DEFINITIONS AND METHODS OF CALCULATION OF THE TEMPERATURE-PROGRAMMED RETENTION INDEX, I_{TP}

I. THE RELATIONSHIP BETWEEN I_{TP} AND THE NET RETENTION VOLUME FOR n-ALKANES

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SUMMARY

Definitions and methods of calculation of the temperature-programmed retention index, I_{TP}, are presented. A more accurate regression equation describing the relationship between I_{TP} and the net retention volume, V, or the net retention time, t, for n-alkanes in temperature-programmed gas chromatography is proposed

$$I_{TP} = a_0 + a_1 \ln Y + a_2 Y^B$$

where a_0, a_1, a_2 and B are constants, Y may be V or t. The equation can be applied to any temperature programme.

INTRODUCTION

The retention index, I_V, defined according to Kováts[1] is based on the linear relationship between the logarithm of the net retention volume and the carbon number of n-alkanes under isothermal conditions

$$I_{V(x)} = 100N + 100 \cdot \frac{\ln V_x - \ln V_N}{\ln V_{N+1} - \ln V_N} \tag{1}$$

where V is the net retention volume, the subscripts N and $N + 1$ are the numbers of carbon atoms in the n-alkanes and the subscript x represents the unknown compound. Under isothermal conditions, V can be replaced by the net retention time, t.

Temperature programming is generally used in the analysis of complex organic mixtures having a wide range of boiling points. Van den Dool and Kratz[2] proposed the following definition of the temperature-programmed retention index, I_{TP}

$$I_{TP(x)} = 100N + 100 \cdot \frac{T_{R(x)} - T_{R(N)}}{T_{R(N+1)} - T_{R(N)}} \qquad (2a)$$

or

$$I_{TP(x)} = 100N + 100 \cdot \frac{t_{R(x)} - t_{R(N)}}{t_{R(N+1)} - t_{R(N)}} \qquad (2b)$$

where T_R is the retention temperature and t_R is the retention time. The above equations have been accepted as the fundamental definition of I_{TP}. However, there are three weaknesses in this definition:

(1) It is based on the linear relationship between T_R and the carbon number of n-alkanes under linear temperature-programming conditions. As pointed out by Harris and Habgood[3], this linear relationship is "less regular and less extensive".

(2) It is only applicable to a linear temperature programme not including isothermal steps.

(3) It is not more closely related to the isothermal retention indices of Kováts[4], I_i. Thus, in correlating I_{TP} with I_i, anomalies are found[5].

Recognizing the non-linearity between T_R or $\ln t_R$ and the carbon number of n-alkanes in temperature-programmed gas chromatography (TPGC), some other definitions of I_{TP} were proposed. Halang et al.[6] and Zenkevich[7] used curve-fitting methods to obtain some critical constants from retention data for n-alkanes and then calculated I_{TP} values by means of special equations. For instance, Zenkevich proposed the following relationship in TPGC:

$$\begin{aligned} I_{TP} &= at + b \log t + c \\ &= a(t + q \log t) + c \end{aligned} \qquad (3)$$

Eqn. 3 shows that a linear relationship exists between I_{TP} and $(t + q \log t)$, so a "Generalized Retention Index (GI)" was defined as follows

$$GI_{t(x)} = 100 N + 100 \cdot \frac{(t_x + q \log t_x) - (t_N + q \log t_N)}{(t_{N+1} + q \log t_{N+1}) - (t_N + q \log t_N)} \qquad (4)$$

where a, b, c and q are constants. The shortcoming of such a treatment is that all the constants used have to be redetermined when the temperature programme is varied. In addition, these methods are limited to simple temperature programmes without isothermal steps.

Some authors have tried to extend the Kováts definition (eqn. 1) to TPGC and succeeded in deriving some rigorous equations to calculate V for any temperature programme. For instance, in the case of a constant mass flow-rate of carrier gas, V can be calculated by the method of Majlát et al.[8]. In the case of a constant inlet pressure of carrier gas, V can be calculated by Zhu's method[9]. Then, I_{TP} can be calculated according to eqn. 1. In this case, eqn. 1 can be called the Extended Kováts Definition.

According to Majlát et al. and Zhu, the Extended Kováts Definition seems to be applicable to any temperature programme. However, the relationship between ln

V and the carbon number of n-alkanes may not be linear in TPGC, so a linear interpolation could result in error.

Because I_{TP} is the most important retention parameter in TPGC and is widely used for peak identification in routine analysis, a great number of I_{TP} data have been collected and additional data are expected to accumulate rapidly. Therefore, it is worthwhile to evaluate critically the different definitions and methods of calculation for I_{TP}.

In this paper, attention is focused on the relationship between the net retention volume, V, and the carbon number of n-alkanes in TPGC, because this relationship forms the basis of the I_{TP} definition. We have improved upon the Zenkevich treatment[7] and a more accurate and universally applicable regression equation is proposed to describe this relationship.

