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Review

Programmed-temperature gas chromatographic retention index

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ABSTRACT

Thirty years of studies on the definitions and calculation methods of the gas chromatographic programmed-temperature retention index values and the various conversion methods between retention values under different gas chromatographic conditions have been reviewed. The programmed-temperature retention value databases compiled in various laboratories are listed. Special emphasis is placed on the recent advances in reproducing programmed-temperature retention indexes under different chromatographic conditions.

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1. INTRODUCTION

Since its advent in the early 1950s [1], gas chromatography (GC) has long been an extraordinarily important and active field in analytical chemistry. Being an excellent separation method, it also serves as an identifying means. Retention values, especially retention indices (I) are generally used for identification in GC. It is usually impossible, however, to obtain unambiguous results solely by means of I identification. In practical analyses, it has to be used in conjunction with other identification means. A number of coupled techniques, such as GC–MS, GC–Fourier transform IR spectrometry and GC–atomic emission spectrometry, have been developed in parallel. Nevertheless, identification by I still attracts much attention owing to several of its characteristic advantages: (1) it is very effective in differentiating isomers giving similar mass spectra; (2) it is the most inexpensive identification method as no special facilities are needed; (3) it is easy in manipulation and (4) it is extremely sensitive, especially when the sample size is too small to be analysed by other techniques, such as MS. These justify the continuous efforts in the study of I values along with the development of the chromatographic technique as a whole. Moreover, the repeatability of I measurements has improved steadily in step with the improvements in chromatographic instrumentation and capillary column technology.

The Kováts retention index system [2] put forward in 1958 has been commonly accepted. It is a very important parameter in the identification of compounds in isothermal GC analysis. Very abundant data on isothermal GC I values have been accumulated over several decades of practical research work.

There have been numerous reports on the study of GC I values in the literature. In 1983 and 1989, Budahegyi *et al.* [3] and Tarjan *et al.* [4] published two exhaustive reviews to commemorate the 25th and 30th anniversaries of the

GC I system, respectively. Nearly 1400 and 500 references were cited respectively, and the advent and subsequent development of the I system and its applications and research on various aspects of the system were put into retrospect. Evans and Haken [5] reviewed research work on I under isothermal conditions.

Programmed-temperature gas chromatography (PTGC), especially linear PTGC (LPTGC), has become the most important technique in GC. About 75% of GC studies were done under programmed-temperature conditions [3]. Retention indices under PTGC conditions (I_{PT}) were studied almost immediately after Kováts put forward his I concept. Judging from the importance of the PTGC technique, however, this kind of study has not won as much popularity. The studies published account for only a small fraction of those on I systems as a whole.

It is known that I values under PTGC conditions depend not only on the characteristics of the stationary phase as in isothermal GC, but also on the conditions prevailing in a PTGC process (initial temperature, programming rate r , column geometry, flow-rate of the carrier gas and its change during the temperature programme, etc.). As a result, without a knowledge of the relationship between I_{PT} values and the numerous parameters involved, they can be reproduced only when all the parameters in a “standard process” are followed rigorously. The problems are that it is difficult to duplicate strictly some parameters of the conditions (exact inner diameter of the column and capillary deactivation are two examples) under which the literature I values were measured, and that it is difficult to define a standard temperature programme that is universally applicable and will win common acceptance by chromatographers who measure I values and who use them for identification. These problems caused some difficulties in reproducing I_{PT} values and applying them for identification.

Nevertheless, studies on I_{PT} systems have been

pushed forward by numerous chromatographers the world over. The first approach to an I_{PT} system was to define it by replacing the $\log t'_R$ terms in Kováts' I definition with retention temperature or time, T_R or t_R , as measured in a PTGC process (see below). On the basis of this system, numerous modifications were put forward. Later, with a better understanding of an I system as a function of the programmed-temperature conditions, different approaches to I_{PT} systems were proposed in an attempt to convert between I values obtained under different conditions. Recently, by allowing for all the relevant parameters in the calculation, has been shown that more fundamental parameters (e.g., enthalpies and entropies of solution of solutes in the stationary phase) can be obtained from the measured retention times under one set of conditions, by using such parameter the I values of the same solutes under any conditions can be calculated.

To commemorate the 35th anniversary of the Kováts I system, studies on I_{PT} systems are reviewed in this paper. It can be seen that, as in science research in general, by studying more and more the fundamentals of the subject, research is pushed continuously forward.

2. DEFINITIONS OF VALUES

2.1. Van den Dool and Kratz equation

The first equation for calculating I_{PT} values was put forward by Van den Dool and Kratz [6] in 1963:

$$I_{PT,x} = 100z + 100 \cdot \frac{T_{R,x} - T_{R,z}}{T_{R,z+1} - T_{R,z}} \quad (1a)$$

$$I_{PT,x} = 100z + 100 \cdot \frac{t_{r,x} - t_{r,z}}{t_{r,z+1} - t_{r,z}} \quad (1b)$$

where $I_{PT,x}$ is the value of the solute being measured, T_R and t_R are retention temperature and retention time, respectively, and x , z , and $z + 1$ denote the solute being measured and two adjacent n -alkanes that elute just before and after the solute, respectively.

It is easier, however, to calculate I values with eqn. 1b. These equations imply a linear relation-

ship between retention temperatures of the n -alkanes and the number of carbon atoms in their molecules. Actually, this linear relationship is only approximate, so the range of validity of the equation is limited. Moreover, this equation is applicable only to temperature programmes without an isothermal period. Nevertheless, I_{PT} values in the literature were generally calculated with this equation.

2.2. Generalized retention index (GI)

In an effort to find the correlation between z and T_R , a number of researchers adopted the method of curve fitting. The term generalized retention index (GI) was first put forward by Zenkevich and Ioffe [7]. In this paper, GI systems will be discussed in a broader sense, including all I_{PT} systems using the curve-fitting method for I definition.

