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Temperature Programmed Retention Indices: Calculation from Isothermal Data

Part 1: Theory

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Summary

Direct conversion of isothermal to temperature programmed indices is not possible. In this work it is shown that linear temperature programmed retention indices can only be calculated from isothermal retention data if the temperature dependence of both the distribution coefficients and the column dead time are taken into account.

Procedures are described which allow calculation of retention temperatures and from these, accurate programmed retention indices. Within certain limits the initial oven temperature and programming rate can be chosen freely. The prerequisite for this calculation is the availability of reliable isothermal retention data (retention times, retention factors, relative retention times, or retention indices) at two different temperatures for one column.

The use of compiled isothermal retention indices at two different temperatures for the calculation of retention temperatures and thus temperature programmed indices is demonstrated. For the column for which programmed retention indices have to be determined, the isothermal retention times of the *n*-alkanes and the column dead time as a function of temperature have to be known in addition to the compiled data for a given stationary phase.

Once the programmed retention indices have been calculated for a given column the concept allows the calculation of temperature programmed indices for columns with different specifications. The characteristics which can be varied are: column length, column inner diameter, phase-ratio, initial oven temperature, and programming rate.

1 Introduction

Since the beginning of gas chromatography numerous authors and committees have discussed and made proposals on the best way to express retention data, to enable the general use of published retention data for the identification of individual compounds and the characterization of stationary phases.

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The Kovats retention index, introduced in 1958 [1] and widely accepted today, has a number of distinct advantages in isothermal gas chromatography over the relative retention time. The retention behavior of the compounds is expressed on a uniform scale, the retention index depends linearly on the column temperature, and the position of a compound in the chromatogram is known from its retention index.

It is evident that the applicability of the retention index as a means of identification greatly depends on the availability of reliable retention data, column stability, reproducibility of column polarity, and the quality of sample introduction, detection, and interfacing. Although much progress has been made with peak identification by means of compilations of retention indices in isothermal gas chromatography (table matching), most analyses are performed preferably with linear temperature programming. Therefore, there was a great need to develop a practical method for identification using temperature programmed retention indices, a concept introduced by *Van der Dool* and *Kratz* in 1963 [2].

Prediction or calculation of temperature programmed retention indices from isothermal retention data, which are available in large quantities, is of course attractive. The first attempts to predict programmed indices using isothermal retention data were made by *Guiochon* [3], *Habgood* and *Harris* [4], and *Giddings* [5]. Their approximations did not account for the influence of the initial oven temperature, programming rate, and column dimensions. *Golovnya* and *Uraletz* [6] and *Erdey et al.* [7] calculated temperature programmed indices taking into account the temperature dependence of the isothermal index. Although they stated the temperature programmed index to be a complex function of experimental conditions, these conditions were not accounted for in the calculations.

Another way of correlating isothermal and temperature programmed indices is the prediction of the retention time

or temperature in a temperature programmed run from isothermal retention data. Elaborating the model of Grant and Hollis [8], this paper presents a procedure for calculation of retention temperatures.

This study is directed towards the development of a theoretical concept for the calculation of temperature programmed retention indices from isothermal retention data. The concept is based also on the conversion of programmed retention indices between columns of different dimensions (length, inner diameter), phase ratio, initial temperature, and programming rate. The results will be reported in a series of publications.

This paper deals with the theoretical concept and the procedure for the calculation of programmed retention indices from isothermal data. The reliability of the method in terms of reproducibility and accuracy as well as its applicability for the conversion of tabulated programmed indices to columns of different dimensions and operating conditions will be discussed in part 2.

2 Theoretical Concept

In the first instance, the isothermal retention index depends on column temperature and structure and purity of the stationary phase. In practice, however, many other factors such as the nature of the carrier gas, column pressure, inertness of the column wall, and instrument quality may cause secondary but significant variations of the retention index. The temperature programmed index is also affected by the initial temperature, the programming rate, the temperature dependence of the distribution coefficient, and the carrier gas velocity. Therefore, high demands on the GC equipment with respect to temperature, column pressure, and flow control are expected. Obviously, the retention behavior of different columns with the same stationary phase must be sufficiently reproducible.

2.1 The Retention Index Concept

The Kovats retention index [1], which is generally accepted as a means of characterizing the separated substances and the column polarity, is defined as:

$$I = 100z + 100 \frac{\log t'_{R,i} - \log t'_{R,z}}{\log t'_{R,z+1} - \log t'_{R,z}} \quad (1)$$

where $t'_{R,z} < t'_{R,i} < t'_{R,z+1}$, $t'_{R,i}$ is the adjusted retention time of a component i , and z , $z+1$ are the numbers of carbon atoms of the n -alkanes.

The retention index equals 100 times the carbon number of a hypothetical n -alkane with the same adjusted retention time. The adjusted retention times may be replaced by the corresponding retention factors.

The linear temperature programmed index was defined by Van der Dool and Kratz [2] as:

$$I^T = 100z + 100 \frac{T_i - T_z}{T_{z+1} - T_z} \quad (2)$$

where $T_z < T_i < T_{z+1}$ and T_i , T_z , T_{z+1} are the retention temperatures of component i and of the bracketing n -alkanes with z and $z+1$ carbon atoms respectively. The retention temperatures can be replaced by the corresponding retention times or the retention factor.

