



Kinetic plots for programmed temperature gas chromatography



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ABSTRACT

The applicability of the kinetic plot theory to temperature-programmed gas chromatography (GC) has been confirmed experimentally by measuring the efficiency of a temperature gradient separation of a simple test mixture on 15, 30, 60 and 120 m long (coupled) columns. It has been shown that the temperature-dependent data needed for the kinetic plot calculation can be obtained from isothermal experiments at the significant temperature, a temperature that characterizes the entire gradient run. Furthermore, optimal flow rates have been calculated for various combinations of column length, diameter, and operating temperature (or significant temperature). The tabulated outcome of these calculations provide good starting points for the optimization of any GC separation.

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1. Introduction

The kinetic plot theory, first developed for LC and recently extended to GC, provides a general framework to compare the quality of different chromatographic systems in a geometry-independent way, as well as to guide system design and determine optimal working conditions [1–4]. In a kinetic plot, a measure for the analysis time (typically the t_0 time, or the time of the last eluting compound) is plotted versus a measure for column efficiency (typically the plate number N or the peak capacity n_p). Whereas in a Van Deemter-plot the length of the column is the same for each data point while the pressure varies, the data points in a kinetic plot all relate to the same maximal, or more generally, optimal pressure drop but to a different column length. Being plotted at the optimal pressure drop, kinetic plots describe, in one single curve, the best performance one can expect from a given chromatographic support (LC) or column diameter (GC) for any possible value of the required efficiency or the allowable analysis time.

Following upon earlier work on the kinetic optimization of GC separations by Giddings [5,6], Cramers [7–9], Blumberg [10,11] and Kurganov et al. [12], we recently extended the kinetic plot theory from the case of LC (incompressible fluid) to isothermal GC (compressible fluid obeying the ideal gas law). In addition, we also derived the exact equations determining the optimal pressure [4]. Contrary to LC, where the optimal pressure is always the maximum

pressure, this optimal pressure is in GC a function of the compound of interest, as well as of the required analysis time. However, the error made by using the maximum pressure drop as the optimal pressure in GC for every compound and column length is rather small. A recent interesting review on the use of kinetic plots for the optimization of separations in LC and GC was published by Kurganov et al. [13].

Whereas our previous work related to isothermal GC, many GC measurements are performed under temperature gradient conditions, the focus of this study was to validate the kinetic plot theory for temperature-programmed GC [14–20].

2. Experimental

All chemicals were HPLC grade from Sigma Aldrich (St. Louis, MO, United States). 4HP-5MS 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). 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 consisted of 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 (t_M -

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compound), 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 a 20:1 split ratio. Separations were performed under gradient conditions with the flow varying between 0.2–5.2 mL/min and the oven temperature running from 80–200 °C at 10 °C/min for the run at 2.4 mL/min. For the runs at other flow rates, the gradient time was scaled proportionally to the void time. 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 HPChemStation. 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 the signal intensity.

3. Theory

A kinetic plot extrapolates the observed efficiency of a given column (with a certain length and stationary phase), measured in the form of a Van Deemter curve, to the expected efficiencies of the same column but at different lengths and all operated at the optimal pressure. A necessary condition for this theory to be valid is that the peak elution pattern is preserved when the column length is changed (i.e. that all peaks retain their relative elution time). In gas chromatography with H₂ as carrier gas the logarithm of the retention factor k is inversely proportional to the carrier gas inlet pressure, however in the range of inlet pressures used in this work (and most GC experiments) this dependency is negligible [21]. For isothermal GC the necessary condition is thus met simply by running all measurements at the same temperature. For temperature gradient GC, it is shown in Ref. [22] that scaling the gradient time proportionally to the void time leads to a constant peak elution pattern.

3.1. Kinetic plot expressions

The general theory for kinetic plots in GC was introduced, and checked for the isothermal case, in a previous paper [4]. It was shown that the kinetic performance limit (KPL) of a given chromatographic system can be calculated by scaling each of the different performance characteristics: length (L), column void time (t_M), and peak capacity (n_p) with a specific elongation factor.

$$L_{KPL} = \lambda_1 L_{exp} \quad (1)$$

$$t_{M,KPL} = \lambda_2 t_{M,exp} \quad (2)$$

$$n_{p,KPL} = 1 + \sqrt{\lambda_3(n_{p,exp} - 1)} \quad (3)$$

This column elongation-based approach is based on the direct physical interpretation of the column length extrapolation process needed to arrive at the kinetic performance limit of a given chromatographic system, transforming a given peak capacity ($n_{p,exp}$) obtained in a given time $t_{M,exp}$ on a column with length L_{exp} and producing a given pressure drop Δp_{exp} into the peak capacity one can expect in a column producing the optimal pressure drop Δp_{opt} while keeping the same mobile phase outlet velocity (and hence having an adapted length L_{KPL}).

