



The modeling of overloaded elution band profiles in supercritical fluid chromatography



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ARTICLE INFO

Article history:

Received 30 October 2013

Received in revised form 11 January 2014

Accepted 13 January 2014

Available online 31 January 2014

Keywords:

Average volumetric flow rate

Supercritical fluid chromatography

Equilibrium-dispersive model

ABSTRACT

Three methods were used to analyze elution bands of methanol on silica, using pure CO₂ as the eluent. The results of these analyses were applied to calculate overloaded elution band profiles in supercritical fluid chromatography. The results obtained are compared. To ensure that the mobile phase density varies widely along the column bed, high volumetric flow rates of the mobile phase (CO₂) were applied to two columns packed with neat, porous silica. Then, even a slight error made in the determination of the isotherm parameters or during the numerical calculations should be magnified compared to those obtained with a low pressure drop along the column. During the determination of the isotherms of adsorption of methanol from liquid carbon dioxide onto silica, the inlet and outlet pressure of the column, the mass flow rate and the temperature were monitored continuously. Based on these parameters, overloaded elution bands were calculated numerically using three calculation methods. The results are compared with experimental ones.

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1. Introduction

The availability of reliable procedures permitting the accurate calculation of the profiles of overloaded elution bands was proved to be necessary for the computer-assisted optimization of the experimental conditions used in preparative-scale liquid chromatography [1]. The basis of all the calculation procedures available is a numerical solution of the mass-balance equation of the compounds considered in the column. During the last twenty years, several approaches were introduced to determine the profiles of overloaded elution bands in large scale separations [1]. The results obtained when using several isotherm models were compared with experimental chromatograms [2–4]. The conclusion was that, when a proper numerical algorithm and a suitable isotherm model are used, it is possible to design large scale separations that achieve maximum productivity at relatively low cost [5,6]. Our purpose is to modify the classical procedures used in liquid chromatography and apply them to supercritical fluid chromatography (SFC).

The foundation of all the procedures used to calculate the profiles of overloaded elution bands is a deep understanding of the retention mechanism taking place in the chromatographic system used. A precise and accurate determination of the adsorption isotherm parameters is also an important requirement for the

success of the calculation process [7–9]. There are more experimental parameters to affect the reproducibility and the accuracy of the isotherm parameters and the optimization of large scale separations in SFC than in liquid chromatography. These factors were reviewed and discussed by Guiochon and Tarafder [10].

The adsorption properties of small molecules on silica surface have been studied by various methods. Scott and Kucera [11] showed that polar molecules able to give hydrogen bonding, such as isopropyl alcohol or ethyl acetate dissolved in n-heptane, interact with silica surface and form a monolayer at low concentrations or an adsorbed double layer at high concentrations. Lochmüller and Mink [12] measured the adsorption isotherm of ethyl-acetate on a silica adsorbent from supercritical carbon dioxide and modeled the adsorption isotherm with the Langmuir isotherm model.

Recently, the nonlinear adsorption characteristics of the naproxen enantiomers were investigated, and several methods of isotherm determination were compared to estimate their adsorption isotherm parameters [13]. The transfer of isotherm determination methods from liquid chromatography to supercritical fluid chromatography is now actively discussed. The issues affecting the transfer into SFC of the Elution by Characteristic Points, the Retention Time Method, the Inverse Method and the Perturbation Peak method were investigated under quasi isopycnic conditions [14].

This work discusses the consequences of the choice made between different approaches of modeling overloaded elution band profiles. To investigate the influence of the pressure drop along the column on the adsorption properties, our experiments were carried

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out with high pressure drops along the column. The calculations were based on the adsorption data of methanol on two silicagel adsorbents. Such a system is suitable to investigate adsorption mechanisms. All our calculations used the isotherm parameters determined by frontal analysis experiments. Three approaches were investigated for these calculations. In all cases, we used the continuous plate model. The calculations were done first by using the volumetric flow rate set with fixed isotherm parameters in each column section. Second, this flow rate was replaced by an average volumetric flow rate calculated from the mass flow of the mobile phase and its average density inside the column and the calculations were carried out using fixed isotherm parameters. In the third approach, the isotherm parameters and the linear velocity were changed in each column section.

