CHROM. 19 252

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

III. A SIMPLIFIED CALCULATION METHOD BASED ON THE EXTENDED KOVÁTS DEFINITION

TIANSONG WANG

Beijing Institute of Labour Hygiene and Occupational Diseases, Dong Da Qiao, Beijing (China)

and

BIANXIAO ZHONG, MINBO CHEN and YILIANG SUN*

Department of Chemistry, Peking University, Beijing (China)

(First received March 20th, 1986; revised manuscript received October 28th, 1986)

SUMMARY

When the temperature-programmed retention index, I_{TP}, of a compound is calculated according to the Extended Kováts Definition, the net retention volume, V, of the compound should be used. However, it has been found that I_{TP} values calculated from the net retention time, t, are almost the same as those from V, and in general the differences are less than 0.5 i.u. The mathematical justification for this is presented. Therefore, for the calculation of I_{TP}, the substitution of t for V in the Extended Kováts Definition is not only very convenient in practice but also reasonable in principle.

INTRODUCTION

The retention index defined originally by Kováts can be written as follows[1]:

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

Under isothermal conditions, the net retention volume, V, can be replaced by the net retention time, t, yielding the equation

$$I_{t(x)} = 100N + 100 \cdot \frac{\ln t_x - \ln t_N}{\ln t_{N+1} - \ln t_N} \tag{2}$$

which is much simpler to calculate.

In temperature-programmed gas chromatography (TPGC) the temperature-programmed retention index, I_{TP}, is used for routine analysis. One of the definitions

of I_{TP} as mentioned previously[1] is the Extended Kováts Definition proposed by Maj-lát *et al.*[2] and Zhu[3]. For instance, in the case of a constant mass flow-rate of carrier gas and for the program shown in Fig. 1, the net retention volume of compound A can be calculated according to Majlát *et al.*[2]

$$V_{(A)} = F\left[j_1 t_1 + t_2 \int_{P_1}^{P_3} j \, dP/(P_3 - P_1) + j_3 t_3 \right] \tag{3}$$

where F is the flow-rate of carrier gas, j is the gas compressibility correction factor, t_1, t_2 and t_3 are times (see Fig. 1) and P is the ratio of the carrier gas pressure at the inlet of the column to that at the outlet. In the case of a constant inlet pressure, $V_{(A)}$ can be calculated by Zhu's method[3]

$$V_{(A)} = K \left\{ (AT_1^{-1/2} - BT_1^{1/2})\, t_1 + \left[\frac{2A}{T_1^{1/2} + T_2^{1/2}} - \frac{2B}{3} \times \right.\right.$$

$$\left.\left. \times \frac{T_1 + T_2 + (T_1 T_2)^{1/2}}{T_1^{1/2} + T_2^{1/2}} \right] t_2 + (AT_2^{-1/2} - BT_2^{1/2})\, t_3 \right\} \tag{4}$$

where K, A and B are constants, T_1 and T_2 are the oven temperatures (see Fig. 1). V_N and V_{N+1} can be evaluated similarly using eqn. 3 or 4, then I_{TP} is calculated by eqn. 1.

   Although the Extended Kováts Definition, I_E, is only approximate, the error (1–3 i.u.)[4] in using it for simple temperature programme seems tolerable. Its major disadvantage seems to be inconvenience in calculation, especially in the case of a constant mass flow-rate of carrier gas.

   We have found that for any temperature programme the I_{TP} values calculated directly by eqn. 2 are almost equal to those calculated rigorously according to eqn. 1. This has been shown experimentally and is proven mathematically in the present paper.
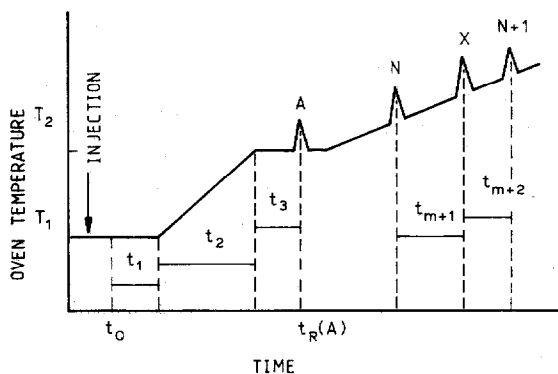

Fig. 1. Schematic diagram of a temperature programme.

