Note

Correlation of retention indices obtained with two temperature programmes

TIANSONG WANG and YILIANG SUN*

Department of Chemistry, Peking University, Beijing (China)

(First received December 3rd, 1984; revised manuscript received April 3rd, 1985)

Combined gas chromatography–mass spectrometry (GC–MS) has been widely utilized for the identification of the components of complex organic samples. However, the information provided by MS itself is usually insufficient for the complete identification of peaks separated by GC. Therefore, many workers have proposed the use of retention indices obtained with temperature programming, I_{TP}, as an auxiliary means of identification[1,2]. Many I_{TP} values have been published[3,4]. As I_{TP} is a function of the temperature programme parameters, one should specify these parameters (initial temperature, heating rate, carrier gas flow-rate, etc) when reporting I_{TP} values. Nevertheless, the parameters chosen are not necessarily the optima, so it is useful to establish the relationship, even approximately, between the I_{TP} values obtained using particular parameters for convenience and those reported in the literature.

Golovnya and Uraletz[5] proposed the following equation for correlating I_{TP} and the isothermal retention index (I_i):

$$I_{TP} = I_{T_0} + \frac{T_r - T_0}{2} \cdot \frac{dI}{dT} \tag{1}$$

where T_r is the retention temperature of the solute, T_0 is the initial column temperature and I_{T_0} represents the isothermal retention index at T_0. Later Erdey *et al.*[6] derived an equation for calculating I_{TP} from any pair of values of the initial temperature and the retention temperature of a solute.

In this study, it was found that many anomalies exist in calculating I_{TP} value from I_{T_0} by Golovnya and Uraletz's equation. We therefore considered it to be of value to derive a new equation for the correlation of retention indices. A new equation has been derived for correlating I_{TP} of one temperature programme with that of another temperature programme. Although the new equation originates from that of Golovnya and Uraletz it gives a better correlation.

EXPERIMENTAL

A Shimadzu GC-9A gas chromatograph equipped with a flame ionization detector, a C-R2A microprocessor and two glass capillary columns [OV-101 (50 m × 0.27

mm I.D.) and PEG 20M (62 m × 0.27 mm I.D.)] were used for retention index measurement and the values of dI/dT were calculated form the I_i versus T curves. The test mixture was injected, then n-alkanes were pre-mixed and then the mixture was injected into the column. The I_{TP} values were calculated in terms of T_r and the I_i values in terms of log t'_r. The standard deviations of the I_{TP} measurement were in the range 0.2–0.9 i.u. ($n = 4$).

For most compounds tested the I_i versus T curves were linear over the whole range from T_0 to T_r and dI/dT was simply the slope of the straight line. However, for n-heptanol and anisaldehyde on the OV-101 column and n-heptanol on the PEG 20M column, the I_i versus T curves deviated considerably from linearity and for these three compounds dI/dT in the initial temperature correction term (see below) was approximated by $\Delta I/\Delta T$, equal to $(I_{T_{02}} - I_{T_{01}})/(T_{02} - T_{01})$. dI/dT in the retention temperature correction term (see below) was treated similarly. When eqn. 1 is used, a straight line should be drawn to approximate the relevant curve and the slope thus obtained is used as an approximation for dI/dT.

RESULTS AND DISCUSSION

According to eqn. 1, for a solute with dI/dT greater than zero, the I_{TP} should be greater than the corresponding I_{T_0}. This inference from eqn. 1 cannot always be verified by experiment, as is shown in Table I. All the compounds in Table I show a positive temperature coefficient of the isothermal retention index, but $I_{TP} < I_{T_0}$. The cause of these anomalies is unclear. However, it is apparent that eqn. 1 is inapplicable in these instances.

Based on Golovnya and Uraletz's equation, the I_{TP} values of two different temperature programmes can be expressed as follows:

$$I_{TP_1} = I_{T_{01}} + \frac{(T_{r_1} - T_{0_1})}{2} \cdot \frac{dI}{dT} \tag{2a}$$

$$I_{TP_2} = T_{T_{02}} + \frac{(T_{r_2} - T_{0_2})}{2} \cdot \frac{dI}{dT} \tag{2b}$$

where T_{r_1}, T_{r_2} represent the retention temperatures of the solute for the two pro-

TABLE I

SOME PAIRS OF $I_{TP} - I_i$ VALUES UNPREDICTABLE WITH GOLOVNYA AND URALETZ'S EQUATION (EQN. 1)

Parameter*	PEG 20M column				OV-101 column	
	Cyclo-hexane	2-pentan-one	n-Butyl-acetate	1-dode-cene	2-pentan-one	p-Xylene
$\Delta I/\Delta T$ (i.u./°C)	+0.42	+0.23	+0.07	+0.07	+0.03	+0.25
I_{TP} ($T_0 = 80°C$, $r = 2°C/min$)	737.0	984.4	1073.7	1243.7	661.4	861.8
I_i ($T_c = 80°C$)	742.0	986.3	1077.6	1246.4	668.1	862.7

* T_0 = Initial temperature; r = heating rate; T_c = column temperature (isothermal).

