



Kinetic plots for gas chromatography: Theory and experimental verification



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ABSTRACT

Mathematical kinetic plot expressions have been established for the correct extrapolation of the kinetic performance measured in a thin-film capillary GC column with fixed length into the performance that can be expected in a longer column used at the same outlet velocity but at either the maximal inlet pressure or at the optimal inlet pressure, i.e., the one leading to an operation at the kinetic performance limit of the given capillary size. To determine this optimal pressure, analytical solutions have been established for the three roots of the corresponding cubic equation. Experimental confirmation of the kinetic plot extrapolations in GC has been obtained measuring the efficiency of a simple test mixture on 30, 60, 90 and 120 m long (coupled) columns.

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1. Introduction

In a series of papers [1–3], two different methods have been established to directly calculate and compare the kinetic performance limit (KPL) of different liquid chromatography (LC) systems, in short referred to as the kinetic plot method. A kinetic performance limit plot directly relates the optimized separation efficiency to the minimal required analysis time. This information obviously is more of a practical relevance, while the traditional Van Deemter-plot (plate height versus mobile phase velocity) is more suited for theoretical analysis. More specifically, the kinetic plot method allows to recalculate a set of experimental measurements of time and efficiency obtained on a column with fixed length into a set of data points forming the KPL of the chromatographic support in the test column. This KPL combines the band broadening as well as the pressure drop characteristics of the support into a single curve, thus providing a unique signature of its kinetic performance under a given set of operating conditions (mobile phase composition, column type, temperature). The single assumption underlying the method is that the plate height is independent of the column length, an assumption which in LC is theoretically sound, at least when neglecting some practical length-dependent issues. A detailed discussion of these issues can be found in literature [3–7].

Whereas earlier work on kinetic plots [8–10] used iterative algorithms to construct plots of time versus efficiency, and was therefore limited to theoretical data, the simple kinetic plot expressions developed in [1–3] for liquid chromatography only involve a few multiplications and divisions and can be readily applied to any set of experimental data. As a consequence, the method has now become quite popular and has been used by many authors to assess the true kinetic merits of the systems they are developing or investigating [11–33].

The first of the two methods proposed in [1–3], further referred to as the plate height-based method, rely on the measurement of the plate height H_{obs} , the velocity u_o of the non-retained component marker and the column permeability. The second method, referred to as the column elongation-method, directly uses the t_m -time of the non-retained component and the corresponding separation efficiency N or peak capacity (n_p) measured on a given column. Whereas the first method is better suited to understand and visualize the link between the traditional Van Deemter curve and the KPL-curve, the advantage of the second method is that it also works for programmed temporal changes in the mobile phase composition (gradient LC) as rigorously shown in [3] and applied in [6,18,22,24,26–29,31,34].

The column-elongation method also works for conditions where the mobile phase velocity undergoes temporal changes, as occurs for example in constant-pressure gradient LC [35,36].

Whereas the work in [1–3] was restricted to LC, where the spatial pressure-gradient to a first approximation scales linearly with

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the column length, the question remained to which extent the established methods can still be used in cases with a significant mobile phase compressibility, as occurs in SFC and GC. In SFC, the additional strong dependency of retention on pressure (through the mobile phase density) obviously complicates the extrapolation and prohibits the derivation of an analytical mathematical expression. However, by measuring the performance as a function of flow rate for a fixed average column pressure (i.e., the so-called isopycnic method), a good approximation of the kinetic performance limits could be obtained [25,30,37].

Seminal work on the kinetic optimization of GC separations has been carried out by, amongst others, Giddings [8,38], Cramers [39–41] and Blumberg [42,43]. Kurganov et al. [44] recently proposed to extend the plate-height based kinetic plot method to account for the compressibility effects occurring in the case of ideal gas chromatography (GC). They applied their method to describe the kinetic performance of a set of monolithic GC columns used under isothermal conditions [44]. In the present study, we reviewed their work and also extended the column elongation-variant of the kinetic plot method to GC. This led to expressions for the extrapolation to the maximal inlet pressure (Section 3.1), as well as for the extrapolation to the optimal inlet pressure (Section 3.3). In LC, both extrapolations are the same. In GC, they differ because of the inlet pressure dependency of the observed plate height when different column lengths operating at the same outlet velocity are compared.

2. Experimental

All chemicals were HPLC grade from Sigma–Aldrich (St. Louis, MO, United States). 4 HP-5 MS columns (30 m × 250 μm × 0.25 μm) were obtained from Agilent (Santa Clara, CA, United States). An Agilent 6890 gas chromatograph with FID detector and split/split less injection was used. The H₂ carrier gas was supplied by a Parker Balston Hydrogen Generator H2PD-300-220 (Haverhill, MA, United States). The maximum pressure drop of this system was 184 kPa due to limitations on the gas generation rate. Polyimide sealing resin from Grace Davison Discovery Sciences (Columbia, MD, United States) and universal 2-way fused silica unions from Agilent were used to couple the columns according to the included instructions.

The test mixture contained ethyl-caprate, tridecane and pentadecane dissolved in 2,2,4-trimethylpentane at a concentration of 50 ppm for each component. A headspace sample was made to determine the elution time of 2,2,4-trimethylpentane, while a separate sample of 50 ppm was made for each of the three components to determine their elution order.

