hardly evaluated. Whereas there is a clear integration formula available to determine the moments from experimentally observed profiles, there is no simple connection between the thermodynamic and kinetic parameters of the chromatographic models, the operating parameters of the process and the corresponding theoretical moments. For the simplified situation of linear distribution equilibria for many of the chromatography models the moment generating property of the Laplace transform can be efficiently used to derive analytical expressions for the temporal moments. The method develops a new strategy for the analysis of chromatographic behavior beyond the ordinary plate and rate theories of chromatography [5–10].

Moment analysis has been comprehensively elaborated in the chromatographic literature [2,7–20]. In these partly classical papers analytical moments were derived for specific chromatographic models and boundary conditions. The analysis typically covered just the most important first and second moments, i.e. retention times and band broadening. Beside the first and second moments, in a few studies also the third moment, which describes the peak asymmetry, was derived and evaluated, e.g. in the work of Prof. G. Guiochon [5,6]. In our recently published couple of papers, we addressed several aspects that have not been considered to this depth up to now [21–25]. Apart from considering the three standard chromatographic models, we derived and compared also the fourth order moment, i.e. the kurtosis or flatness of the profile. Using low-noise detectors and complete capture of the responses this moment appears to be still experimentally accessible. As discussion on the influence of the boundary conditions (BCs) were often ignored in the literature, we compared the moment analysis for Dirichlet and Danckwerts BCs considering both rectangular pulses and steps as inlet profiles. For quantitative comparison, the first four moments of the General Rate Model (GRM), the Lumped Kinetic Model (LKM), and the Equilibrium Dispersive Model (EDM) were derived. With this analysis it was intended to elucidate the connections between the specific kinetic parameters, including for the first time the results for the fourth moments. Finally, going beyond previous studies, we provided a comparisons of the analytically derived moments with moments calculated independently by integrating numerically calculated effluent profiles. For this purpose advanced high resolution finite volume scheme was applied, which is capable to treat also the more general case of nonlinear equilibria [26]. We have recently extended the aforementioned analysis to core-shell particles using the GRM [25]. Core-shell particles were invented and pioneered by Horvath et al. [27] with the specific purpose of preparing columns that could provide highly efficient HPLC separation of high molecular weight compounds of biological origin. They are beneficial over fully porous beads in reducing diffusional mass transfer resistances in particle macropores and separation times. Furthermore, they can be also useful to regulate bead densities. Several researchers, including Guiochon and his co-authors, worked on the understanding and improvement of coreshell particles performance [28–35]. The analysis of one-dimensional (1D) models was recently extended to the analysis of two-dimensional (2D) models describing the movement of a solute in a two-dimensional chromatographic column of radial geometry [24]. In this case, the finite Hankel and Laplace transformations were simultaneously applied to solve the model equations. After eliminating the radial coordinate by Hankel transformation, the Laplace transformation was applied to solve the model equations analogously to the solution of 1D models.

In this review article, we provide a summary of the above mentioned instructive solutions by focusing on the: a) derivation of analytical expressions of first four temporal moments for the GRM and LKM using fully porous particles, b) derivation of first three temporal moments of GRM for core-shell particles, and on the c) derivation of first four temporal moments for the 2D GRM. To derive analytical moment expressions for the latter case, the Hankel transformation needs to be applied initially. The analysis is mainly focused on the derivation of temporal moments for the general rate model (GRM), while the temporal moments of LKM are derived as limiting cases of the GRM moments. The moments of simplified Equilibrium Dispersive Model (EDM) can be deduced from the moments of LKM by considering fast transport.

The structure of the article is as follows. In Section 2, the 1D GRM, 1D LKM and 2D GRM are briefly introduced. Section 3 presents the moments of 1D GRM and LKM for fully porous particles using Dirichlet BC. Section 4 presents the temporal moments of the 1D GRM for core-shell particles considering both Dirichlet and Danckwerts BCs. The first four temporal moments of 2D GRM are presented in Section 5 for Dirichlet BC. A few selected numerical test problems are presented in Section 6 for illustrating the results. Concluding remarks are given in Section 7.

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