Halang *et al.* [8] adopted a T_R cubic spline interpolation for the calculation of retention. Cubic splines are functions composed of third-order polynomials pieced together in the data points. It is claimed that this method offers the following advantages: smoothness, no introduction of extraneous oscillations, easy computability and good fit to both non-linear and linear data sets.

Messadi *et al.* [9] compared the retention indices computed by the spline and the linear methods. It was found that retention indices computed by the two methods may differ by as much as 49 index units (i.u.), generally the spline method yields better results. Zenkevich and Ioffe [7] obtained

$$I_{pt} = at'_R + b \log t'_R + c \\ = a(t'_R + q \log t'_R) + c \quad (2a)$$

where t'_R is the adjusted retention time of an n -alkane. On the basis of the above relationship, the so-called linear-logarithmic (generalized) retention index was defined:

$$GI = 100z + \\ \Delta I \cdot \frac{(t'_{R,x} + q \log t'_{R,x}) - (t'_{R,z} + q \log t'_{R,z})}{(t'_{R,z+k} + q \log t'_{R,z+k}) - (t'_{R,z} + q \log t'_{R,z})} \quad (2b)$$

where a , b , c and $q = b/a$ are constants, ΔI is the difference between the I_{PT} values of two n -alkanes and k is the difference between the carbon numbers in two n -alkane molecules ($k \geq 1$). Similarly, Wang and Sun [10] obtained a relationship between I_{PT} and parameters such as retention volume or its ratio with carrier gas velocity or partition coefficient of the solute, and defining their GI on the basis of I_{PT} , they obtained

$$\begin{aligned} I_{PT} &= a_0 + a_1 \ln Y + a_2 10^{b \ln Y} \\ &= a_0 + a_1 \ln Y + a_2 Y^B \\ &= a_0 + a_2 (q \ln Y + Y^B) \end{aligned} \quad (3a)$$

where $q = a_1/a_2$, a_0 , a_1 , a_2 , b , B and q are constants. Y could be one of the parameters V , V/F or V/K , where F is the carrier gas velocity, V the retention volume and K the partition coefficient of the solute, respectively. On the basis of the linear relationship shown above, GI can be defined as

$$GI(x) = 100z + 100 \cdot \frac{(q \ln Y_x + Y_x^B) - (q \ln Y_z + Y_z^B)}{(q \ln Y_z + 1 + Y_{z+1}^B) - (q \ln Y_z + Y_z^B)} \quad (3b)$$

Although these GI systems have some advantages, they both have the shortcoming that the constants a , b , c and q (or a_0 , a_1 , a_2 , q and B) have to be re-calibrated every time the temperature programme changes.

Podmaniczky *et al.* [11] rewrote Van den Dool and Kratz's equation using the capacity factor, k' , as follows:

$$I_{PT} = 100z + 100 \cdot \frac{k'_x - k'_z}{k'_{z+1} - k'_z} \quad (4a)$$

They tried to correlate k'_{PT} vs. z by different functions. The best correlation was obtained by parabolic regression:

$$k'_{PT} = b_2 z^2 + b_1 z + b_0 \quad (4b)$$

where b_0 , b_1 and b_2 are constants. The I_{PT} value

can be calculated as

$$I_{PT} = 100 \left(\sqrt{\frac{k'_{PT} - b_0}{b_2} + \frac{b_1^2}{4b_2^2}} - \frac{b_1}{2b_2} \right) \quad (4c)$$

2.3. Extended Kováts retention index

This definition is so-called in this paper only because of its resemblance in form to the Kováts isothermal I . It is applicable to complex programmed-temperature processes with isothermal periods:

$$I_v(x) = 100z + 100 \cdot \frac{\ln V_{N,x} - \ln V_{N,z}}{\ln V_{N,z+1} - \ln V_{N,z}} \quad (5)$$

where $V_{N,x}$, $V_{N,z}$ and $V_{N,z+1}$ are the net retention volume of the solute being measured and those of the n -alkanes with z and $z + 1$ carbon atoms, respectively.

In the calculation of I_{PT} with this equation, it is critical to obtain the correct net retention volume. For a constant flow-rate-controlled chromatograph, V_N can be obtained with Majlat *et al.*'s method [12]:

$$V_N(A) = F \left[j_1 t_1 + t_2 \int_{P_1}^{P_2} j dP / (P_2 - P_1) + j_3 t_3 \right] \quad (6)$$

where F is the carrier gas velocity, J is the gas compressibility correction factor and t_1 , t_2 and t_3 are times (see Fig. 1).

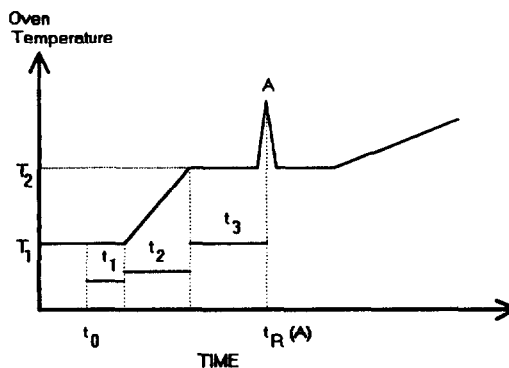


Fig. 1. Schematic diagram of a temperature programme.

Zhu [13] suggested calculating the retention volume on a constant pressure-controlled chromatograph with the following equation:

$$V_N(A) = K \left[(AT_1^{-1/2} - BT_1^{1/2})t_1 + \left(\frac{2A}{T_1^{1/2} + T_2^{1/2}} - \frac{2B}{3} \cdot \frac{[T_1 + T_2 + (T_1 T_2)^{1/2}]}{T_1^{1/2} + T_2^{1/2}} \right) t_2 + (AT_2^{-1/2} - BT_2^{1/2})t_3 \right] \quad (7)$$

where K , A and B are constants and T_1 and T_2 are column temperatures (see Fig. 1).