EXPERIMENTAL

Shimadzu GC-9A (constant mass flow-rate) and Varian 3770 (constant inlet pressure) gas chromatographs were used with a flame ionization detector. 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 test compounds were premixed with n-alkanes and then injected with a splitting ratio of 1:90. The standard deviations for the I_{TP} measurements ranged from 0.2 to 0.9 i.u. (n = 3, calculation based on eqn. 2).

In the case of a constant mass flow-rate, the column inlet pressure, P_i, was measured by an U-shaped mercury pressure gauge at different column temperatures, T_c, and a good linear regression equation for P_i versus T_c was obtained. From the retention temperatures of the solutes and the regression equation, the corresponding column inlet pressure and then P, the ratio of the pressures at the column inlet and outlet, can be calculated.

The calculation of V based on eqns. 3 and 4 was carried out on a NEC/PC-8801B computer. The calculation of I_{TP} (I_V and I_t) was based on the same set of data for each experiment.

RESULTS AND DISCUSSION

The values of I_{TP} calculated by different methods are compared in Table I. For the sake of clarity, the statistical results of the comparison are shown in Table II. It is evident that the values of I_t are almost equal to those of I_V obtained by rigorous calculation based on the Extended Kováts Definition, the average discrepancies amounting only to 0.12 i.u. for a constant inlet pressure and 0.04 i.u. for a constant mass flow-rate; the maximum discrepancy does not exceed 0.46 i.u. in each case. The discrepancy is comparable with the standard deviation of the I_{TP} measurement, 0.2–0.9 i.u.

In order to evaluate the net retention volume, according to Majlát's or Zhu's method, the variation of the column inlet pressure or column temperature during the temperature programme should be taken into account. Let f_i be the correction factor with respect to the column inlet pressure or the column temperature, then the net retention volume of a compound can be written as:

$$V = \sum_{i=1}^{n} f_i t_i \tag{5}$$

It is well known that

$$\ln(1 + x) = \sum_{n=1}^{\infty} \frac{(-1)^{n-1}}{n} \cdot x^n \qquad (0 \leqslant x < 1) \tag{6}$$

and

$$\frac{x + dx}{y + dy} = \frac{x}{y} + \frac{x}{y}\left(\frac{dx}{x} - \frac{dy}{y}\right) \tag{7}$$

TABLE I

I_{TP} VALUES CALCULATED BY DIFFERENT METHODS ON AN OV-101 COLUMN

Underlined values correspond to compounds eluted during the isothermal step.

