



Possibilities and limitations of the kinetic plot method in supercritical fluid chromatography



Ruben De Pauw, Gert Desmet, Ken Broeckhoven*

Vrije Universiteit Brussel, Department of Chemical Engineering (CHIS-IR), Pleinlaan 2, 1050 Brussels, Belgium

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ABSTRACT

Although supercritical fluid chromatography (SFC) is becoming a technique of increasing importance in the field of analytical chromatography, methods to compare the performance of SFC-columns and separations in an unbiased way are not fully developed. The present study uses mathematical models to investigate the possibilities and limitations of the kinetic plot method in SFC as this easily allows to investigate a wide range of operating pressures, retention and mobile phase conditions. The variable column length (L) kinetic plot method was further investigated in this work. Since the pressure history is identical for each measurement, this method gives the true kinetic performance limit in SFC. The deviations of the traditional way of measuring the performance as a function of flow rate (fixed back pressure and column length) and the isopycnic method with respect to this variable column length method were investigated under a wide range of operational conditions. It is found that using the variable L method, extrapolations towards other pressure drops are not valid in SFC (deviation of ~15% for extrapolation from 50 to 200 bar pressure drop). The isopycnic method provides the best prediction but its use is limited when operating closer towards critical point conditions. When an organic modifier is used, the predictions are improved for both methods with respect to the variable L method (e.g. deviations decreases from 20% to 2% when 20 mol% of methanol is added).

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1. Introduction

Supercritical fluid chromatography (SFC), using CO₂ as a mobile phase, is becoming a technique of increasing importance in the field of analytical chromatography to achieve faster and better separations. The advantages of using CO₂ lie in the higher diffusivity of analytes, yielding higher optimal flow rates compared to high performance liquid chromatography (HPLC), and the much lower viscosity of CO₂ compared to the typical HPLC solvents. The latter allows the use of longer columns (higher efficiency) and/or higher flow rates (faster analysis). As a result of these key assets, an increasing number of manufacturers have nowadays dedicated SFC systems and the number of publications on the topic has remarkably increased over the last few years.

The properties of the highly compressible mobile phase in SFC however complicate the interpretation of the kinetic performance data and predictions towards other operating conditions. The chromatographic properties of the mobile phase have a complex non-linear dependency on temperature and pressure. The effect of pressure on the mobile phase density (ρ) has been extensively described in literature [1]. Recently Tarafder and Guiochon

[2] pointed out that in fact the mass flow rate is the only constant parameter along the column, at least in isocratic elution. This is due to the fact that the pressure drop along the column results in a significant density drop, resulting in an increase in volumetric flow rate along the column. When going to gradient elution even the mass flow rate is no longer constant. Due to the high compressibility, a significant cooling effect can be expected as well [3]. In addition, the non-linear behavior of SFC also makes it difficult to predict the kinetic performance. For example, the influence of the back pressure has already been pointed out in [4]. When experiments are performed at a higher back pressure, the mobile phase density will increase which results in a lower retention. In addition the mobile phase viscosity (η) increases, which leads to a lower diffusion of analytes. The classical way of determining the kinetic performance in HPLC (further referred to as the “HPLC method” in the present study) is with a fixed column length at a constant back pressure by changing the flow rate. This, however, leads to a large increase in average column pressure when the flow rate is raised. In SFC this will result in changes in retention and diffusion of the analytes throughout the experiments and the effect of solely the flow rate on performance cannot be investigated. An excellent elucidation was given by Poe and Schroden and Xu et al. [5,6], where it was pointed out that when measuring the plate height H as a function of the flow rate, the average column density should remain constant and thus the column back pressure needs to be adjusted throughout

* Corresponding author. Tel.: +32 26293781; fax: +32 26293248.
E-mail address: kbroeckh@vub.ac.be (K. Broeckhoven).

Table 1

Fitting parameters ρ'_{ij} for the density (kg/m³) of pure CO₂, using the values provided by NIST REFPROP software in a pressure and temperature range of [130 bar, 400 bar] and [305 K, 330 K]. The deviation was always smaller than 2% between the calculated data from REFPROP and the fitting (using Eq. (3)). Values for σ_P , σ_T , μ_P and μ_T are 78.24 bar, 8.068 K, 265 bar and 317.2 K.

$i \setminus j$	0	1	2	3	4	5
0	871.6	54.34	-7.821	1.042	-2.801	1.347
1	-35.02	6.384	-1.433	3.061	-1.699	0
2	-0.3799	0.2005	-1.073	0.7054	0	0

Table 2

Fitting parameters η'_{ij} for the viscosity (mPa s) of pure CO₂, using the values provided by NIST REFPROP software. The deviation was always smaller than 1% between the calculated data from REFPROP and the fitting (using Eq. (3)). Other parameters same as in Table 1.