For programmed-temperature processes other than that shown in Fig. 1, the calculation equation for $V_N(A)$ should be modified accordingly.

Chen *et al.* [14] proposed calculating the I_{PT} values with Kováts' definition:

$$I_{PT} = 100 \left(z + \frac{\log t'_{R,x} - \log t'_{R,z}}{\log t'_{R,z+1} - \log t'_{R,z}} \right) \quad (8a)$$

However, in a temperature programme the temperature ranges to which the compounds of interest and the n -alkanes are exposed are different from each other. Therefore, the influences of carrier gas velocity (which is in turn influenced by temperature) on the retention times of the compound of interest and the n -alkanes are also different. In order to obtain results comparable with the isothermal retention indices, the influence of the gas velocity due to temperature change should be considered. They suggested to use the adjusted retention times $t'_{R,z}(T)$ and $t'_{R,z+1}(T)$ instead of $t'_{R,z}$ and $t'_{R,z+1}$, respectively. $t'_{R,z}(T)$ and $t'_{R,z+1}(T)$ can be calculated with the equations

$$t'_{R,z}(T) = t'_{R,z}(T_z) 10^{B(1/T - 1/T_z)} + \alpha t'_{R,z}(T_z) (T^m T_z^m) \quad (8b)$$

$$t'_{R,z+1}(T) = t'_{R,z+1}(T_{z+1}) 10^{B(1/T - 1/T_{z+1})} + \alpha t'_{R,z+1}(T_{z+1}) (T^m T_{z+1}^m) \quad (8c)$$

where T is the average retention temperature of the compound, T_z and T_{z+1} are the average retention temperatures of the respective n -al-

kanes, α and B can be obtained from the gas hold-up times at two or more different temperatures and from the adjusted retention times for the n -alkanes at two or more different programming rates and m is a constant, the value of which is 0.725 for nitrogen. The data calculated by this method are in good agreement with the isothermal retention indices.

The extended Kováts I system has the advantage of being applicable to those programming processes having an isothermal period, even those having multi-ramps with more than one isothermal period. The calculations involved are very tedious, however, and no reports on the application of these calculation methods have appeared in the literature.

Jennings and Shibamoto [15] used a simplified calculation method on the basis of the extended Kováts concept:

$$I_{Pt,x} = 100z + 100 \cdot \frac{\ln t'_{R,x} - \ln t'_{R,z}}{\ln t'_{R,z+1} + \ln t'_{R,z}} \quad (9)$$

where $t'_{R,x}$, $t'_{R,z}$ and $t'_{R,z+1}$ are the adjusted retention times of the solute under investigation and the n -alkanes with z and $z+1$ carbon atoms, respectively. However, they did not give a sound proof for the justification of using $t'_{R,x}$ as a substitute for $V_{N,x}$ for calculating I_{PT} with eqn. 5. Wang and Sun [16] showed experimentally that there were only slight differences between the results of the exact (with eqns. 5–7) and the approximate (with eqn. 9) calculation methods under different temperature programming conditions (the maximum deviation is less than 0.5 i.u. in extreme cases). A mathematical explanation of this result was also given. This substitution of adjusted retention time for net retention volume greatly simplifies the calculation of extended Kováts I values.

2.4. Other methods

Janssens [17] suggested adding n -alkanes with only odd or even numbers of carbon atoms to the sample. The larger systematic error introduced by fewer reference compounds could be compensated for by a proposed improved linear

interpolation, *i.e.*, setting an imaginary reference point between two consecutive *n*-alkanes.

Watts and Kekwick [18] defined retention index by a simple parameter, the relative elution temperature (T_{re}), *i.e.*, the ratio of the elution temperature of any compound to that of a standard. They found that both the logarithms of the retention volume, $\log V_R$, and T_{re} vary with boiling points in an identical manner. This implies that there is a direct relationship between $\log V_R$ and T_{re} . They derived a relationship between I_{PT} and the elution temperature T_e .

2.5. Comparison of retention index definitions

Wang and Sun [19] made a comparison of the values calculated according to three definitions (eqns. 1a, 3b and 5). The advantages and shortcomings of these definitions were discussed in terms of their theoretical basis, accuracy, ease of calculation and applicability. They found that eqn. 3b seems to be the best definition of I_{PT} except for its complexity in calculation, while eqns. 1a and 5 are approximate methods for calculating I_{PT} and can be applied only to simple temperature programmes. In the early stages of a simple temperature programme without an initial isothermal step, the I_{PT} values calculated by eqn. 1a may be 7 i.u. smaller than those given by eqn. 3b and may give rise to anomalous results in the correlation between I_{PT} and I_{iso} , while the difference in the I_{PT} values calculated with eqns. 3b and 5 is about 1–3 i.u.

Garcia Dominguez and Santiuste [20] compared I_{PT} values obtained with the cubic spline method, which they considered to be the most reliable, with those calculated with the methods of Van den Dool and Kratz [6], Halang *et al.* [8], Zenkevich and Ioffe [7], Pdmniczky *et al.* [11], Wang and Sun [10] and Chen *et al.* [14] and with the isothermal Kováts method. They concluded that Van den Dool and Kratz's method is consistently one of the surest methods, but it works worse with high- T_R solutes. The $\log t_R$ cubic interpolation appeared to be the most reliable method. As comparison is made with Halang *et al.*'s T_R cubic spline interpolation, this seems to be natural. Zenkevich and Ioffe's and Wang and Sun's methods are also reliable, and all these

methods have the advantage that they need only retention times in their calculations. The Podmaniczky *et al.* method appears to be less reliable.

In summary, in order to establish a widely applicable I_{PT} system, numerous proposals have been made, but most of the I_{PT} values reported in the literature were still calculated with Van den Dool and Kratz's definition of I_{PT} .