EXPERIMENTAL

A Varian 3770 gas chromatograph (constant inlet pressure of carrier gas) equipped with a flame ionization detector and a C-R1B microprocessor was used. The open-tubular glass capillary columns were coated with OV-101 (24 m × 0.26 mm I.D., film thickness, $d_f = 0.5$ μm) or PEG-20M (25 m × 0.26 mm I.D., $d_f = 0.2$ μm).

The C_7–C_{23} n-alkanes were dissolved in n-pentane and then injected with a splitting ratio of 1:90.

V/K values (K = constant, see ref. 9) for the n-alkanes were calculated and the equations describing I_{TP} *versus* V/K or t were established by means of stepwise regression analysis; then GI values were calculated according to eqn. 6 (see below).

A preliminary calculation showed that the maxima discrepancy between GI_t and GI_V (see below) existed at about $(100N + 50)$ i.u., so a series of hypothetical compounds with $t_x = t_N + (t_{N+1} - t_N)/2$ was assigned for comparison of the discrepancy.

A NEC/PC-8801 B computer was used for the calculations.

RESULTS AND DISCUSSION

Eqn. 3 proposed by Zenkevich was first used to calculate I_{TP}, but the results were comparatively unsatisfactory as the multiple correlation coefficient, R, was only 0.999–0.9999 and the estimated standard error (S.E.) was as large as 10 i.u. S.E. is the statistical result of the discrepancies between the I_{TP} values calculated by the regression equation and the theoretical I_{TP} values of n-alkanes $(100N)$.

By means of stepwise regression analysis, a more accurate regression equation has been found

$$\begin{aligned}
I_{TP} &= a_0 + a_1 \ln Y + a_2 \cdot 10^{\,b \ln Y} \\
&= a_0 + a_1 \ln Y + a_2 Y^B \\
&= a_0 + a_2(q \ln Y + Y^B)
\end{aligned} \qquad (5)$$

where $q = a_1/a_2$, a_0, a_1, a_2, b and B are constants, Y may be V, V/F (F is flow-rate of carrier gas, see ref. 8), V/K or t. Then, GI can be redefined as follows:

TABLE I

CONSTANTS IN EQNS. 5 AND 6 WHEN $Y = V/K$ (OV-101 COLUMN)

Temperature programme	Span	a_0	a_1	a_2	B	q	Regression	
							R	S.E. (i.u.)
80 to 210°C at 2°C/min	C_7–C_{13} ($r = 2$°C/min)	1096.00	145.7	139.2	1.428	1.047	0.999999	0.39
	C_{13}–C_{19} ($r = 2$°C/min)	1157.92	192.7	77.48	1.958	2.487	0.999999	0.31
	C_{19}–C_{23} ($t = 0$)	2537.64	70.39	−4285.9	−1.800	−0.01642	0.999998	0.38
80 to 240°C at 6°C/min	C_7–C_{13} ($r = 6$°C/min)	1145.73	156.9	585.7	1.635	0.2679	>0.999999	0.28
	C_{13}–C_{18} ($r = 6$°C/min)	1236.47	201.4	531.9	2.050	0.3786	0.999999	0.41
	C_{18}–C_{23} ($r = 0$)	3610.87	2970	−1846	0.800	−1.609	0.999996	0.65
80 (9 min) to 230°C at 6°C/min	C_9–C_{17} ($r = 6$°C/min)	988.08	97.19	301.3	2.418	0.3225	0.999999	0.39
80 (5 min) to 136°C at 2°C/min then to 240°C at 9°C/min	C_8–C_{13} ($r = 2$°C/min)	1050.61	132.1	119.1	1.566	1.109	>0.999999	0.16
	C_{13}–C_{17} ($r = 9$°C/min)	1249.16	−78.53	9.947	5.988	−7.894	>0.999999	0.14
	C_{18}–C_{23} ($r = 0$)	3108.07	−272.3	−8845	−3.000	0.03078	0.999997	0.63

$$GI_{(x)} = 100N + 100 \frac{(q \ln Y_x + Y_x^B) - (q \ln Y_N + Y_N^B)}{(q \ln Y_{N+1} + Y_{N+1}^B) - (q \ln Y_N + Y_N^B)} \qquad (6)$$

The constants in eqn. 5 have to be determined based on the Y values of n-alkanes and they have to be redetermined when the temperature programme or the column used is varied. In Table I, the constants of eqn. 5 for typical temperature programmes are compared. All of the regression equations are sufficiently accurate with $R \geqslant 0.999996$, S.E. $\leqslant 0.65$ i.u.

