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## DETERMINATION OF THE TEMPERATURE-DEPENDENCE OF THE RETENTION INDEX IN GAS-LIQUID CHROMATOGRAPHY BY COMPUTER

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## SUMMARY

As already shown by the authors<sup>1</sup>, the temperature-dependence of the retention index can be expressed by a first-order fractional function of the column temperature:

$$I_{\text{stationary phase}}^{\text{substance}}(T) = A + \frac{B}{T + C}$$

In the present paper, a least-squares computational method is used to determine by computer the constants to account for all the experimental variables. The equation expressing the temperature-dependence of the retention index has a shorter or longer linear portion depending on the natures of the substances involved and the stationary phase in the temperature range generally used in gas-liquid chromatography. The temperature-dependence of the retention index is significant from both the practical and the theoretical viewpoint. It has an important role in research on the structures and interactions of molecules.

## INTRODUCTION

It is well known that auxiliary methods are used for the identification of peaks in qualitative gas-liquid chromatography when appropriate standards are not available. An important advance was achieved with the Kováts system of retention indices<sup>2</sup>, and many investigators have dealt with the problems concerning this system<sup>3</sup>. Thorough examinations were made to elucidate the relationship between column temperature and retention index<sup>4-10</sup>, but no unambiguous resolution was obtained, in spite of the remarkable results.

We have already shown<sup>1</sup> that the temperature-dependence of the retention index can be expressed by eqn. 1:

$$I_{\text{stationary phase}}^{\text{substance}}(T) = A + \frac{B}{T + C} \quad (1)$$

where  $I$  is the isothermal retention index (index units);  $T$  is the column temperature ( $^{\circ}\text{K}$ ); and  $A$ ,  $B$  and  $C$  are constants. Under given gas chromatographic conditions, as used in the laboratory,  $A$ ,  $B$  and  $C$  are defined by the substance involved and by the properties of the stationary phase. The physicochemical derivations of these constants according to PURNELL<sup>4</sup> are as follows:

$$A = c_1 + 100z \quad (2)$$

$$B = c_2(\Delta H)_x - (\Delta H)_{nP_{z+1}} + c_3(\Delta H)_{nP_z} - (\Delta H)_{nP_{z+1}} + c_4(\Delta H)_{nP_z} - (\Delta H)_x \quad (3)$$

$$C = \frac{(\Delta H)_{nP_z} - (\Delta H)_{nP_{z+1}}}{c_5} \quad (4)$$

where  $c_1$ - $c_5$  are constants;  $\Delta H$  is the differential molar heat of evaporation from solution;  $z$  is the number of carbon atoms;  $x$  refers to the substance to be analyzed; and  $nP_z$  and  $nP_{z+1}$  refer to paraffin hydrocarbons having  $z$  and  $z+1$  carbon atoms, respectively.

Although the differential molar heat of evaporation from solution is theoretically not independent of the column temperature<sup>17</sup>, our laboratory experience has shown that the results obtained from this assumption are significant within a relatively wide temperature range. Two problems concerning the temperature have arisen from the practical application of this assumption: (a) the variation of the temperature interval over which linear dependence is valid; and (b) the number of estimations necessary to define the three constants in eqn. 1.

#### THEORETICAL

As we have already stated<sup>1</sup>, in almost every case the length of the linear portion of eqn. 1 varies in the temperature interval of gas chromatographic measurements. The length of this portion is initially determined from the interactions between the substance investigated and the stationary phase.

The fact that the length of this portion may in certain cases be extremely long, *e.g.*, when using squalane or Apiezon L as the stationary phase, does not mean that the theoretical function of the retention index is therefore a linear function of the column temperature.

We must emphasize that although a linear approximation may be quite sufficient on some apolar stationary phases, its accuracy is less than that of the approximation by a first-order fractional function. However, the linear approximation may, in the case of a polar stationary phase, be a frequent source of serious error.

The method used previously<sup>1</sup> for determining the constants in eqn. 1 for practical purposes yielded quite reasonable results, but did not have sufficient

accuracy for investigating theoretical problems. Therefore, the least-squares method has been used for determining the constants to account for all experimental variables<sup>18,19</sup>:

$$F = \sum_{i=1}^n \left( I_i - A - \frac{B}{T_i + C} \right)^2 = \text{minimum!} \quad (5)$$

where  $F$  is a function;  $I_i$  and  $T_i$  are the measured data;  $A$ ,  $B$  and  $C$  are the constants in eqn. 1;  $i$  is a series of numbers; and  $n$  is the number of measurements.

The condition of the minimum is:

$$\frac{\partial F}{\partial A} = \frac{\partial F}{\partial B} = \frac{\partial F}{\partial C} = 0 \quad (6)$$

As the system of eqn. 6 is, in our case, non-linear, its solution cannot be expressed in a closed form. Therefore, it is usually solved by approximations starting from an appropriate set of initial values,  $A_0$ ,  $B_0$  and  $C_0$ , which may be calculated, for example, by the method described previously<sup>1</sup>.

In the course of our calculations an approximation procedure has been used; namely, the function  $F$  has been expressed at its starting point by its power expansion, neglecting higher-order members.