TABLE II

COMPARISON OF I_{TP} VALUES CALCULATED BY EQNS. 1 AND 5 WITH THAT MEASURED EXPERIMENTALLY ON AN OV-101 COLUMN

Compound	I_{TP} ($T_0 = 80°C$, $r = 3°C/min$)			I_{TP} ($T_0 = 80°C$, $r = 4°C/min$)			I_{TP} ($T_0 = 95°C$, $r = 2°C/min$)			I_{TP} ($T_0 = 110°C$, $r = 2°C/min$)			I_{TP} ($T_0 = 125°C$, $r = 2°C/min$)		
	Measured	Calculated		Measured	Calculated		Measured	Calculated		Measured	Calculated		Measured	Calculated	
		Eqn. 5*	Eqn. 1		Eqn. 5*	Eqn. 1		Eqn. 5*	Eqn. 1		Eqn. 5*	Eqn. 1		Eqn. 5*	Eqn. 1
2-Pentanone	662.0	661.5	668.5	662.4	661.6	668.6	661.9	661.8	668.6	662.8	662.3	669.2	664.1	662.7	669.7
Isobutyl acetate	749.7	749.0	755.3	749.9	748.6	755.0	747.9	748.3	754.6	746.8	747.2	753.6	746.3	746.1	752.6
p-Xylene	863.7	863.1	867.5	865.2	864.2	868.6	864.1	864.8	869.1	867.1	868.0	872.3	870.8	871.5	875.7
n-Heptanol							952.8	953.9	957.2	951.2	953.3	955.8	950.0	952.4	954.8
Limonene	1029.6	1029.0	1029.7	1031.3	1030.5	1031.2	1028.7	1030.1	1030.7	1030.9	1033.4	1034.0	1033.5	1037.0	1037.7
Ethyl benzoate	1154.7	1153.9	1153.2	1156.4	1155.4	1154.7	1153.0	1154.6	1155.3	1154.3	1157.3	1156.2	1155.9	1160.3	1159.1
Anisaldehyde	1238.0	1237.5	1236.2	1240.5	1240.0	1238.3	1235.7	1237.2	1236.0	1237.6	1240.3	1238.7	1239.7	1243.7	1241.5

* I_{TP_1} in eqn. 5 was measured under the conditions $T_0 = 80°C$, $r = 2°C/min$.

TABLE III

COMPARISON OF I_{TP} VALUES CALCULATED BY EQNS. 1 AND 5 WITH THAT MEASURED EXPERIMENTALLY ON A PEG 20M COLUMN

Compound	I_{TP} ($T_0 = 70°C$, $r = 3°C/min$)			I_{TP} ($T_0 = 70°C$, $r = 4°C/min$)			I_{TP} ($T_0 = 80°C$, $r = 2°C/min$)			I_{TP} ($T_0 = 90°C$, $r = 2°C/min$)			I_{TP} ($T_0 = 100°C$, $r = 2°C/min$)		
	Measured	Calculated		Measured	Calculated		Measured	Calculated		Measured	Calculated		Measured	Calculated	
		Eqn. 5*	Eqn. 1		Eqn. 5*	Eqn. 1		Eqn. 5*	Eqn. 1		Eqn. 5*	Eqn. 1		Eqn. 5*	Eqn. 1
Diisopropyl ether	659.0	659.0	665.6	658.3	658.5	665.1	657.0	656.9	664.6	655.4	655.4	662.5			
Cyclohexane	734.0	734.4	742.6	735.5	736.0	744.2	737.0	737.0	745.2	741.7	741.1	749.0			
2-Pentanone	983.4	983.1	987.3	984.3	984.2	988.3	984.4	984.1	988.5	987.0	986.2	990.7			
n-Butyl acetate	1074.0	1073.6	1077.9	1074.4	1073.9	1078.3	1073.7	1073.9	1078.4	1074.1	1074.5	1080.6	1074.5	1075.2	1079.5
p-Xylene	1143.4	1143.3	1148.7	1146.0	1145.9	1151.3	1143.9	1145.7	1150.3	1148.7	1150.1	1154.8	1153.2	1154.8	1159.7
Cyclopentanone	1200	1200.6	1201.9	1203.1	1204.3	1205.6	1200	1201.7	1203.4	1206.3	1207.4	1208.9	1211.7	1213.4	1215.7
1-Dodecene	1245.1	1244.7	1247.1	1245.9	1245.1	1247.5	1243.7	1245.5	1247.5	1244.0	1245.9	1247.9	1244.2	1246.5	1248.9
Anisole	1348.2	1347.9	1350.2	1351.0	1350.9	1353.3	1348.0	1349.4	1349.6	1350.9	1352.9	1353.9	1353.8	1357.0	1358.0
n-Heptanol	1449.8	1449.7	1449.4	1449.3	1449.2	1449.0	1449.2	1450.0	1449.9	1448.4	1449.7	1449.6	1447.4	1449.4	1449.9
Camphor	1532.7	1531.8	1524.9	1539.5	1538.8	1531.9	1526.3	1529.9	1523.1	1531.3	1536.4	1529.6	1536.6	1543.8	1538.1

