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Prediction of retention times in temperature programmed gas chromatography using the retention equation derived from crystallization behavior of polymer

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ABSTRACT

Based on the enlightenment from the crystallization behavior of polymer, a novel retention equation constructed with only three pairs of isothermal retention data was proposed to predict retention times in temperature programmed gas chromatography (TPGC). The new retention equation worked beautifully in both the single- and the multiple-ramp temperature-programmed modes, yielding the average absolute relative errors of 0.65% for single-ramp TPGC across all the 18 analytes in 3 temperature programmed experiments and 0.30% for multiple-ramp TPGC across all the 8 analytes in 6 temperature programmed experiments tested in this work. Moreover, to compare with the new retention equation systematically and thoroughly, another 13 retention equations determined by two or three parameters were derived from a universal formula $\ln k = a_0 + a_1/T + a_2/T^2 + a_3 \ln T + a_4 T + a_5 T^2$ as a combination of the relationships between $\ln k$ and T with reference to four widely used retention equations in publications. Calculated by these 14 retention equations with the same experimental data, the absolute relative errors of prediction retention times for single-ramp TPGC mode were compared by means of statistical analysis. At a very high significance level of 1%, statistical evidences of paired *t*-test strictly implied that the new retention equation yielded the best prediction results among all of the 14 retention equations. In addition, remarkably, among the 13 retention equations, three seldom used in publications retention equations also worked nicely, yielding satisfactory average absolute relative errors of 0.78%, 0.81% and 0.84% for single-ramp TPGC.

1. Introduction

Temperature-programmed gas chromatography (TPGC) is nowadays an advantageous and effective technique for separating components in complex mixtures [1,2], but the optimization of separations for complex samples with a wide boiling points range is often a tedious and time-consuming task. Aiming to circumvent complicated labor intensive trial and error optimizations, various computer-assisted calculation methods have been addressed, a large number of which attempt to describe chromatography retention behavior such as to predict the retention time, the relative retention, or the Kováts retention index.

Many calculating methods have been utilized and proved to be efficient in predicting retention times in the field of GC, such as the finite element method (FEM) [3], the quantitative structure–retention relationships (QSRRs) [4], the quantitative structure–property relationships (QSPRs) [5] and the basic physical model of differential and integral [6,7]. In terms of the widely used basic model of differential and integral, the main source of prediction relative errors of retention times, on large scale, comes from whether the described retention behavior can closely match up with the actual. The approximately described retention behavior is computed through the retention equation, which is defined as the temperature dependence of the natural logarithm of retention factor data ($\ln k$ versus T) and can be determined by several parameters calculated by known experimental retention data.

For the purpose of optimizing TPGC separations feasibly, obtaining higher prediction precise with fewer input experiments is the terminal target of predicting retention times in TPGC. Nevertheless, several boundaries limited the application of predicting retention times based on retention equations.

On one respect, the target itself seems contradictory. To guarantee the accuracy of prediction, it is undoubtedly correct that the more fitting parameters you construct the retention equation with, the less difference between the actual and calculated retention behavior you observe. Hence, in order to obtain adequate experimental retention data to construct the retention equation, numerous input-runs requiring considerable time and intensive

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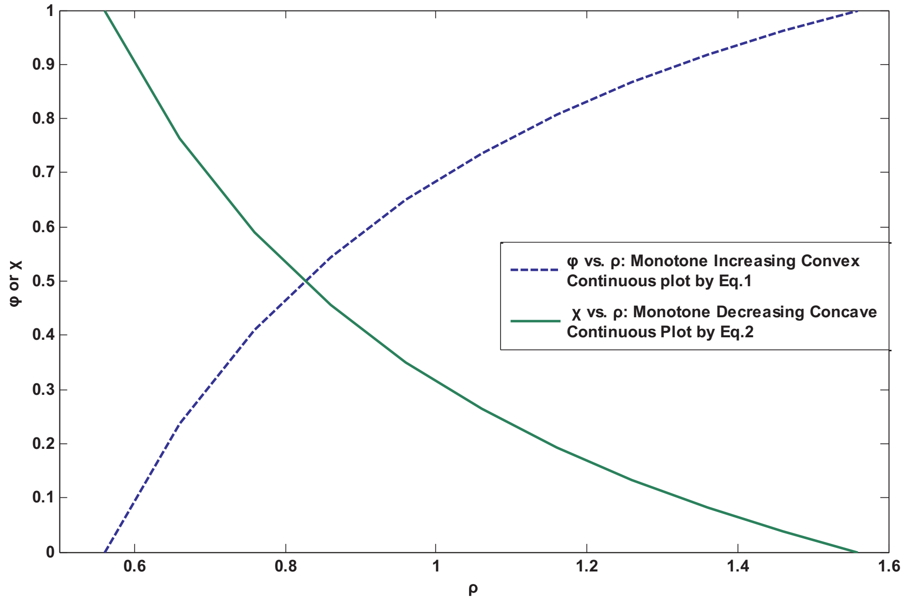

Fig. 1. Plot of φ vs. ρ, and plot of χ vs. ρ: the blue dash line: the monotone increasing convex plot by Eq. (1); The green solid line: the monotone decreasing concave plot by Eq. (2). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

labor have to be performed. Consequently, however, this will complicate the prediction procedure. In this sense, with fewer parameters, constructing a kind of retention equation which is capable to yield precise prediction retention times in TPGC is essential.