3. CONVERSIONS BETWEEN RETENTION VALUES UNDER DIFFERENT GC CONDITIONS

3.1. Conversion of I values under isothermal conditions or other isothermal retention values into values under PTGC conditions I_{pt}

Although PTGC has received widespread application, the lack of standard PTRI data results in inconvenience in identification by means of I_{PT} . It is logical, therefore, to find the relationship between I_{PT} and I_{iso} (or other isothermal retention values, such as k or t'_R), so that widely accepted and accumulated isothermal data can be used for PTGC identification. This was for a long time one of the focal points in research and many papers have been published on this topic.

Since the 1960s in studies on the relationship between I_{PT} and I_{iso} , many researchers have tried to find a certain equivalent temperature T_e , so that $I_{PT} = I_{iso}(T_e)$. Among the earlier chromatographers who tried to find T_e with empirical or semi-empirical approximation are Guiochon [21], Giddings [22] and Habgood and Harris [23]. Guiochon proposed that $T_e = T_R - 20^\circ\text{C}$. Giddings suggested that $T_e = 0.92 T_R$. Harris and Habgood, on the basis of many of their investigations on cyclohydrocarbons, pointed out that T_e should be 30–50°C lower than T_R . Lee and Taylor [24] showed that T_e should be the harmonic mean between retention temperature T_R and the initial oven temperature T_0 : $T_e = 2T_R T_0 / (T_R + T_0)$. Later, Akporhonor *et al.* [25] compared the fitness of the calculated I_{PT} with $T_e = 0.92 T_R$ and $T_e = 2T_R T_0 / (T_R + T_0)$. The results showed that under the condition of lower T_0 , I_{PT} corresponds better with I_{iso} if the former T_e values are applied, whereas under higher T_0 the latter gives better results. When the initial

temperatures are the same, at higher programming rates the former T_e and at lower programming rates the latter give better results.

All the above workers based their conclusion on experiments, but as the ranges of solutes under investigation were limited and the precision of I_{PT} measurements on packed columns is less satisfactory than on capillary columns, the conclusions are of limited validity. The approximate calculations proposed by these workers are easy to perform, but they are truly empirical. The influence of some important parameters such as programming rate, geometry of the column, film thickness of the stationary phase and other operating conditions on equivalent T_e has not been taken into consideration.

Said *et al.* [26] tried to make a theoretical study of the problem. They deduced the relationship between the programmed-temperature and isothermal retention indices in chromatography. The relationship was given in the form of a chart from which the equivalent isothermal temperature T_e is plotted vs. $\Delta T'$ with I_{PT} as the parameter, $\Delta T'$ is a function of both the inlet and outlet temperatures during the temperature programme and T_e is the temperature at which the isothermal retention index is equal to the programmed-temperature retention index I_{PT} .

In order to reflect the overall dependence of retention temperature in LPTGC on various chromatographic parameters, Grant and Hollis [27] derived the following equation:

$$\int_{T_0}^{T_R} \frac{dT}{[1 + \alpha/\beta \exp(\Delta H/RT)]} = \int_0^L r \cdot \frac{dx}{u_x} \quad (10a)$$

where u_x is the linear gas velocity at point x , β column phase ratio, ΔH the molar heat of solution of the solute in the stationary phase at the column temperature T , $a = \exp(\Delta S/R)$ is constant for a given solute, ΔS the molar entropy of solution at the column temperature, r the programming rate ($^{\circ}\text{C}/\text{min}$), L the column length, R the gas constant, T_0 the initial programme temperature (K) and T_r retention temperature of the solute (K). In order to simplify the treatment, the following assumptions are made: during a period corresponding to the column dead time, the solute is transported a

negligible distance; and the dead time is assumed to be constant during temperature programming.

On the basis of the assumptions, for aromatic compounds the following equation was determined by the authors:

$$T_R = \frac{T_b}{A + 0.22 \log(0.0012 T_b/A^2)} \quad (10b)$$

where T_b is the boiling point of the solute, $A = 0.44 - 0.22 \log r\phi$, $\phi = aL/\beta\bar{u}$, L is the column length and \bar{u} is the average linear velocity of the carrier gas.

Curvers *et al.* [28] stressed that 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 owing to changes in the carrier gas viscosity and thermal expansion of the carrier gas. They continued the treatment without any simplifications and derived the following equation:

$$\int_{T_0}^{T_R} \frac{dT}{t_0(T)[1 + \alpha/\beta \exp(\Delta H/RT)]} = r \quad (11a)$$

where $t_0(T)$, the dead retention time, is a function of temperature. They further pointed out [28] that the parameters in eqn. 11a could be obtained as follows without any preconditions:

(1) Calculation of a/β and $\Delta H/RT$: for an isothermal GC process,

$$\ln k = \ln(a/\beta) + \Delta H/RT \quad (11b)$$

From measurements at two or more temperatures, a $\ln k$ versus $1/T$ curve can be obtained; a/β and $\Delta H/RT$ in turn can be obtained from the slope and the intercept of the regression line.

(2) Calculation of $t_0(T)$: according to Ettre's theory [29], there is a linear relationship between the viscosity of a gas and temperature T . Hence $t_0(T)$ can be obtained from the following equation:

$$t_0(T) = \frac{4L^2(P^3 - 1)}{3P_0(P^2 - 1)} \cdot \frac{32}{d_c^2} \cdot \eta(T) \quad (11c)$$

and experiments, where $P = P_i/P_0$, P_0 and P_i are the pressures at the outlet and the inlet of the column, respectively, and d_c and L are the inner diameter and the length of the column, respec-

tively. By using the above-mentioned relationships, the retention temperature of the solute T_R can be calculated with the temperature programme parameters T_0 and r provided and I_{PT} can be further calculated by Van den Dool and Kratz's equation. This procedure for calculating linear programmed temperature retention indices was evaluated using five different non-polar columns with OV-1 as the stationary phase. The results were compared with the measured values (*e.g.*, see Table 1). It was believed that the isothermal retention information obtained on one column can be transferred to another column containing the same stationary phase with different phase ratio.