Injection of 1 μL sample was done at 250 °C and 20:1 split ratio. Separations were performed under isothermal conditions with the flow varying between 0.2 and 1.2 mL/min and oven temperature set at 100 °C. The detector temperature was set at 300 °C, H₂ flow at 40 mL/min, air flow at 300 mL/min and makeup flow at 20 mL/min. Data was analyzed with HPCore ChemStation. Measurements on the 120 m column were performed using a mixture containing 100 ppm of each component and a split ratio of 10:1 to increase sensitivity.

3. Derivation of the theoretical expressions

3.1. Expressions for the extrapolation to maximal inlet pressure performance

3.1.1. Plate height-based extrapolation method

As shown in [1,2], the performance on a column with given length L_{exp} and operated with a pressure difference Δp_{exp} can be directly extrapolated to the performance on a column operating at

the maximal pressure drop but with the same outlet velocity by combining the three basic equations for efficiency, mobile phase velocity and pressure drop in chromatography, adapted here to account for the specific compressibility of the carrier medium in ideal gas GC [45] (see Supplementary Material SM for details):

$$N_{\text{exp}} = \frac{L_{\text{exp}}}{H_{\text{obs}}} \quad (1)$$

$$t_{\text{m,exp}} = \frac{L_{\text{exp}}}{\bar{u}_{t,\text{exp}}} = \frac{L_{\text{exp}}}{u_{o,\text{exp}}} \frac{2(P_{\text{exp}}^3 - 1)}{3(P_{\text{exp}}^2 - 1)} \quad (2)$$

$$\begin{aligned} \Delta p_{\text{exp}} &= \frac{\eta L_{\text{exp}} \bar{u}_{x,\text{exp}}}{K_v} = \frac{\eta L_{\text{exp}} u_{o,\text{exp}}}{K_v} \frac{2(P_{\text{exp}} - 1)}{(P_{\text{exp}}^2 - 1)} \\ &= \frac{\eta L_{\text{exp}} u_{o,\text{exp}}}{K_v} f_{0,\text{exp}} \end{aligned} \quad (3)$$

wherein H_{obs} is the observed plate height, L the column length, N_{exp} the observed plate number, $t_{\text{m,exp}}$ the experimentally observed elution time of a non-retained compound (in LC this is often written as t_0), Δp_{exp} the experimental pressure drop over the column, $u_{o,\text{exp}}$ the mobile phase outlet velocity, η the mobile phase dynamic viscosity, K_v the column permeability and P_{exp} the ratio of inlet pressure to outlet pressure during the experiment:

$$P_{\text{exp}} = \frac{p_{i,\text{exp}}}{p_{o,\text{exp}}} = \frac{\Delta p_{\text{exp}} + p_{o,\text{exp}}}{p_{o,\text{exp}}} \quad (3b)$$

Because of the mobile phase compressibility, the carrier gas in GC expands from the high pressure inlet toward the low pressure outlet. One of the consequences of this expansion is that the elution time of the non-retained compound ($t_{\text{m,exp}}$) is determined by \bar{u}_t , the time-averaged mobile phase velocity (Eq. (S-4) in SM), whereas the pressure drop (Δp_{exp}) depends on \bar{u}_x , the space-averaged mobile phase velocity (Eq. (S-11) in SM) [39,40,46]. In an incompressible liquid, both velocities are equal, such that this distinction does not need to be made in LC (even under UHPLC conditions where the liquid displays some compressibility, the effect is minor). For a fluid following the ideal gas law, the relation between \bar{u}_t and \bar{u}_x is given by Eqs. (S-12) and (S-13) of the SM, and can also be found in literature [47].

In GC, the observed plate height can generally be written as [42,48,49].

$$H_{\text{obs}} = H_0 f_{1,\text{exp}} + C_s u_{o,\text{exp}} f_{2,\text{exp}} \quad (4)$$

with:

$$H_0 = \frac{B}{p_{o,\text{exp}} u_{o,\text{exp}}} + C_m u_{o,\text{exp}} p_{o,\text{exp}} \quad (5)$$

$$f_{1,\text{exp}} = \frac{9(P_{\text{exp}}^4 - 1)(P_{\text{exp}}^2 - 1)}{8(P_{\text{exp}}^3 - 1)^2} \quad (6)$$

$$f_{2,\text{exp}} = \frac{3(P_{\text{exp}}^2 - 1)}{2(P_{\text{exp}}^3 - 1)} \quad (7)$$

Extrapolating an experimentally measured efficiency on a column with given length into an extrapolated efficiency expected in a column containing the same support but now elongated such that it generates a given maximal pressure drop while keeping the same outlet velocity is only correct if this extrapolation leaves the plate height H_{obs} unchanged. This is (approximately) true in LC, but clearly not in GC, given the inlet pressure dependency of H_{obs} via f_1 and f_2 in Eq. (4). However, making the approximation that the film mass transfer is negligible (C_s very small), which holds for most open-tubular GC systems, the dependency which exists between H_{obs} and column length at the same outlet velocity u_o can be expressed using a single flow-dependent factor H_0 and a single

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