From Table I it is seen that the constant B increases with increasing heating rate, r, and with increasing isothermal time at the initial column temperature. When r is changed abruptly, for example, from 2 to 9°C/min or from an isothermal step to a heating step or *vice versa*, the B value changes dramatically. So the regression equation has to be obtained from, and is only useful to, a single step of a complex temperature programme.

The constant q represents the relative contribution of the $\ln Y$ and Y^B terms to I_{TP}. For the most simple temperature programmes (from 80 to 210°C at 2°C/min and from 80 to 240°C at 6°C/min excluding a final isothermal step), with decreasing heating rate, q increases and B decreases; this means a greater contribution from $\ln Y$ to I_{TP} compared with Y^B.

In addition, from Table I, the values of B and q for the earlier stage of a linear heating step are different from those for the later stage, so if an highly accurate regression equation is necessary the span of eqn. 5 should not be too large, say six to eight consecutive n-alkanes.

From the experimental results in Table II, it is seen that when V/K is small, the $\ln (V/K)$ term provides the main contribution to I_{TP}, and with increasing V/K the contribution of $(V/K)^B$ rapidly rises. Also, neither $\ln Y$ nor Y^B can be neglected (if the contribution of a term is less than 1 i.u., the term can be neglected), even at low heating rates.

In our opinion, Y in eqns. 5 and 6 should be the net retention volume, V (also including V/F and V/K), so that the equation has a closer theoretical relationship to

TABLE II

COMPARISON OF CONTRIBUTIONS OF $\ln Y$ AND Y^B TO I_{TP} FOR HYPOTHETICAL COMPOUNDS (OV-101 COLUMN)

Temperature programme	$V/K^\star$	I_{TP}	a_0	$a_1 \ln (V/K)$ (i.u.)	$a_2 (V/K)^B$ (i.u.)
80 (9 min) to 230°C at 6°C/min	0.43899	949.23	988.08	−80.01	41.16
80 to 240°C at 6°C/min	0.21557	952.59	1145.73	−240.79	47.65
	0.81890	1549.40	1236.47	−40.23	353.16
	1.23515	2051.97	3610.87	627.29	−2186.19
80 to 210°C at 2°C/min	0.09490	757.66	1096.00	−343.16	4.82

$\star$ See ref. 9.

TABLE III

COMPARISON OF GI_t ($Y = t$) WITH GI_V ($Y = V/K$) FOR HYPOTHETICAL COMPOUNDS ON AN OV-101 COLUMN

Hypothetical compound*	80 to 240°C at 6°C/min			80 (5 min) to 136°C at 2°C/min then to 240°C at 9°C/min		
	GI_t	GI_V	ΔGI**	GI_t	GI_V	ΔGI
A	756.80	756.85	−0.05			
B	854.31	854.31	0.00	857.18	857.19	−0.01
C	952.75	952.72	0.03	954.67	954.63	0.04
D	1051.45	1051.44	0.01	1052.36	1052.33	0.03
E	1150.56	1150.60	−0.04	1150.83	1150.88	−0.05
F	1249.92	1250.00	−0.08	1250.03	1250.15	−0.12
G	1349.54	1349.50	0.04	1340.66	1340.55	0.11
H	1449.45	1449.43	0.02	1445.59	1445.57	0.02
I	1549.42	1549.42	0.00	1547.06	1547.09	−0.03
J	1649.44	1649.46	−0.02	1648.04	1648.09	−0.05
K	1749.71	1749.75	−0.04			
L	1851.94	1851.96	−0.02	1852.13	1852.12	0.01
M	1952.09	1952.08	0.01	1952.07	1952.06	0.01
N	2052.37	2052.37	0.00	2052.60	2052.60	0.00
O	2152.87	2152.88	−0.01	2153.07	2153.07	0.00
P	2253.55	2253.59	−0.04	2253.68	2253.69	−0.01

  * There is a maximum discrepancy between GI_t and GI_V for these compounds.
  ** $\Delta GI = GI_t - GI_V$.

Kováts definition (eqn. 1). However, we found that GI_t ($Y = t$) was very close to GI_V ($Y = V/K$). The experimental results are in Table III, from which it is seen that $GI_t - GI_V$ is generally less than 0.1 i.u. So the substitution of t for V in eqns. 5 and 6 is reasonable and this facilitates the calculation. The previous discussions on GI_V are also valid for GI_t.

The results obtained on the PEG-20M column were similar to those on the OV-101 column.

CONCLUSIONS

The relationship between I_{TP} and V or t for n-alkanes in TPGC can be described more accurately by eqn. 5, which could be used for any step of a complex temperature programme. When the span of eqn. 5 was properly chosen, the accuracy of I_{TP} was generally better than 1 i.u. Based on eqn. 5, the generalized retention index (GI) can be calculated more accurately by eqn. 6 and has a closer theoretical relationship to Kováts definition. In addition, the observed similarity of GI_t to GI_V makes it easier to calculate GI in practice.

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