Guan *et al.* [30] pointed out, however, that the entropy and enthalpy terms in eqn. 11a are not independent of the stationary phase film thickness or even of the carrier gas velocity. Hence it is not correct to transfer the entropy and enthalpy terms obtained from one column to those for another as proposed by Curvers *et al.* They suggested evaluating these terms from two or more isothermal Kováts I measurements with some new equations:

$$\ln k_i = \frac{I_i - 100z}{100} \cdot \ln \left(\frac{k_{z+1}}{k_z} \right) + \ln K_z \quad (12a)$$

$$\ln k_{i,T} = \ln \left(\frac{a_i}{\beta} \right) - \frac{\Delta H_i}{RT} \quad (12b)$$

Together with eqn. 12a, they obtained the desired equations:

$$-\frac{\Delta H_i}{R} = (\ln k_{i,T_1} - \ln k_{i,T_2}) \frac{T_1 T_2}{T_2 - T_1} \quad (12c)$$

and

$$\frac{a_i}{\beta} = \exp \left(\ln k_{i,T} - \frac{\Delta H_i}{RT} \right) \quad (12d)$$

where T can be T_1 or T_2 . The differences between calculated and experimentally determined I_{PT} values usually fall within 0.5 i.u. (*e.g.*, see Table 2).

Guan and Zhou [31] used their modified calculation method to evaluate retention times obtained under multi-step temperature programmes with equal success (*e.g.*, see Table 3). Guan *et al.* [32] applied their calculation method

to the identification of unknown components in a simple mixture.

Similarly, on the basis of the work of Grant and Hollis [27], Podmaniczky *et al.* [33] developed a method for the calculation of k'_{PT} (capacity factor in a PTGC process) and then calculated the retention indices using eqn. 4c. The mean difference in the retention indices measured and calculated is 5 i.u.

Krupcik and co-workers [34,35] derived an equation for the prediction of T_R for a compound of interest, measured by LPTGC, from isothermal Kováts retention indices I . The temperature coefficient, dI/dT , and retention temperatures of n -alkanes, $T_{R,z}$, $T_{R,z+1}$, were found via LPTGC.

$$T_R = \frac{[I_{T_0} - 100z + (dI/dT)T_0][T_{R,z+1} - T_{R,z}] + 100T_{R,z}}{100 - (dI/dT)(T_{R,z+1} - T_{R,z})} \quad (13)$$

where I_{T_0} is the isothermal retention index at the initial temperature. The predicted retention temperature can be used to calculate I_{PT} with Van den Dool and Kratz's eqn. 1a.

Examples of other methods without using T_c are as follows:

$$I_{T_0/r} = (I_{T_r} + I_{T_0})/2 \quad (14)$$

This equation was put forward by Golovnya and Uraletz [36], where $I_{T_0/r}$ is the PTGC retention index under the conditions of programming rate r and initial temperature T_0 and I_{T_r} and I_{T_0} are the isothermal retention indices at temperatures of T_r and T_0 , respectively.

Erdey *et al.* [37] put forward

$$I_{PT} = A + \frac{2.3B \log [(T_R + C)/(T_0 + C)]}{T_R - T_0} \quad (15)$$

where A , B and C are constants in Antoine-type equations.

Further, Akporhonor *et al.* [38–40] described procedures for the calculation of programmed-temperature retention times, elution tempera-

TABLE 1

PREDICTION OF RETENTION VALUES ACCORDING TO CURVERS *ET AL.*'S [28]

Comparison between measured and calculated retention temperatures and retention indices for column 2. Reproduced from Table 8 in ref. 28.

Retention parameter	Component	Programming rate (°C/min)								
		2			4			8		
		Measured	Calculated	Difference	Measured	Calculated	Difference	Measured	Calculated	Difference
Retention temperature	<i>n</i> -Octane	345.13	345.12	-0.11	360.26	360.37	-0.12	384.08	363.82	+0.28
	<i>n</i> -Dodecane	401.24	400.78	+0.46	423.42	422.95	+0.46	453.39	452.11	+1.28
	Heptanol	363.90	400.78	-0.33	382.99	383.02	-0.04	410.13	409.06	+1.06
	Decanol	409.36	409.04	+0.32	431.88	431.39	+0.49	462.32	460.69	+1.63
	3-Pentanone	336.24	336.34	-0.11	347.49	347.62	-0.13	367.48	367.38	+0.10
	3-Octanone	359.74	360.08	-0.34	378.48	378.61	-0.13	405.46	404.68	+0.78
	2,4,4-Trimethyl-1-pentene	338.18	338.29	-0.12	350.52	350.64	-0.12	371.78	371.62	+0.15
	1-Tridecene	414.31	414.04	+0.27	437.08	436.49	+0.59	467.72	465.91	+1.81
	Toluene	341.29	341.44	-0.16	355.16	355.32	-0.16	378.04	377.87	+0.17
	1,2-Dimethylbenzene	353.98	354.24	-0.26	371.94	372.09	-0.16	398.53	397.98	+0.54
	Isobutylbenzene	370.10	370.34	-0.25	Coincides with <i>n</i> -C-10			419.52	418.07	+1.45
Retention index	Heptanol	951.56	952.07	-0.51	951.56	951.97	-0.42	-		
	Decanol	1255.19	1255.40	-0.21	1255.32	1255.64	-0.32	-		
	3-Pentanone	670.49	672.79	-2.30	660.58	662.59	-2.01	672.89	673.41	-0.52
	3-Octanone	922.24	923.06	-0.82	923.72	924.33	-0.61	925.57	925.51	+0.06
	2,2,4-Trimethyl-1-pentene	709.05	710.09	-1.04	710.32	710.98	-0.66	911.96	711.61	+0.35
	1-Tridecene	1288.85	1288.93	-0.08	1289.36	1289.31	+0.05	1289.70	1289.81	-0.11
	Toluene	749.73	750.84	-1.12	753.06	753.80	-0.74	756.98	756.40	+0.58
	1,2-Trimethylbenzene	877.19	877.92	-0.73	881.20	881.62	+0.41	885.87	885.60	+0.17
		Isobutylbenzene	995.33	994.95	+0.37	Coincides with <i>n</i> -C-10			1004.21	1003.88

