



# Modeling of thermal processes in very high pressure liquid chromatography for column immersed in a water bath: Application of the selected models

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## ARTICLE INFO

### Article history:

Received 16 March 2010

Received in revised form 3 May 2010

Accepted 7 May 2010

Available online 19 May 2010

### Keywords:

VHPLC

Heat generation

Viscous friction

Peak profiles

Equilibrium-dispersive model

Transport-dispersive model

POR model

Column efficiency

## ABSTRACT

Currently, chromatographic analyses are carried out by operating columns packed with sub-2  $\mu\text{m}$  particles under very high pressure gradients, up to 1200 bar for 5 cm long columns. This provides the high flow rates that are necessary for the achievement of high column efficiencies and short analysis times. However, operating columns at high flow rates under such high pressure gradients generate a large amount of heat due to the viscous friction of the mobile phase stream that percolates through a low permeability bed. The evacuation of this heat causes the formation of significant or even large axial and radial gradients of all the physico-chemical parameters characterizing the packing material and the mobile phase, eventually resulting in a loss of column efficiency. We previously developed and successfully applied a model combining the heat and the mass balances of a chromatographic column operated under very high pressure gradients (VHPLC). The use of this model requires accurate estimates of the dispersion coefficients at each applied mobile phase velocity. This work reports on a modification of the mass balance model such that only one measurement is now necessary to accurately predict elution peak profiles in a wide range of mobile phase velocities. The conditions under which the simple equilibrium-dispersive (ED) and transport-dispersive (TD) models are applicable in VHPLC are also discussed. This work proves that the new combination of the heat transfer and the ED model discussed in this work enables the calculation of accurate profiles for peaks eluted under extreme conditions, like when the column is thermostated in a water bath.

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## 1. Introduction

Analysts in the pharmaceutical and fine chemical industries are under strong pressure to increase considerably the speed and throughput of HPLC analyses while keeping constant or even increasing peak resolutions. For these reasons, manufacturers of packing materials are preparing and packing new brands of finer silica particles. Various types of columns packed with sub-2  $\mu\text{m}$  particles are now commercially available. The permeability of these columns is much lower than that of conventional columns but the velocity under which they should be operated for optimum results is larger. In order to fully exploit the potential of these new columns, analysts need to operate them under high inlet pressures, up to 1000 bar or more. However, high linear velocities of the mobile phase require steep pressure gradients along the columns and these combine to generate important amounts of heat. This heat, due to

the friction of the mobile phase against the bed through which it percolates, escapes through axial convection, radial and axial conduction. This evacuation causes an important thermal heterogeneity of the column and losses of its efficiency that depend on the thermal environment of the column.

An abundant literature [1–19] deals with theoretical and experimental investigations of the consequences of heat generation by viscous friction in chromatographic columns: (1) the degree of thermal heterogeneity due to the evacuation of this heat; (2) the distributions throughout the columns of the temperature, hence the mobile phase velocity, the viscosity and the density, and (3) the resulting column efficiency. Recently, the profiles of peaks eluted from a column immersed in a water bath were determined in a wide range of mobile phase flow rates and at several bath temperatures [20]. It was shown that, when the temperature of the column wall is kept constant, the peak profiles are Gaussian at low flow rates and become trapezoidal at high flow rates (i.e., at very high inlet pressures).

We previously [21,22] described a new model accounting for column behavior under such conditions. This model combines the heat balance of the column and its mass balance in the equilibrium-

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**Nomenclature**

$C$	concentration in mobile phase
$\bar{C}_p$	average concentration in the mobile phase
$d_p$	adsorbent diameter
$D_{eff}$	effective particle diffusivity
$D_{z,a}$	axial apparent dispersion coefficient
$D_L$	axial dispersion coefficients
$D_{r,a}$	radial apparent dispersion coefficient
$D_m$	molecular diffusion coefficient
$E$	activation energy
$F$	phase ratio
$F_v$	volumetric mobile phase flow
$H$	Henry constant
$k$	overall mass transfer coefficient
$k_{ext}$	external mass transfer coefficient
$k_f$	apparent overall mass transfer coefficient
$L$	column length
$N$	number of theoretical plates
$q$	concentration in stationary phase
$q^*$	equilibrium concentration in solid phase
$q_s$	saturation capacity
$\bar{q}$	average concentration in stationary phase
$R$	gas constant
$R_p$	the particle radius
$t$	time
$t_p$	injection time
$T$	temperature
$u$	superficial velocity
$V_m$	partial molar volume
$w$	interstitial velocity