To enable direct conversion of isothermal into programmed retention indices one should consider that the isothermal retention index is a relation between distribution coefficients (K) which are constant for a given temperature. The programmed retention index, however, is calculated from temperature dependent variables (e.g. distribution coefficients and carrier gas viscosity and velocity, respectively) which changes continuously during a temperature programmed run. Furthermore, the temperature variation of the distribution coefficient is different for the n -alkanes and the different types of solutes. The isothermal index is a relation between adjusted retention times. The adjusted retention time, which is the time period during which the solute is retained by the stationary phase, cannot easily be calculated for temperature programming because of varying column dead time. From the above it can be concluded that a direct conversion of isothermal to temperature programmed indices is not feasible. For an accurate calculation of programmed retention indices from isothermal retention data (retention time, retention factors, relative retention times, or retention indices), the actual dead times and distribution coefficients should be used in the calculations.

2.2 Calculation of the Retention Temperature

The velocity of a specific segment in an open tubular column depends on the oven temperature, T , and the linear carrier gas velocity, u_x . Suppose the segment is transported over a distance of dx cm in dt seconds, then:

$$dt = \frac{dx}{u_x} \left(1 + \frac{K(T)}{\beta} \right) \quad (3)$$

where u_x is the linear gas velocity at a position x in the column, $K(T)$ the distribution coefficient of the solute at a temperature T , β the column phase ratio, and $K(T)/\beta$ the retention factor (k).

The distribution coefficient can be expressed as:

$$K(T) = \exp \left(-\frac{\Delta G}{RT} \right) = a \cdot \exp \left(\frac{\Delta H}{RT} \right) \quad (4)$$

where ΔG is the molar free energy of solution, R the ideal gas constant, $a = \exp(\Delta S/R)$, ΔH is the molar enthalpy of solution (expressed positive), and ΔS the molar entropy of solution.

In isothermal gas chromatography, the mean linear gas velocity is $u = L/t_0$, L being the column length and t_0 the column dead time. A combined substitution of this relation and Eq. (4) in Eq. (3) and integration over the column length yields:

$$t_{R,i} = t_0 \left[1 + \frac{a}{\beta} \cdot \exp\left(\frac{\Delta H}{RT}\right) \right] \quad (5)$$

This equation can be rearranged to give:

$$\ln k = \ln \frac{a}{\beta} + \frac{\Delta H}{RT} \quad (6)$$

Eq. (6) describes isothermal gas chromatography in terms of the distribution coefficient. By plotting the retention factor versus the reciprocal temperatures the values for a/β and $\Delta H/R$ can be obtained.

In linear temperature programmed gas chromatography, the oven temperature increases during the analysis according to:

$$T = T_0 + r \cdot t \quad (7)$$

where T_0 is the initial oven temperature and r the programming rate.

Differentiation and substitution in Eq. (3) together with Eq. (4) yields:

$$\frac{dT}{1 + \frac{a}{\beta} \cdot \exp\left(\frac{\Delta H}{RT}\right)} = r \cdot \frac{dx}{u_x} \quad (8)$$

After integration of Eq. (8), the left-hand side between the initial temperature T_0 and the elution temperature T_R , and the right-hand side over the column length L , an expression describing linear temperature programmed gas chromatography is obtained:

$$\int_{T_0}^{T_R} \frac{dT}{1 + \frac{a}{\beta} \cdot \exp\left(\frac{\Delta H}{RT}\right)} = \int_0^L r \cdot \frac{dx}{u_x} \quad (9)$$

At this point, various simplifications have been introduced in the literature to simplify the calculation of the retention temperatures. The following assumptions have been proposed [8]: during a period corresponding to the column dead time, the solute is transported a negligible distance along the column and the dead time is assumed constant during temperature programming. Clearly, the first assumption will not hold for components with relatively short retention times except when an extremely low (sub-ambient) initial temperature is used. The second assumption is not valid due to changes in the carrier gas viscosity and thermal expansion of the carrier gas. We continue the treatment without any simplifications.

In Eq. (9), dx/u_x , integrated over the column length, represents the column dead-time, t_0 , which is temperature dependent. Transferring the dead time to the left-hand side leads to an equation suitable for calculating elution temperatures in temperature programmed gas chromatography:

$$\int_{T_0}^{T_R} \frac{dT}{t_0(T) \left[1 + \frac{a}{\beta} \cdot \exp\left(\frac{\Delta H}{RT}\right) \right]} = r \quad (10)$$

The denominator of the left-hand side represents the retention time under isothermal conditions at temperature T (cf. Eq. (5)).

2.3 Calculation of $t_0(T)$

The mean carrier gas velocity can be described (9) by:

$$u = \frac{3 \cdot p_0 (P^2 - 1)^2}{4 \cdot \eta \cdot L \cdot (P^3 - 1)} \cdot \frac{d_c^2}{32} \quad (11)$$

where u is the mean carrier gas velocity, p_0 the column outlet pressure, P the pressure ratio (in/out), d_c the column inner diameter, η the dynamic carrier gas velocity, and L the column length.

