Journal of Chromatography A, 1216 (2009) 134–139

Contents lists available at ScienceDirect

Journal of Chromatography A

journal homepage: www.elsevier.com/locate/chroma

Prediction of retention times and peak widths in temperature-programmed gas chromatography using the finite element method

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ARTICLE INFO

Article history:
Received 31 October 2007
Received in revised form 7 November 2008
Accepted 13 November 2008
Available online 19 November 2008

Keywords:
Gas chromatography
Finite elements
Chromatogram prediction
Computer simulation
Optimization

ABSTRACT

Optimization of separations in gas chromatography is often a time-consuming task. However, computer simulations of chromatographic experiments may greatly reduce the time required. In this study, the finite element method was used to predict the retention times and peak widths of three analytes eluting from each of four columns during chromatographic separations with two temperature programs. The data acquired were displayed in predicted chromatograms that were then compared to experimentally acquired chromatograms. The differences between the predicted and measured retention times were typically less than 0.1%, although the experimental peak widths were typically 10% larger than expected from the idealized calculations. Input data for the retention and peak dispersion calculations were obtained from isothermal experiments, and converted to thermodynamic parameters.

1. Introduction

Gas chromatography [1] is a robust, consistent technique for separating analytes in samples, but optimizing the separation of complex samples can be very time-consuming. The development of good calculation tools is therefore an important task that has been addressed by several authors [2–26].

The finite element method has been applied for diverse purposes in physico-chemical investigations, for instance to model the transport of various substances through different media [27,28], the migration of additives in polymeric packages during contact with food [29], the convection, diffusion and reactions of particles [30] and stress distributions in liquid chromatography columns [31]. It has also been used to predict the retention times and peak widths of analytes during liquid chromatography [32], two-phase partition chromatography [33], and acoustic chromatography [34]. However, it has not previously been applied to gas chromatography.

Several commercial software packages are now available for finite element calculations, for instance Ansys (Ansys Inc., USA), Comsol Multiphysics (Comsol AB, Sweden) and Flux-Expert® (Astek, France). The finite element method is very flexible since a wide variety of differential equations may be used, it often gives accurate and reliable results, and the calculations are no longer very time-consuming (which used to be a major drawback of the method) since standard office computers are much faster than they were just a few years ago.

In this paper, we present a theoretical model for the prediction of retention times and peak widths in gas chromatography that can be solved by the finite element method. The retention and peak dispersion parameters are determined for each of three test analytes in chromatographic separations with four types of columns and (in each case) two temperature gradients, using thermodynamic data for the chromatographic system acquired from isothermal experiments. The predicted results are then compared to experimental data acquired under the same running conditions.

1.1. Theory

In the finite element method, a differential equation is solved in a solution domain divided into small mesh elements. In gas chromatography applications, the column can be considered as a one-dimensional domain wherein an appropriate equation is solved. Within each element, parameters such as temperature, pressure, and mobile phase velocity are considered constant.

During a non-isothermal separation, *e.g.* in a temperature-programmed experiment, the temperature can be regarded as a function of time

$$T = f(t) \tag{1}$$

When an analyte is moving through a column during a separation under such conditions in a gas chromatograph, the concentration c at a position x along the column axis at a time t may

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doi:10.1016/j.chroma.2008.11.038

be determined by using a one-dimensional transient convection-diffusion equation [35,36]

$$\frac{\partial c}{\partial t} = -\frac{\partial}{\partial x}(u_{\mathrm{eff}}c) + \frac{\partial}{\partial x}\left(D_{\mathrm{eff}}\frac{\partial c}{\partial x}\right) \tag{2}$$

where u_{eff} and D_{eff} are, respectively, the effective velocity and the effective diffusion of the analyte. The effective velocity can be calculated from the velocity $u_{\mathrm{M}}(x, t)$ of the mobile phase and the temperature-dependent (and hence time-dependent in a non-isothermal experiment) retention factor kĭ of the analyte in the column used

$$u_{\mathrm{eff}}(x, t) = \frac{u_{\mathrm{M}}(x, t)}{1 + k(t)} \tag{3}$$

The effective diffusion can be calculated from

$$D_{\mathrm{eff}}(x, t) = \frac{D_{\mathrm{M}}(x, t)}{1 + k(t)} \tag{4}$$

where $D(x, t)$ is a local dispersion term that depends not only on static longitudinal diffusion but also on dynamic diffusion caused by the resistance to mass transfer in the mobile and stationary phases.

The local dispersion $D(x, t)$ may be expressed as

$$D(x, t) = \frac{u_{\mathrm{M}}}{2}H(x, t) \tag{5}$$

where $H(x, t)$ is the local plate height is defined [36] as

$$H(x, t) = \lim_{\sigma^2 \to 0} \frac{\mathrm{d}\sigma^2}{\mathrm{d}x} \tag{6}$$

In this equation, $\mathrm{d}(\sigma^2)$ is the incremental second moment (*i.e.* variance) of a normalized packet of gaseous analyte. The quantity $\mathrm{d}(\sigma^2)$ may be found from the following differential equation [35,36]:

$$\mathrm{d}(\sigma^2) = \left(H(x, t) + \frac{2}{u_{\mathrm{eff}}(x, t)} \cdot \frac{\partial u_{\mathrm{eff}}(x, t)}{\partial x} \cdot \sigma^2\right) \mathrm{d}x \tag{7}$$