* I_{TP} in eqn. 5 was measured under the conditions $T_0 = 70°C$, $r = 2°C/min$.

grammes, T_{0_1}, T_{0_2} denote the initial column temperatures and $I_{T_{01}}$, $I_{T_{02}}$ the isothermal retention indices at T_{0_1} and T_{0_2}, respectively.

It is reasonable to assume that the temperature coefficient of the isothermal retention index, dI/dT, remains constant or approximately so over a small temperature range, i.e.,

$$I_{T_{02}} = I_{T_{01}} + (T_{0_2} - T_{0_1})\frac{dI}{dT} \tag{3}$$

By substituting eqn. 3 into eqn. 2b, we obtain

$$I_{TP_2} = I_{T_{01}} + (T_{0_2} - T_{0_1})\frac{dI}{dT} + \frac{(T_{r_2} - T_{0_2})}{2} \cdot \frac{dI}{dT} \tag{4}$$

By subtracting eqn. 2a from eqn. 4 and after rearrangement, we finally obtain

$$I_{TP_2} = I_{TP_1} + \frac{(T_{0_2} - T_{0_1})}{2} \cdot \frac{dI}{dT} + \frac{(T_{r_2} - T_{r_1})}{2} \cdot \frac{dI}{dT} \tag{5}$$

This is the new equation for correlating the I_{TP} values of two different temperature programme. The second term on the right-hand side may be called the initial temperature correction term and the last term the retention temperature correction term.

The differences between the I_{TP} values calculated by eqns. 5 and 1 and that determined by experiment are given in Tables II and III. In general, when eqn. 5 is used for the calculation of I_{TP}, the discrepancies between calculation and experiment are smaller, amounting to 1.2 i.u. on average. In particular, for those temperature programmes in which the initial temperature (T_0) is kept unchanged while the heating rate (r) is varied, the discrepancies become even smaller, amounting to only 0.5 i.u. on average. On the other hand, when eqn. 1 is applied for correlation, the discrepancies become larger with an average of 4.1 i.u.; the smaller the T_{TP} value, the larger the deviation becomes.

Erdey et al.'s equation was also used for calculating the I_{TP} values of some of the test compounds and the results were similar to those given by eqn. 1.

For temperature programmes with different T_0 values, in certain instances the accuracy of I_{TP} calculated by the new equation is poorer than that calculated by the old equation, e.g., camphor on the PEG 20M column and anisaldehyde on the OV-101 column. This is probably due to the fact that T_{0_1} and/or T_{0_2} in eqn. 5 are too low with respect to their retention temperatures. How one should utilize eqn. 5 in this instance is still under investigation.

REFERENCES

1 C. D. Ma, A. J. Huang, Z. M. Lin, H. Tang, X. Bu, Y. L. Sun, S. W. Sun, Y. P. Ma, Q. Z. Cheng, X. L. Luo and T. M. Lin, Hua Xue Tong Bao, 3 (1983) 15.
2 K. Yamaguchi and T. Shibamoto, J. Agr. Food Chem., 29 (1981) 366.
3 W. Jennings and T. Shibamoto, Qualitative Analysis of Flavor and Fragrance Volatiles by Glass Capillary Gas Chromatography, Academic Press, New York,, 1980, p. 26.
4 B. J. Perrigo and H. W. Peel., J. Chromatogr. Sci., 19 (1981) 219.
5 R. V. Golovnya and V. P. Uraletz, J. Chromatogr., 36 (1968) 276.
6 L. Erdey, J. Takács and É. Szalánczy, J. Chromatogr., 46 (1970) 29.