On the other, the brief common retention equation, $\ln k = A + B/T$, works well only across a narrow temperature range, across which a general assumption of thermodynamics postulates that the changes in both enthalpy and entropy associated with movements of the analytes between the stationary and mobile phases do not vary as the temperature changes [8]. Unfortunately, however, when the temperature changes across a wide range, the enthalpy and entropy should be described as a complicated variable rather than as a constant, and the curve of $\ln k$ vs. T therefore present diversified nonlinear expressions instead of a simple linear tendency. In this sense, a kind of retention equation which is able to approximately describe the nonlinear relationship between $\ln k$ and T is urgently demanded.

In addition, published prediction results were calculated by diversified retention equations determined by experimental data varying in quantities and temperature ranges [9–15], thus the prediction errors calculated by different retention equations cannot be compared systematically.

Table 1
Fourteen retention equations for predicting retention times.

Type	Parameters			Retention equation	Abbreviation
a	–	–	–	The crystallization model	Eq.a
b	a_0	a_1	a_2	$\ln k = a_0 + a_1/T + a_2/T^2$	Eq.b
c	a_0	a_1	a_3	$\ln k = a_0 + a_1/T + a_3 \ln T$	Eq.c
d	a_0	a_1	a_4	$\ln k = a_0 + a_1/T + a_4 T$	Eq.d
e	a_0	a_1	a_5	$\ln k = a_0 + a_1/T + a_5 T^2$	Eq.e
f	a_0	a_2	a_3	$\ln k = a_0 + a_2/T^2 + a_3 \ln T$	Eq.f
g	a_0	a_2	a_4	$\ln k = a_0 + a_2/T^2 + a_4 T$	Eq.g
h	a_0	a_2	a_5	$\ln k = a_0 + a_2/T^2 + a_5 T^2$	Eq.h
i	a_0	a_3	a_4	$\ln k = a_0 + a_3 \ln T + a_4 T$	Eq.i
j	a_0	a_3	a_5	$\ln k = a_0 + a_3 \ln T + a_5 T^2$	Eq.j
k	a_0	a_4	a_5	$\ln k = a_0 + a_4 T + a_5 T^2$	Eq.k
l	a_0, a_1			$\ln k = a_0 + a_1/T$	Eq.l
m	a_0, a_4			$\ln k = a_0 + a_4 T$	Eq.m
n	a_0, a_4, A_0, A_4			$\ln k = a_0 + a_4 T$ and $\ln k = A_0 + A_4 T$	Eq.n

2. Theory

2.1. New retention equation derivation from crystallization behavior of polymer

The crystallinity formula of polymer described simply by a two-parameter nonlinear curve can nicely meet the requirements for retention equation we mentioned above. On this ground, we derived the new retention equation from the crystallization behavior in this section.

For polymer with the same molecular weight and the same kind of material, the density of a crystalline polymer is greater than an amorphous one because the chains are more closely packed together for the crystalline structure. The degree of crystallinity by weight may be determined from accurate density measurements, according to Eq. (1) as demonstrated [16].

$$\varphi = \frac{\rho_c}{\rho} \cdot \frac{\rho - \rho_a}{\rho_c - \rho_a} \tag{1}$$

where ρ is the density of a specimen for which the crystallinity φ is to be determined, ρ_a is the density of totally amorphous polymer, and ρ_c is the density of the perfectly crystalline polymer, and there are $\rho \in [\rho_a, \rho_c]$, $\varphi \in [0,1]$.

As shown in Eq. (1), the relationship between the density of a polymer and the degree of crystallinity by weight is considered nonlinear variation and can be obtained with only two pairs of known data (ρ, φ). Evidently, there comes the relationship: $0 < \rho_a \le \rho \le \rho_c$. And within the definition domain, φ is the monotone increasing convex continuous function of ρ, as presented in Fig. 1 (dash line) ranged in density from 0.56 to 1.56 g cm^{-3} according to the reference.

Since the retention factor k always serves as a decreasing concave function of temperature T, which is obtained from experimental results, we changed the shape of the curve by transforming the monotone increasing convex function into a monotone decreasing concave one. This was done by defining a new