2. Theory

2.1. The model of supercritical fluid chromatography

The equilibrium-dispersive model of chromatography is widely used to describe the migration of large volumes of molecules at high concentrations along a chromatographic column when the mass transfer kinetics is fast. The main difference between the well known mass-balance equation introduced in liquid chromatography and the one needed in SFC is the need to incorporate the influence of the significant change of the mobile phase velocity along the column. The mass-balance equation for a chromatographic system that is operated with a compressible mobile phase can be written [1,15]:

$$\frac{\partial C_i(z)}{\partial t} + F \frac{\partial q_i(z)}{\partial t} + \frac{\partial(C_i(z) \times u(z))}{\partial z} = D_{a,i} \frac{\partial^2 C_i(z)}{\partial z^2} \quad (1)$$

where $C_i(z)$ and $q_i(z)$ are the concentrations of compound i in the mobile and the stationary phases at equilibrium, respectively, while $u(z)$ is the mobile phase linear velocity. All of these variables are function of the position along the column axis, z , since the mobile phase density varies along the column, due to its compressibility. In Eq. (1) t is the time and F is the phase ratio – independent from the density change of the mobile phase – or the ratio of the volumes of the stationary V_s and the mobile phase V_0 inside the column:

$$F = \frac{V_s}{V_0} \quad (2)$$

$D_{a,i}$ is the apparent dispersion coefficient. All the kinetic effects are lumped into this term.

2.2. Frontal analysis

The simplest model of nonlinear chromatography is the ideal model. It assumes the column efficiency to be infinite, with no axial dispersion and constant equilibrium between the two phases. This model neglects completely the influence of the mass transfer kinetics and of axial dispersion on the band profiles. Consistent with the basic assumptions of the ideal model, the band profiles obtained as solutions of this model agree well with experimental chromatograms recorded for large samples eluted on highly efficient columns, in which case the deviation of the equilibrium isotherm from linear behavior is important and the dispersive effects of a finite column efficiency are small. According to the above assumptions, Eq. (1) reduces to:

$$\frac{\partial C_i(z)}{\partial t} + F \frac{\partial q_i(z)}{\partial t} + \frac{\partial(C_i(z) \times u(z))}{\partial z} = 0 \quad (3)$$

The retention time of the breakthrough front, $t_{R,F,i}$, of component i during a frontal analysis measurement is provided by a solution of Eq. (3):

$$t_{R,F,i} = \int_0^L \frac{1}{u(z)} \left[1 + F \frac{q_i(z)}{C_i(z)} \right] dz \quad (4)$$

where L is the column length. When several simplifications and assumptions are introduced, Eq. (4) can be transformed into an equation that is practically more relevant.

1. It is possible to accurately estimate the temperature, the pressure and the mass flow rate of the mobile phase at any point in the instrument used, including the column.
2. Based on the known pressure and temperature, the mobile phase density can be calculated accurately in any place along the column z axis. Using this calculated density profile, an average density value $\tilde{\rho}$ can be introduced.

$$\rho(z) \simeq \tilde{\rho} \quad (5)$$

The value of $\tilde{\rho}$ reflects properly the density variation along the column.

3. The variable linear velocity along the column can be replaced by the average linear velocity derived from the average density of the mobile phase through the equation

$$u(z) \simeq u(\tilde{\rho}) \quad (6)$$

4. The linear velocity is independent of the adsorption process taking place along the column. In gas chromatography, it was shown that, when the adsorption of one compound affects the flow rate, a well defined deviation from the ideal band profile can be observed [16]. Such deviations have never yet been reported to take place in supercritical fluid chromatography. Frontal analysis measurements provide sharp fronts, as the ideal model suggests that they should.

5. The adsorbed concentration of a compound on the adsorbent surface that is variable along the column can be accurately replaced by an average value derived from the average mobile phase density.

$$q_i(z) \simeq q_i(\tilde{\rho}) \quad (7)$$

6. The equilibrium mobile phase concentration of component i varies due with the density of the mobile phase. It can be replaced by an average value, equal to its feed concentration.

$$C_i(z) \simeq C_i(\tilde{\rho}) \simeq C_i \quad (8)$$

With the above assumptions Eq. (4) simplifies to:

$$t_{R,F,i} = \frac{L}{u(\tilde{\rho})} \left[1 + F \frac{q_i(\tilde{\rho})}{C_i} \right] \quad (9)$$

By rearranging Eq. (9) and using $t_0 = L/u(\tilde{\rho})$ we obtain:

$$q_i(\tilde{\rho}) = \frac{C_i}{F} \frac{t_{R,F,i} - t_0}{t_0} = C_i \frac{V_0}{V_s} \frac{t_{R,F,i} - t_0}{t_0} \quad (10)$$

Introducing the average volumetric flow rate of the mobile phase, \tilde{F}_V , when the column is connected to the chromatograph and using:

$$V_0 = \tilde{F}_V \times t_0 \quad \text{and} \quad V_{R,F,i} = \tilde{F}_V \times t_{R,F,i} \quad (11)$$

provides

$$q_i(\tilde{\rho}) = \frac{C_i(V_{R,F,i} - V_0)}{V_s} \quad (12)$$

To take into account the contribution of the extra-column volume of the instrument, particularly those of the mixer and the connecting tubes to the retention volume of the breakthrough front measured, an extra parameter must be introduced, the retention volume of

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