Compound	Constant inlet pressure								
	80 to 240°C at 6°C/min			80 (9 min) to 230°C at 6°C/min			80 (5.7 min) to 100°C at 2°C/min, then to 130°C at 3°C/min, to 170°C at 4°C/min and to 205°C at 5°C/min		
	I_V*	I_t**	ΔI***	I_V	I_t	ΔI	I_V	I_t	ΔI
Tetrahydro-furan	–	–	–	618.74	618.74	–	620.21	620.21	–
Isobutyl acetate	754.51	754.45	0.06	754.93	754.93	–	754.93	754.93	–
p-Xylene	867.02	866.94	0.08	861.87	861.87	–	863.70	863.60	0.10
n-Heptanol	953.33	953.20	0.13	959.27	958.81	0.46	954.53	954.41	0.12
Limonene	1030.85	1030.73	0.12	1028.02	1027.77	0.25	1026.33	1026.17	0.16
Camphor	1134.87	1134.74	0.13	1127.46	1127.28	0.18	1123.69	1123.54	0.15
Anisyl aldehyde	–	–	–	1219.60	1219.48	0.12	1215.65	1215.52	0.13
Eugenol	1335.95	1335.83	0.12	1334.41	1334.26	0.15	1330.73	1330.56	0.17
Diphenyl ether	1384.67	1384.60	0.07	1382.23	1382.14	0.09	1376.07	1375.92	0.15
Caryophyllene	1435.18	1435.06	0.12	1432.31	1432.19	0.12	1422.86	1422.81	0.05
β-Ionone	1472.75	1472.65	0.10	1471.99	1471.88	0.11	1466.97	1466.81	0.16
n-Hexyl benzoate	1559.39	1559.28	0.11	1559.88	1559.76	0.12	1554.17	1553.99	0.18
cis-3-Hexenyl salicylate	1654.66	1654.55	0.11	1656.14	1656.02	0.12	1646.49	1646.59	−0.10
Benzyl benzoate	–	–	–	1740.91	1740.99	−0.08	1728.10	1728.18	−0.08

* I_{TP} value calculated by eqn. 1.
** I_{TP} value calculated by eqn. 2.
*** $\Delta I = I_V - I_t$.

Utilizing the above equations, after a series of mathematical expansions and approximations, the following equation can be derived from eqn. 1

$$
I_V - I_t \doteq \frac{100 t_{m+1}}{t_{m+1} + t_{m+2}} \left(\frac{1 - t_{m+1}/(2t_N) + t_{m+1}^2/(3t_N^2)}{1 - c/2 + c^2/3} \right) \times
$$

$$
\times \left[b \cdot \frac{t_{m+2} f_{m+1}}{(t_{m+1} + t_{m+2}) \bar{f}} \left(\frac{1 - \dfrac{f_{m+1}}{\bar{f}} \cdot c + \dfrac{f_{m+1}^2}{\bar{f}^2} \cdot c^2}{1 - c/2 + c^2/3} \right) + \right.
$$

$$
\left. - a \cdot \frac{t_{m+2}}{t_N} \left(\frac{h_2/2 - 4h_3 c/3 + 2h_3 t_{m+2}/(3t_N)}{1 - c + \dfrac{t_{m+2}}{t_N} \left(\dfrac{1}{2} + \dfrac{t_{m+2}}{3t_N} \right) + \dfrac{11}{12} c \left(c - \dfrac{t_{m+2}}{t_N} \right)} \right) \right] \tag{8}
$$

Constant mass flow-rate

80 to 240°C at 6°C/min			80 (6.6 min) to 198°C at 6°C/min			80 (6.6 min) to 111°C at 2°C/min, then to 147°C at 3°C/min and to 198°C at 4°C/min		
I_V	I_t	ΔI	I_V	I_t	ΔI	I_V	I_t	ΔI
620.71	620.70	0.01	618.98	618.98	—	618.86	618.86	—
755.55	755.52	0.03	754.96	754.96	—	755.00	755.00	—
867.77	867.74	0.03	866.20	866.09	0.11	863.55	863.51	0.04
952.78	952.74	0.04	956.23	956.12	0.11	954.37	954.31	0.06
1031.87	1031.82	0.05	1028.68	1028.61	0.07	1025.64	1025.59	0.05
1136.37	1136.31	0.06	1130.05	1129.98	0.07	1123.79	1123.70	0.09
1224.34	1224.30	0.04	1220.52	1220.48	0.04	1213.89	1213.86	0.03
1336.65	1336.60	0.05	1335.04	1334.99	0.05	1331.33	1331.21	0.12
1385.16	1385.13	0.03	1382.90	1382.87	0.03	1375.42	1375.31	0.11
1435.76	1435.71	0.05	1432.72	1432.67	0.05	1420.53	1420.48	0.05
1473.19	1473.14	0.05	1471.82	1471.77	0.05	1465.84	1465.77	0.07
1559.93	1559.89	0.04	1556.13	1556.19	−0.06	1554.40	1554.33	0.07
1655.18	1655.14	0.04	1649.81	1649.86	−0.05	1644.28	1644.28	0.00
1737.75	1737.71	0.04	1730.43	1730.48	−0.05	1724.47	1724.50	−0.03