*Greek symbol*

$\varepsilon_e$	external porosity
$\varepsilon_t$	total column porosity
$\varepsilon_p$	particle porosity
$\gamma_1, \gamma_2$	geometrical constant
$\eta$	viscosity
$\rho$	density
$\tau$	tortuosity parameter

*Subscripts*

$F$	inlet value
$ext$	external

dispersive (ED) model with an isotherm model for the analyte, and the equations accounting for flow in porous media. It takes into account the influence of the axial and radial distributions of the local temperature and pressure on the values of the viscosity and density of the mobile phase, on its velocity, and on the Henry constant of the analyte. This model was validated by its correct predictions of the temperature distribution along the walls of columns packed with either conventional 5  $\mu\text{m}$  particles or sub-2  $\mu\text{m}$  particles, and of elution band profiles of analytes. Noteworthy were the correct predictions of peak profiles eluted from a sub-2  $\mu\text{m}$  particle column held in a water bath at 299 K. This good agreement between calculated and recorded peak profiles was achieved, however, only because the apparent axial dispersion coefficient needed in the ED model was estimated separately, by parameter identification, at each mobile phase velocity studied.

The efficiency of columns operated under VHPLC conditions at constant wall temperature can be extremely low, as low as a

few hundred theoretical plates. At such low efficiencies, the solution of the classical ED or TD models may differ considerably from that given by the general rate (GR) or the lumped pore diffusion model (POR). We previously proposed [23,24] the use of correlations between the apparent dispersion coefficient (for the ED model) or the effective overall mass transfer coefficient (for the TD model) and proved that these models could be applied to predict the profiles of bands eluted from very low efficiency columns. However, the applicability of these correlations has never been checked yet for chromatographic systems in which the physico-chemical parameters vary along and across the column because this column is thermally heterogeneous.

The goals of this work are: (1) a discussion of the conditions of applicability of the simple equilibrium-dispersive (ED) and transport-dispersive (TD) models under VHPLC conditions; (2) a presentation of a modified mass balance model enabling the prediction of the elution profiles of solutes in a wide range of mobile phase velocities based on the measurement of a single kinetic parameter requiring only one experiment; and (3) the validation of the proposed model for columns operated at different wall temperatures.

To validate the proposed model, we chose the experimental conditions that are the most unfavorable and difficult for this modeling, the thermal environment in which the chromatographic column is immersed in a liquid bath with a fast, turbulent water flow. Under such conditions, the column wall temperature is kept constant, equal to the water temperature, due to the very high external heat transfer between the column wall and the water in the bath. On other hand and due to the radial heat flux, a steep radial temperature gradient, hence steep radial gradients of mobile phase velocity, viscosity, and density, and of retention factors form across the column. Shallow axial gradients of all these parameters also are formed. If the model is validated under such conditions, it should also correctly predict the column behavior under the less severe conditions that are typically chosen in laboratory practice, with the column operated in a closed, still air bath.

**2. Mathematical models**

The mathematical model developed to account for the consequences of the heat generated in the column by the friction of the mobile phase percolating through the bed consists in the fusion of three separate models: (1) a model of heat transfer; (2) a model of mobile phase velocity distribution; and (3) a model of mass transfer. The first of these models expresses how heat is generated by viscous friction and how it is evacuated from the column under steady-state conditions. The boundary conditions for this model assume a constant wall temperature equal to that of the temperature-controlled water bath. The second model accounts for the distribution of mobile phase velocities across the column, which depend on the local temperature and pressure provided by the first model and on the equations of hydrodynamics in porous media. These two models are exactly the same as those described in our previous paper [22] and need not be described again. To solve these two models, we need the eluent density, viscosity, thermal expansion coefficient, and heat capacity as a function of pressure and temperature. These values and the effective thermal conductivity of the bed were calculated using the correlations given in [22].

The third model accounts for the propagation of a compound band along a column that is no longer isothermal. Then, the equilibrium constant depends on the local temperature and pressure; so does the migration velocity of a concentration. In this work we applied a modified equilibrium-dispersive (ED), a transport-dispersive (TD), and the lumped pore diffusion model (POR) [23,24].

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