$i \setminus j$	0	1	2	3	4	5
0	0.08497	0.01166	-0.001017	0.0002074	-0.0002502	0.0001111
1	-0.0075	8.739E-05	-0.0001265	0.0002231	-0.0001162	0
2	-0.0004091	1.401E-05	-4.404E-05	2.77E-05	0	0

the measurements. This approach, further referred to as the “isopycnic method”, should result in a nearly constant retention factor. It is a similar approach to the constant average column pressure P_{av} method described by Mourier et al. [7]. In the present paper the isopycnic method, which implies a constant average density, will be considered to be the same as a constant average pressure method because the latter is the only experimentally straightforward method and in the investigated conditions the density profile along a column is only slightly non-linear with pressure.

When defining an ideal method to measure the performance of a column for a compressible fluid, one would want to keep the same inlet and outlet pressure. As a result, when changing the flow rate, the column length needs to be adjusted. This method will be referred to as the variable Length (L) method [4]. This ensures an identical pressure history throughout the experiments, i.e. at each relative location $z' = z/L$ in the columns, the components experience the same pressure. From a practical point of view however one would need many columns with different lengths to calculate the performance of the column of interest.

Recently, the variable L method was experimentally investigated by Delahaye et al. [4] for pressure drops up to 80 bar and Gritti and Guiochon [8] theoretically compared the KPL of different packing materials and particle sizes, using this method. The present work will study in more detail the behavior of the variable L method and will also determine if the more practical approaches (isopycnic and HPLC-method) are valid and under what range of conditions. The key questions that need to be answered are:

- Does the variable L method behaves the same in a SFC system with its a non-linear characteristics as in a HPLC system, i.e. can kinetic performance data be extrapolated towards other operating pressure drops and particle sizes?
- Can the variable L method be omitted and a more practical approach such as the isopycnic or the HPLC-method be used?
- What are the deviations between the methods and how are they influenced by the chromatographic parameters?

Quantifying the limits and validity of the various techniques can be done by using the so-called kinetic plots. This technique allows to objectively compare the performance of different chromatographic systems (different column length, particle size, etc.). The kinetic performance data is translated into a kinetic plot. These plots describe the kinetic performance limit (KPL) of a system, providing a graphical representation of the shortest analysis time for a given efficiency or the highest efficiency in a given time that can be achieved with a certain system [9]. Whereas the experimental investigation was made by Delahaye et al. [4], the validation and limitations of the kinetic plot method in SFC are examined, in this

study, with mathematical models. This allows an investigation of the kinetic plot method in SFC over a much wider range of conditions such as particle size, pressure drop, average pressure and mobile phase composition. It also extends the recent theoretical study by Gritti and Guiochon [8], who's results were limited to the variable length method for a single inlet and outlet pressure and pure CO₂ as mobile phase.

2. Theory

2.1. Mobile phase properties

In order to model the SFC system as accurately as possible, all the necessary mobile phase parameters need to be fitted in the employed pressure and temperature range. The density ρ (kg/m³), the viscosity η (mPa s), the heat capacity c_p (kJ/kg K) and the thermal expansion coefficient α (K⁻¹) were fitted as a function of a normalized pressure, P_{norm} , and temperature, T_{norm} . These are defined as:

$$P_{norm} = \frac{P - \mu_P}{\sigma_P} \quad (1)$$

$$T_{norm} = \frac{T - \mu_T}{\sigma_T} \quad (2)$$

where the pressure P (bar) and the temperature T (K) are normalized with the mean, μ , and standard deviation, σ , of the fitting range. In general, these mobile phase parameters can be fitted using the following general function:

$$\gamma = \sum_i \sum_j \gamma'_{ij} \cdot T_{norm}^i \cdot P_{norm}^j \quad (3)$$

where γ either represents ρ , η or c_p and γ'_{ij} represent the corresponding fitting parameter. The values for ρ'_{ij} , η'_{ij} and c'_{pij} are given in Tables 1–3 for pure CO₂ and in Tables 5–7 for a mixture of 80/20 mol% of CO₂ and methanol. The thermal expansion coefficient, α , is defined as:

$$\alpha = \frac{1}{\rho} \frac{d\rho}{dT} \quad (4)$$

The derivative of the density with respect to the temperature, $d\rho/dT$, was fitted as a function of the previous defined normalized pressure and temperature as in Eq. (3). The fitting parameters are provided in Table 4 for pure CO₂ and in Table 8 for a mixture of 80/20 mol% of CO₂ and methanol. At typical inlet conditions (330 bar and 312 K) this corresponds to a mass and volumetric fraction of respectively 15.4% and 12.4% of methanol.

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