Whereas in LC the expressions for λ are very simple [3], the expressions for the pressure dependency of the λ – elongation factors for thin-film GC are more complex, and have in Ref. [4] been shown to be given by:

$$\lambda_1 = \frac{\Delta p_{opt} \left(\frac{P_{opt}^2 - 1}{P_{opt} - 1} \right)}{\Delta p_{exp} \left(\frac{P_{exp}^2 - 1}{P_{exp} - 1} \right)} = \left[\frac{\Delta p_{opt}}{\Delta p_{exp}} \right] \frac{f_{0,exp}}{f_{0,opt}} \quad (4)$$

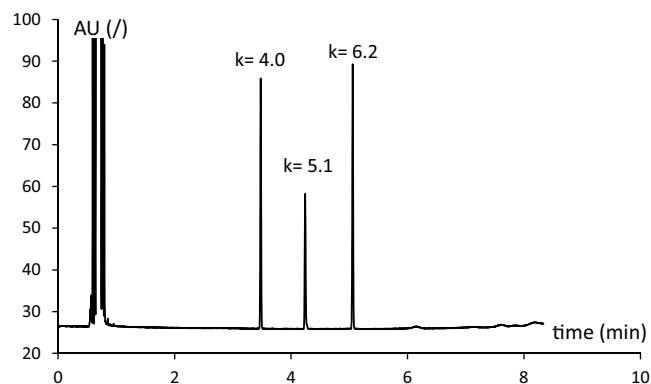


Fig. 1. Chromatogram of the separation of tridecane ($k=4.0$), ethyl-caprate ($k=5.1$) and pentadecane ($k=6.2$) in 2,2,4-trimethylpentane on the 15 m column at the optimal flow rate for pentadecane. T_{oven} : 80–200 °C, $F=2.3$ mL/min, $t_{gradient}=5.3$ min.

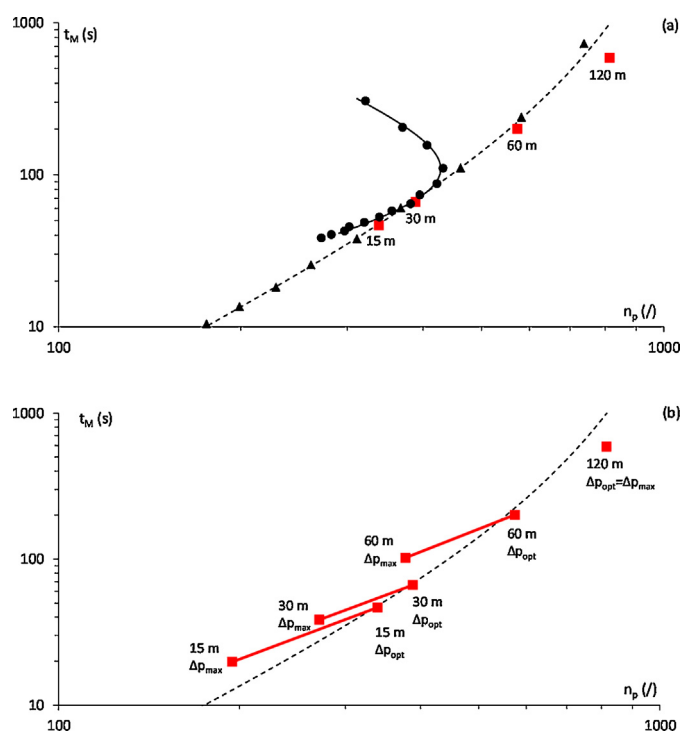


Fig. 2. (a) Experimental measurements of peak capacity at different flow rates on a 30 m column (circles) and corresponding fit (full line), using Eq. (20). The kinetic plot extrapolations of the experimental data points and fit, with Eqs. (2), (3), are represented by the triangles and dashed line, respectively. Experimental measurements on columns of different length, at the optimal flow rates for tridecane, are shown as well (red squares). The peak capacities were calculated using the width of the tridecane peak. (b) The kinetic plot for tridecane (dashed line) is shown, as well as experimental measurements at the optimal and the maximum flow for tridecane at each column length (squares) are shown. At 120 m the optimal flow and the maximum flow are equal. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

$$\lambda_2 = \frac{\Delta p_{opt} \left(\frac{P_{opt}^3 - 1}{P_{opt} - 1} \right)}{\Delta p_{exp} \left(\frac{P_{exp}^3 - 1}{P_{exp} - 1} \right)} = \left[\frac{\Delta p_{opt}}{\Delta p_{exp}} \right] \frac{f_{4,opt}}{f_{4,exp}} \quad (5)$$

$$\lambda_3 = \frac{\Delta p_{opt} \left(\frac{P_{opt}^3 - 1}{P_{opt} - 1} \right)^2}{\Delta p_{exp} \left(\frac{P_{exp}^3 - 1}{P_{exp} - 1} \right)^2} = \left[\frac{\Delta p_{opt}}{\Delta p_{exp}} \right] \frac{f_{3,opt}}{f_{3,exp}} \quad (6)$$

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