TABLE II

STATISTICAL RESULTS OF THE COMPARISON OF I_{TP} CALCULATED BY DIFFERENT METHODS ON AN OV-101 COLUMN

Carrier gas control	Calculation method used	$\overline{\Delta I}$	S.D.	n
Constant mass flow-rate	$I_V - I_t$	0.04	± 0.04	38
Constant inlet pressure	$I_V - I_t$	0.12	± 0.09	34

TABLE III

COMPARISON OF THE VALUES OF $I_V - I_t$

Compound	$t^\star$ (min)	$\bar{f}_{m+1}$ ($K^{\star\star}$)	f_{m+2} (K)	$\bar{f}$ (K)	a	b	c	$I_V - I_t$ (i.u.)		
								Exptl.*	Eqn. 8	Eqn. 9
n-Decane	11.19			0.0487						
Limonene	12.19	0.0465			0.045	0.019	0.36	0.25	0.26	0.22
n-Undecane	15.23		0.0456							
n-Heptadecane	31.20			0.0448						
Benzyl benzoate	32.08	0.0386			0.138	0.000	0.07	-0.08	-0.10	-0.11
n-Octadecane	33.39		0.0386							

* At constant inlet pressure, on an OV-101 column; 80 (9 min) to 230°C at 6°C/min, see Table I.

** According to Zhu³, K is a constant in the case of a constant inlet pressure.

where t_{m+1} and t_{m+2} are time intervals (see Fig. 1), $\bar{f}$ is the average correction factor, $\bar{f} = V_N/t_N$, $a = 1 - f_{m+1}/\bar{f}$ (in general, $0 \leqslant a \leqslant 0.2$), $b = 1 - f_{m+2}/f_{m+1}$ (in general, $0 \leqslant b \leqslant 0.03$), $c = (t_{m+1} + t_{m+2})/t_N$ (in general, $0 < c < 0.5$), $h_2 = (1 + f_{m+1}/\bar{f})/2$ and $h_3 = (1 + f_{m+1}/\bar{f} + f_{m+1}^2/\bar{f}^2)/3$.

In eqn. 8 the effect of the pressure or temperature of the carrier gas on the retention volume has been expressed as a- and b-containing terms. It is evident that both terms are not only very small, but also counteract each other. Therefore, the difference between I_V and I_t is restricted to a small range.

- For extremum analysis, eqn. 8 can be simplified further:

$$I_V - I_t \doteq \frac{100 t_{m+1}}{t_{m+1} + t_{m+2}} \left(1 + \frac{t_{m+2}}{2t_N}\right) \left[b \cdot \frac{t_{m+2}f_{m+1}}{\bar{f}(t_{m+1} + t_{m+2})} \times \right.$$

$$\left. \times (1 - c/2 + c^2/6) - a(1/2 - 5c/6 + 5t_{m+2}/12t_N) \, t_{m+2}/t_N \right] \quad (9)$$

In order to verify the validity of eqns. 8 and 9, some data calculated with them are compared with experimental values in Table III.