TABLE 2

PREDICTION OF RETENTION VALUES ACCORDING TO GUAN ET AL.'S METHOD [30]

Comparison of calculated and measured LPTGC I values on column 4. $T_0 = 40^\circ\text{C}$. Reproduced from Table V in ref. 30.

Component	Isothermal		Programming rate ($^\circ\text{C}/\text{min}$)					
	45.0 $^\circ\text{C}$	65.0 $^\circ\text{C}$	2		4		8	
			$I_{\text{calc.}}$	ΔI	$I_{\text{calc.}}$	ΔI	$I_{\text{calc.}}$	ΔI
2-Methyl-2-butene	520.0	519.8	513.7	0.0	514.1	0.1	514.7	0.1
4-Methyl-1-pentene	556.7	557.1	546.0	0.2	546.9	0.3	548.2	0.4
2,3-Dimethylbutane	566.3	567.2	556.2	0.2	557.1	0.2	558.6	0.3
2-Methyl-1-pentene	588.0	588.0	583.0	0.1	583.5	-0.1	584.1	0.0
Methylcyclopentane	628.2	631.3	620.9	0.1	622.3	0.1		
2,4-Dimethylpentane	630.4	631.3	623.0	0.0	624.2	0.0		
Benzene	651.3	655.4	642.0	0.2	644.2	0.5	647.2	0.6
Cyclohexane	660.6	665.6	651.6	0.2	654.0	0.4	657.3	0.6
2-Methylhexane	667.6	667.7	659.5	0.1	661.0	0.0	662.8	0.0
1-Heptane	688.6	688.7	684.7	0.0	685.5	0.0	686.4	0.0

ture, retention indices and two kinds of equivalent temperature from isothermal chromatographic data. The first equivalent temperature, $T_e(1)$, is the temperature at which the isothermal retention time t_{iso} equals t_{PT} , the programmed temperature retention time, and the second, $T_e(2)$, is the temperature at which the isothermal retention index I_{iso} equals the programmed-temperature retention index I_{PT} .

Engewald and Maurer [41] used the retention index concept in systems of series-coupled columns without intermediate trapping for the identification of individual components in a complex mixture. Recently, Wright and Walling [42] demonstrated the calculation of retention times for temperature-programmed serially linked capillary columns from isothermal chromatographic data.

In summary, many researchers have made contributions to the study of the relationships between I_{PT} and isothermal retention values in an effort to make use of the I_{iso} standard data system in LPTGC analysis. However, the equivalent temperature approach gave less accurate predictions than those given by the approaches of Curvers *et al.* [28] and Guan *et al.* [30].

3.2. Conversion of I_{PT} values under one set of PTGC conditions into those under another set of PTGC conditions

All studies on the conversion of I_{PT} values under one set of PTGC conditions into those under another set of conditions are based on Golovnyia and Uraletz's work [36]. On studying the relationship between I_{iso} and I_{PT} , they obtained

$$I_{\text{PT}} = I_{T_0} + \frac{T_{\text{R}} - T_0}{2} \cdot \frac{dI}{dT} \quad (16)$$

where T_{R} is the retention temperature of the solute, T_0 is the initial temperature, I_{T_0} is the isothermal retention index of the solute at T_0 and dI/dT is the temperature coefficient of the isothermal retention index.

On the basis of eqn. 16, Wang and Sun [43] derived the following equation to define the LPTGC I values of a certain solute under different temperature programming conditions:

$$I_{\text{PT}}(1) = I_{T_{01}} + \frac{T_{\text{R}1} - T_{01}}{2} \cdot \frac{dI}{dT} \quad (17a)$$

and

TABLE 3

PREDICTION OF RETENTION TIMES ACCORDING TO GUAN AND ZHOU'S METHOD [31]

Retention time (min) calculation for column 2. Temperature programming conditions as indicated. Reproduced from Tables IV and V in ref. 31.

Component	Programme A		Programme B		Programme C		Programme D	
	Calculated	Measured	Calculated	Measured	Calculated	Measured	Calculated	Measured
Decane	2.32	2.35	—	—	1.88	1.90	2.60	2.63
<i>o</i> -Cresol	3.57	3.50	3.53	3.50	2.68	2.62	4.04	4.05
<i>p</i> -Cresol	4.10	4.04	3.95	3.94	3.01	2.94 ^a	4.60	4.62
Undecane	3.91	2.92	3.80	3.81	2.91	2.94 ^a	4.39	4.39
Dodecane	6.59	6.60	5.54	5.55	4.88	4.88	7.33	7.34
1-Decanol	8.55	8.53	6.85	6.84	7.12	7.13	10.57	10.56
Tridecane	9.07	9.09	7.22	7.22	7.84	7.90	11.48	11.49
Tetradecane	11.21	11.20	8.76	8.76	11.15	11.21	15.82	15.82
Methyl dodecanoate	11.76	11.75	9.15	9.15	12.06	12.09	16.75	16.73
Pentadecane	13.53	13.52	10.17	10.17	14.74	14.79	18.72	18.72
Methyl deodecanoate	14.31	14.29	10.55	10.57	15.97	15.99	19.33	19.34
Hexadecane	16.98	16.94	11.78	11.81	20.23	20.22	20.80	20.84