Combination with $t_0 = L/u$ yields an expression for the temperature dependence of the column dead time:

$$t_0(T) = \frac{4 \cdot L^2 \cdot (P^3 - 1)}{3 \cdot p_0 \cdot (P^2 - 1)^2} \cdot \frac{32}{d_c^2} \cdot \eta(T) \quad (12)$$

According to *Ettre* [11], the relation between viscosity and temperature is linear in the range normally used in gas chromatography, so the relation between column dead time and temperature may be assumed linear also. The applicability of Eq. (12) will be discussed in part 2.

2.4 Procedure for Calculation of Retention Indices

The retention temperature can be computed from Eq. (10) using the 'Simpson-rule', if T_0 , r , $t_0(T)$, the entropy-term (a/β), and the enthalpy-term ($\Delta H/R$) are known. The initial temperature, T_0 , and programming rate, r , can be chosen in accordance with the required separation and the boiling range of the sample components. The column dead time as a function of temperature, $t_0(T)$, must either be determined experimentally or calculated according to Eq. (12). The entropy- and enthalpy-terms are obtained according to Eq. (6) after determination of the retention factors at two or more temperatures.

Finally, when the retention temperatures of the solutes and the appropriate n -alkanes are known, linear temperature programmed indices are calculated according to Eq. (2).

The applicability of the concept is illustrated in **Tables 1** and **2**. Three main procedures, differing with respect to the manner in which the isothermal retention information is

Table 1

Two procedures for calculating temperature programmed indices. Applicable for a given column A.

Chromatographic conditions chosen	Experimental data obtained from column A	Compiled isothermal data	Calculated for column A
1) T_o r	$t_o(T)$ k <i>n</i> -alkanes k solutes (at 2 or more temperatures)	-	$\Delta H/R, a/\beta$ ↓ $T_R \rightarrow I^T$
2) T_o r	$t_o(T)$ t_R <i>n</i> -alkanes at temp. T_1, T_2	relative retention or ↓ at temp. T_1, T_2	$\Delta H/R, a/\beta$ $T_R \rightarrow I^T$

obtained, are presented. In all cases the temperature dependence of the column dead time has to be established for the very column for which temperature programmed indices are to be calculated. This linear temperature dependence is obtained either by experiment or by calculation according to Eq. (12).

The two procedures given in Table 1 refer to one specific column for which the linear temperature programmed retention indices have to be calculated. The isothermal data needed have to be measured on the same column. In the first procedure, all necessary isothermal information, retention factors for both the *n*-alkanes and solutes, are determined *experimentally* at two or more temperatures. The second procedure uses compiled retention data, relative retentions or retention indices of a column with the same stationary phase. In addition to the compiled isothermal retention data, the retention times for the *n*-alkanes have to be determined experimentally at two or more temperatures to enable the calculation of retention factors for the solutes.

Both procedures yield values of the retention factors at two or more temperatures for the solutes as well as the *n*-alkanes. They enable the calculation of the entropy- and enthalpy-terms (Eq. (6)). Together with the temperature dependence of the column dead time and the chosen initial temperature and programming rate, the retention temperatures (Eq. (10)) and subsequently temperature programmed indices (Eq. (2)) are calculated.

The third procedure, presented in Table 2, enables calculation of temperature programmed indices for any column from data obtained on other columns with the same stationary phase. As in the case of the procedures 1 and 2, the column dead time as a function of temperature must be determined by experiment or by calculation.

The procedure starts with the entropy- and enthalpy-terms, as determined by the procedures 1 or 2. These terms describe the temperature dependence of the distribution coefficient (Eq. (4)) for a given solute and stationary phase.

Table 2

Procedure for calculating temperature programmed indices. Applicable for any column using entropy- and enthalpy terms obtained from column A.

Chromatographic conditions chosen	Experimental data obtained for any column	Compiled isothermal data	Calculated for any column
3) T_o r	$T_R(T)$ k for one specific solute	$\Delta H/R, a/\beta$ from procedure 1 or 2	$T_R \rightarrow I^T$

Compiled entropy- and enthalpy terms obtained by procedure 1 or 2 for one column allow direct calculation for other columns with different column dimensions and/or phase ratios. Except for the determination of the column dead time as a function of temperature, which could also be calculated, the only additional experimental effort is establishing a retention factor for one specific component to correct the entropy-term (a/β) for a different phase ratio.

Within certain limits the initial oven temperature and programming rate may be chosen freely. The initial oven temperature should preferably be below the boiling point of the first eluting component. The programming rate must be selected such that all components elute during the linear temperature rise.

The difference between calculated and experimental data is about $0.4 I^T$ units for most solutes. The accuracy depends on the selected temperatures at which the entropy and enthalpy terms are obtained. The selection criteria will be discussed in part 2. Tabulated entropy- and enthalpy-terms can also be used to calculate isothermal retention indices for all temperatures within the appropriate temperature range.

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