Since the local plate height may be expressed as [37]

$$H(x, t) = \frac{2D_{\mathrm{M}}}{u_{\mathrm{M}}} + \frac{1 + 6k + 11k^2}{24(1 + k)^2}\frac{{r_{\mathrm{M}}}^2}{D_{\mathrm{M}}}u_{\mathrm{M}} + \frac{2k}{3(1 + k)^2}\frac{{d_{\mathrm{f}}}^2}{D_{\mathrm{S}}}u_{\mathrm{M}} \tag{8}$$

The local dispersion term can also be formulated as [37]

$$D(x, t) = D_{\mathrm{M}}(x, t) + \frac{C_M(x, t) + C_{\mathrm{S}}(x, t)}{2}u_{\mathrm{M}}(x, t)^2 \tag{9}$$

where

$$C_{\mathrm{M}}(x, t) = \frac{1 + 6k(t) + 11k(t)^2}{24(1 + k(t))^2}\frac{r_{\mathrm{M}}^2}{D_{\mathrm{M}}(x, t)} \tag{10}$$

$$C_{\mathrm{S}}(x, t) = \frac{2k(t)}{3(1 + k(t))^2}\frac{d_{\mathrm{f}}^2}{D_{\mathrm{S}}(x, t)} \tag{11}$$

The diffusion constant in the mobile phase may be calculated [38] from

$$D_{\mathrm{M}}(x, t) = D_{\mathrm{C}}\frac{T(t)^{1.75}}{p(x)} \tag{12}$$

where D_{C} is a constant that depends on the molar weights together with the atomic and structural diffusion volumes of the analyte and mobile phase molecules.

The local pressure $p(x)$ may be determined [39] from the inlet and outlet pressures, p_{in} and p_{out} (*i.e.* the pressures at, $x = 0$ and $x = L$, respectively) from the equation:

$$p(x) = \sqrt{p_{\mathrm{in}}^2 - (p_{\mathrm{in}}^2 - p_{\mathrm{out}}^2)\frac{x}{L}} \tag{13}$$

The prediction of the diffusion constant in the stationary phase is an important but very difficult task that has been addressed by several authors. It is however today impossible to find a single model that give good accuracy for all systems that include a liquid solvent [40]. In this paper, the approximation by Snijders et al. 18] assuming a linear relationship between the diffusion constants in the mobile and the stationary phase was used:

$$D_{\mathrm{S}}(x, t) = \frac{D_{\mathrm{M}}(x, t)}{5 \times 10^4} \tag{14}$$

The effect of different equations based on known values of solvent viscosities, *etc.* will be considered in a future paper.

The velocity of the mobile phase may be calculated using the equation

$$u_{\mathrm{M}}(x, t) = \frac{r_{\mathrm{M}}^2}{16\eta(t)L}\frac{1}{p(x)}(p_{\mathrm{in}}^2 - p_{\mathrm{out}}^2) \tag{15}$$

where the viscosity [39] η for a temperature T may be determined from

$$\eta(t) = \eta_0\left(\frac{T(t)}{T_0}\right)^{\alpha_\eta} \tag{16}$$

provided that the gas type dependent exponent α_η and the viscosity η_0 at a reference temperature T_0 are known. The retention factor can be determined from

$$k(t) = \frac{K(t)}{\beta} \tag{17}$$

where K is the distribution coefficient, and the phase ratio β is defined as

$$\beta = \frac{(d_{\mathrm{i}} - 2d_{\mathrm{f}})^2}{d_{\mathrm{i}}^2 - (d_{\mathrm{i}} - 2d_{\mathrm{f}})^2} \tag{18}$$

The distribution coefficient may be calculated from

$$\ln K(t) = -\frac{\Delta H}{RT(t)} + \frac{\Delta S}{R} \tag{19}$$

where ΔH and ΔS are the changes in enthalpy and entropy, respectively, associated with a movement of the analyte from the mobile phase to the stationary phase, and R is the molar gas constant. If ΔH and ΔS depend on the temperature, and hence on the time in the temperature program, then

$$\Delta H(t) = \Delta H(T_{\mathrm{ref}}) + \Delta C_p \cdot (T(t) - T_{\mathrm{ref}}) \tag{20}$$

$$\Delta S(t) = \Delta S(T_{\mathrm{ref}}) + \Delta C_{\mathrm{p}} \cdot (\ln T(t) - \ln T_{\mathrm{ref}}) \tag{21}$$

where ΔC_{p} is the difference in isobaric heat capacity associated with movement of the analyte between the mobile and the stationary phase. Eq. (19) may then be expressed as

$$\ln K(t) = -\frac{\Delta H(T_{\mathrm{ref}})}{R} \cdot \frac{1}{T(t)} + \frac{\Delta S(T_{\mathrm{ref}})}{R} - \frac{\Delta C_{\mathrm{p}}}{R} \cdot \left(1 - \frac{T_{\mathrm{ref}}}{T(t)} - \ln\left(\frac{T_{\mathrm{ref}}}{T(t)}\right)\right) \tag{22}$$

Hence, if values of $\ln K$ are known for at least three temperatures T, it is possible to determine $\Delta H(T_{\mathrm{ref}})$, $\Delta S(T_{\mathrm{ref}})$ and ΔC_{p} for an arbitrary T_{ref}. The distribution coefficient may then be determined for all temperatures within the interval used to determine the parameters.

The analytes may be assumed to have a Gaussian distribution at the start, and thus the initial concentration (*i.e.* for $t = 0$) for all analytes may be set to

$$c(x, 0) = \frac{1}{\sigma\sqrt{2\pi}}\,\mathrm{e}^{-(x - x_0)^2/(2\sigma^2)} \tag{23}$$