Temperature programming conditions

Programme	Step No.	Temperature (°C)	Hold time (min)	Programming rate (°C/min)
A	1	87.0	5.0	8.0
	2	137.0	Hold	
B	1	87.0	3.0	10.0
	2	157.0	Hold	
C	1	97.5	5.0	4.0
	2	127.5	Hold	
D	1	82.5	2.0	2.0
	2	90.0	2.0	4.2
	3	107.0	2.0	8.0
	4	200.0	Hold	

^a Peaks overlap.

$$I_{PT}(2) = I_{T_{02}} + \frac{T_{R2} - T_{02}}{2} \cdot \frac{dI}{dT} \quad (17b)$$

From eqns. 17a and 17b, the following equation can be derived to calculate $I_{PT}(2)$ under PTGC conditions 2 from $I_{PT}(1)$ under conditions 1, assuming dI/dT to be constant:

$$I_{PT}(2) = I_{PT}(1) + \frac{T_{02} - T_{01}}{2} \cdot \frac{dI}{dT} + \frac{T_{R2} - T_{R1}}{2} \cdot \frac{dI}{dT} \quad (17c)$$

Eqn. 17c opens up a new way to expand the application of the PTGC I system.

Chen and Peng [44] obtained the following equation from Kováts' isothermal definition:

$$I_{T_2} = I_{T_1} + \frac{T_2 - T_1}{A + BT_2} \quad (18a)$$

where A and B are constants. Under programmed temperature conditions, if I_{PT} is calculated from eqn. 8a, eqn. 18a can be extended as follows:

$$I_{PT}(2) = I_{PT}(1) + \frac{T_2 - T_1}{A + BT_2} \quad (18b)$$

where T_1 and T_2 are retention temperatures.

3.3. Conversion of I values under PTGC conditions into those under isothermal conditions

A method of calculating I_{iso} from different PTGC I systems was also put forward by Chen *et al.* [45]. This seems to be the only work concerned with the conversion of I_{PT} into I_{iso} .

4. I_{PT} DATABASES

Comparing the measured I values of the solutes to be identified with those in I databases is a very important auxiliary means of identification. Currently, there are two main programmed-temperature retention index data bases.

4.1. Quantitative Analysis of Flavor and Fragrance Volatiles by Glass Capillary Gas Chromatography [15]

The book of the above title collected I values of 1193 organic compounds on PEG-20M and OV-101 columns under programmed-temperature GC conditions. This data system is valuable as a reference to researchers on chromatographic analyses of flavours and fragrances. However, in compiling this data system, glass capillary columns were applied, which are different from fused-silica capillary columns that currently are predominantly used, and some of the chromatographic conditions such as stationary phase film thickness and carrier gas flow-rates are not specified, so it is difficult to reproduce the conditions prevailing in the measurements of the I values. The I_{PT} used in the book was calculated by the extended Kováts definition, which is different from that in other databases using Van den Dool and Kratz's definition.

4.2. Sadtler Standard Capillary Gas Chromatographic Retention Index Library [46]

In 1984, Sadtler Research Laboratories put forward a series of standard capillary chromatographic retention index data. This database is composed of four volumes with retention indices of about 2000 organic compounds under isothermal and temperature-programmed conditions.

This database can serve as a valuable reference in GC identification. The Sadtler data system has the advantage that the experimental conditions are more clearly listed, which might facilitate its application. Weber [47] made use of this database in micropollution monitoring, and discussed the effects of various factors on I_{PT} measurements.

4.3. Others

In addition to the above two larger databases, many laboratories have collected and compiled their own I_{PT} databases for some specific purposes.

Lee and co-workers [48,49] established a linear retention index for capillary PTGC of polycyclic aromatic hydrocarbons (PAHs), polycyclic aromatic heterocyclic and nitrogen-containing polycyclic compounds using naphthalene, phenanthrene, chrysene and picene as reference standards. This system of 310 compounds has been applied to the analysis of diesel particulate material, coal extracts, synthetic fuels, tissues, sediments, air particulate matter and combustion effluents.

Hayes and Pitzer [50] established a I_{PT} library of over 200 hydrocarbons and applied it in the analysis of unknown jet fuel samples.

Emergence (elution, retention) temperature indices and relative retention times of nearly 600 pesticides and industrial chemicals were sequentially tabulated by Saxton [51–53] to provide a basis for the identification of unknowns detected on methylsilicone columns when PTGC is used.

White *et al.* [54] compiled retention indices for 480 compounds, including all possible alkylbenzenes containing ten or fewer carbon atoms, and over 150 monoenes and dienes. The library can be applied to measure gasoline derived from either petroleum or synthetic reactions. The bases of all the above databases are given in Table 4.

Hancock and Peters [55] presented a database of GC retention indices for chemical warfare agents and stimulants, which was applied to the identification of triethyl phosphate, tributyl phosphate and diethyl malonate in water and soil samples.