From eqn. 9, a set of approximate extremum conditions for a, b and t_{m+1}/t_{m+2} has been obtained (see Table IV); then the rigorous extremum condition can be approached by using the following equation which derived directly from eqns. 1, 2 and 5 without any approximation:

$$I_V - I_t = 100 \left\{ \frac{\ln [1 + (1 - a)(c - t_{m+2}/t_N)]}{\ln [1 + (1 - a)(c - bt_{m+2}/t_N)]} + \right.$$

$$\left. - \frac{\ln (1 + c - t_{m+2}/t_N)}{\ln (1 + c)} \right\} \quad (10)$$

At first, a, b and t_{m+1}/t_{m+2} were kept constant and the value of c corresponding to the maximum value of $I_V - I_t$ was found. Subsequently, a, b and this value of c were kept constant and the value of t_{m+1}/t_{m+2} corresponding to the maximum value of $I_V - I_t$ was calculated. The procedure was continued until accurate values of the upper and lower limits of $I_V - I_t$ were obtained (Table IV). The temperature programmes corresponding to the extremum conditions are illustrated in Fig. 2.

From Table IV, it is seen that the maximum deviation of I_t from I_V is at most comparable with the standard deviation of I_{TP} measurement. However, it is usually smaller than the standard deviation under most experimental conditions encountered. According to the experimental results in Table I, the maximum ΔI value is less than 0.5 i.u.

Although the maximum deviations were estimated based on the assumption of $c \leqslant 0.5$, the ΔI values for all the compounds tested with $c > 0.5$ ($I_V < 1000$ i.u. on an OV-101 column, $I_V < 1300$ i.u. on a PEG-20M column) are still below the maximum deviations estimated. Thus, the limits of deviation estimated seem to be universally acceptable. in addition, $c_{max} = 0.5$ is set arbitrarily; if c becomes larger, more terms should be taken into account in the above derivation.

TABLE IV

RESULTS OF EXTREMUM ANALYSIS

Parameter	Upper limit of deviation		Lower limit of deviation	
	Approximate	Accurate	Approximate	Accurate
t_{m+1}/t_{m+2}	1	1	1	0.8
a	0	0	$a_{max}(0.2)$	$a_{max}(0.2)$
b	$b_{max}(0.03)$	$b_{max}(0.03)$	0	0
c	—	$\to 0$	—	$c_{max}(0.5)$
$I_V - I_t$	—	0.75 i.u.	—	−0.86 i.u.

It has been found that the b-containing term is usually larger than the a-containing term during a heating step, although $a > b$. This means the value of b plays a primary rôle in determining the deviation between I_V and I_t, and successive n-alkanes must be used for measurement of I_{TP}.

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

It can be concluded that, as a approximate method for calculating I_{TP}, the substitution of t for V in the Extended Kováts Definition is not only extremely convenient, but also reasonable. We have shown mathematically as well as experimentally that the difference between I_t and I_V usually does not exceed 0.5 i.u. in either case of carrier gas control. Because of this result, the calculation of I_{TP} based on the Extended Kováts Definition becomes very easy.

For those interested in the derivation of eqns. 8 and 9, further details can be obtained on request from the authors.
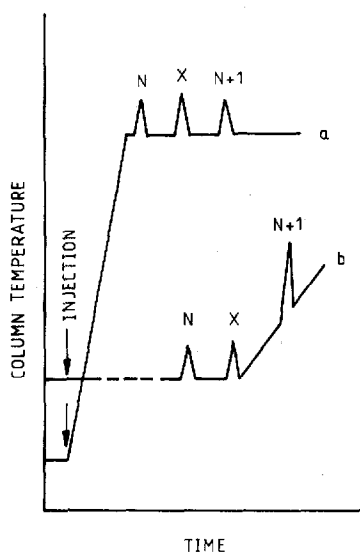

Fig. 2. Schematic diagram of the temperature programmes corresponding to the extremum conditions. (a) Lower limit of $I_V - I_t$ and (b) upper limit of $I_V - I_t$.

REFERENCES

1 T. Wang and Y. Sun, *J. Chromatogr.*, 390 (1987) 261.
2 P. Majlát, Z. Erdös and J. Takaćs, *J. Chromatogr.*, 91 (1974) 89.
3 A. Zhu, *J. Chromatogr.*, 331 (1985) 229.
4 T. Wang and Y. Sun, *J. Chromatogr.*, 390 (1987) 269.