TABLE 4
PROGRAMMED-TEMPERATURE RETENTION VALUE DATABASES

Compiler(s)	No. of compounds	Compound class	Retention value	Definition equation	Column used	Reference standards	Year	Ref.
Jennings and Shibamoto	1193	Flavours and fragrances	I_{PT}	1a	OV-101, PEG-20M	<i>n</i> -Alkanes	1980	15
Sadtler Labs.	2000	Various	I_{PT}	1a	OV-1, SE-54, Carbowax 20M	<i>n</i> -Alkanes	1984	46
Lee <i>et al.</i>	310	Polycyclic aromatics	I_{PT}	1a	SE-52	PAHs	1979	48
Hayes and Pitzer	200	Hydrocarbons	I_{PT}	Kováts	OV-1, OV-17	<i>n</i> -Alkanes	1982	50
White <i>et al.</i>	480	Hydrocarbons	I_{PT}	1a	OV-1	<i>n</i> -Alkanes	1992	54
Saxton	600	Pesticides	T_r, t_r		Methylsilicones	<i>n</i> -Alkanes	1987	51–53

5. STUDY ON THE REPRODUCIBILITY AND TRANSFERABILITY OF I_{PT} VALUES

Compared with I_{iso} measurement, the repeatability of I_{PT} is equally good. However, the reproducibility of I_{PT} measurements between different laboratories or between different groups in a laboratory is usually poor because many authors did not specify exhaustively all the experimental parameters necessary for reproducing their I_{PT} data used in their measurement. In most instances, the poor reproducibility of I_{PT} measurements can be compensated for by using standard samples, although their procurement is often expensive and time consuming. The dependence of this identification method on standard samples is a serious drawback in comparison with spectroscopic identification methods. Also, transferring I_{PT} data obtained under one set of experimental conditions to those under another set even by the same person is considered to be impossible by most chromatographers.

The reliability of the identification by retention indices is based on the reproducibility of retention index measurements. Chromatographs of high quality with highly stable performance have long been available. In addition, capillary columns 0.1–0.53 mm inner diameter, 10–60 m in length and 0.10–5.0 μm film thickness and of high performance are manufactured on a large scale. With high-quality chromatographs and columns, the repeatability of I_{PT} values has attained new levels. Under identical chromato-

graphic conditions, provided that the characteristics of the stationary phases are stable and the samples are not overloaded, the standard deviations of the measurements of I_{PT} can be lower than 0.1 i.u.

Currently, an attractive point in the study of application of I_{PT} values is to increase its reproducibility and to achieve their transferability in order to make full use of their high repeatability. However, many chromatographers pessimistically consider that it is impossible to reproduce I_{PT} values under different experimental conditions. For instance, after a careful study on the effects of column inner diameter, r , $P(P_i/P_o)$, F (gas volumetric velocity), T_0 and the film thickness of the stationary phase, d_f , on measured I_{PT} values, Weber [47] concluded that only on strictly identical columns and with advanced chromatographs was it possible to reproduce standard I_{PT} values, and it was meaningless to compare I_{PT} values obtained in different laboratories and under different conditions.

As early as 1960, Habgood and Harris [56] derived a basic equation for LPTGC:

$$\int_{T_0}^{T_R} \frac{1}{V} \cdot dT = \frac{r}{F} \quad (19)$$

where V is the retention volume of the solute.

In 1983 Knoepfel *et al.* [57], starting from Habgood and Harris's basic equation, proposed that in order to obtain standard I_{PT} values under

different conditions, it was not necessary to standardize all the column characteristics and temperature programming parameters, but only to make the parameters satisfy the condition $raL^2/D^2 = \text{constant}$, where $a = (P^3 - 1)/(P^2 - 1)$, $P = P_i/P_o$, P_i and P_o are the inlet and outlet pressure of the column, respectively, D is the inner diameter of the column, L is the length of the column and r is the programming rate. The authors verified their proposition and found that, when D and L were constants and r and a were adjusted according to aforementioned condition, the reproducibility of I_{PT} values obtained was excellent, but when L changed the reproducibility of I_{PT} suffered.

To solve this problem, Saxton [51–53] proposed a technique of simultaneous parameter compensation: to obtain reproducible I_{PT} values for components in a mixture under different conditions, all the parameters should be adjusted appropriately so as to make the retention temperature T_R of a certain reference compound in the mixture remain unchanged. This simultaneous parameter compensation method seems straightforward and convenient to use but needs a theoretical explanation.

In 1985, Wang and Sun [58] pointed out that it was possible to obtain reproducible I_{PT} values in the I_{PT} measurements on a capillary column heated from the same initial oven temperature. Both the programming rate r and the carrier gas flow-rate F can be varied, but their ratio r/F should be kept constant. In 1987, Wang and Sun [59] furthered their study and also starting from the basic equation of Habgood and Harris they obtained

$$\int_{T_0}^{T_R} \left(V_g + \frac{273V_d}{T_w} \right)^{-1} dT = \frac{rw}{F} \quad (20)$$

where w is the mass of the stationary phase in the column, V_g the specific retention volume of the solute and V_d the column dead retention volume; rw/F is a characteristic parameter for the measurement of retention indices under LPTGC conditions. The authors pointed out that when T_0 and rw/F were kept constant, reproducible I_{PT} values could be obtained with different columns and under different temperature pro-

gramming conditions. Yin and Sun [60] improved and simplified the previous work and pointed out that the ratio rt_0/β , where t_0 is the dead retention time, and β the phase ratio of the column, had the same characteristic in reproducing I_{PT} values as rw/F , while the new characteristic parameter is more convenient to use. Recently, De Paoli *et al.* [61] succeeded in reproducing values on two columns with different phase ratios using Yin and Sun's method.

It can therefore be concluded that reproducing or transferring I_{PT} values under non-identical conditions can be achieved if all the important chromatographic parameters are clearly specified in the original I_{PT} database.

Apart from the work mentioned above, the effects of sample size [62–66] and the amount of the neighbouring solute (large neighbour effect) [67] on reproducing measurements have also been studied. They emphasized the importance of avoiding overloading of injected sample and reference *n*-alkanes and the presence of large neighbouring peaks in order to obtain reproducible I_{PT} measurements. All these studies could help to deepen the understanding on this topic and are of practical significance.

The aforementioned are the main directions in I_{PT} studies in the literature. It should be stated that there are also some publications on studies of the relationship between I_{PT} and molecular structure and thermodynamic parameters. The aim of these studies is to calculate I_{PT} values from structure and thermodynamic parameters. With recent developments in computer technology, more and more chromatographers are following this direction of research. In this review, however, studies in this direction were not included.

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