The function takes the following form at the  $i$ th measured point:

$$F_i \approx I_i - A_0 - \frac{B_0}{T_i + C_0} - dA - \frac{1}{T_i + C_0} dB + \frac{B_0}{(T_i + C_0)^2} dC \quad (7)$$

By using the following symbols:

$$x_i = -1 \quad (8)$$

$$y_i = -\frac{B_0}{T_i + C_0} \quad (9)$$

$$z_i = \frac{B_0}{(T_i + C_0)^2} \quad (10)$$

$$w_i = -\left( I_i - A_0 - \frac{B_0}{T_i + C_0} \right) \quad (11)$$

and inserting them into eqn. 7, then eqn. 12 is obtained:

$$F = \sum_{i=1}^n (x_i dA + y_i dB + z_i dC - w_i)^2 \quad (12)$$

Calculating eqn. 6 by means of eqn. 12, a linear system of equations is obtained from which  $dA$ ,  $dB$  and  $dC$  can be readily calculated. The starting constants are corrected by using the differences obtained and it is checked whether or not the sum of the squares of the deviations have become smaller. If so, the procedure can be continued until the required accuracy is obtained. If necessary, the procedure can be repeated using different starting values.

We have investigated the influence of the incorrectness of the constants on the approximating function. It can be stated on the basis of the partial derivatives that the influence of the constants diminishes in the present example in the order  $A$ ,  $B$ ,  $C$  according to the ratio:

$$\frac{\partial F}{\partial A} : \frac{\partial F}{\partial B} : \frac{\partial F}{\partial C} \approx 1 : 10^{-1} : 10^{-3} \quad (13)$$

## EXPERIMENTAL AND RESULTS

For presentation of the approximation by a fractional function, we have calculated the retention indices of benzene on squalane as stationary phase. The above method of calculation was programmed on a Gier computer (Copenhagen) in Algol-4 (ref. 20). The results are shown in Table I.

TABLE I

DEPENDENCE OF THE RETENTION INDEX OF BENZENE ON THE COLUMN TEMPERATURE ON SQUALANE AS STATIONARY PHASE

Column temperature (°K)	Retention index		Deviation (i.u.)
	Measured (i.u.)	Calculated from eqn. 1 (i.u.)	
295.0	631.0	630.2	+0.8
295.7	631.7	630.5	+1.2
303.0	632.0	633.4	-1.4
313.0	634.0	636.9	-2.9
322.0	639.7 (10)	639.7	0.0
328.0	643.0	641.4	+1.6
340.0	644.6 (10)	644.6	0.0
343.0	645.0	645.3	-0.3
350.0	649.0 (7)	646.9	+2.1
355.0	648.0	648.0	0.0
359.0	648.9 (10)	648.9	0.0
363.0	651.0 (7)	649.7	+1.3
373.0	649.0	651.6	-2.6
393.0	655.0	654.9	+0.1
		Standard deviation	1.58

TABLE II

INITIAL AND CORRECTED VALUES OF THE CONSTANTS IN EQN. 1 FOR BENZENE ON SQUALANE AS STATIONARY PHASE

Constant	Initial values <sup>a</sup>	Corrected values <sup>b</sup>
A	691.00	693.36
B	-8820.00	-9656.22
C	-148.00	-142.03

<sup>a</sup> Calculated from eqn. 1.

<sup>b</sup> Calculated from eqn. 12 by computer.

The initial and the corrected values of the constants are shown in Table II.

The knowledge of the temperature-dependence of the retention indices makes it possible to prepare retention index *vs.* column temperature tables. An example is shown in Table III.

In studying these interactions it is important to know the relationship between the retention index and the column temperature. *e.g.*, on squalane as stationary phase the interaction factor is 0.7455 at 50.0° and 0.7513 at 120.0°. These factors can be calculated only by knowing the temperature-dependence of the retention

index. Their importance is proved by the following calculation<sup>21</sup>:

$$I_{\text{stationary phase substance}}(T) = \frac{I_M}{(1 - f_i)} \quad (14)$$

where  $I_M$  is the molecular index contribution<sup>21</sup> and  $f_i$  is the interaction factor.

TABLE III

DEPENDENCE OF RETENTION INDEX ON COLUMN-TEMPERATURE FOR CYCLOHEXANE WITH SQUALANE AS STATIONARY PHASE

Column temperature (°C)	Retention index									
	0	1	2	3	4	5	6	7	8	9
20	657	658	658	658	658	659	659	659	659	659
30	660	660	660	660	661	661	661	661	662	662
40	662	662	662	663	663	663	663	664	664	664
50	664	664	665	665	665	665	666	666	666	666
60	666	667	667	667	667	668	668	668	668	668
70	669	669	669	669	670	670	670	670	670	671
80	671	671	671	671	672	672	672	672	673	673
90	673	673	673	674	674	674	674	674	675	675
100	675	675	676	676	676	676	676	677	677	677
110	677	677	678	678	678	678	678	679	679	679
120	679	680	680	680	680	680				

Now,  $I_M(\text{benzene}) = 162.92$  index units (i.u.), and therefore:

$$I_{\text{squalane benzene}}(50.0^\circ) = \frac{162.92}{0.2545} = 640.2 \text{ i.u.} \quad (15)$$

$$I_{\text{squalane benzene}}(120.0^\circ) = \frac{162.92}{0.2487} = 655.1 \text{ i.u.} \quad (16)$$

These theoretical data can be compared with the experimental values of 640.0 i.u. at 50.0° and 655.0 i.u. at 120.0°.

As shown in earlier work<sup>22</sup>, eqn. 1 is suitable for the calculation of  $I(\text{TPGC})$  in the case of any temperature programme:

$$I_{\text{stationary phase substance}}(\text{TPGC}) = A + \frac{2.3 \cdot B \cdot \log \left( \frac{T_r + C}{T_0 + C} \right)}{T_r - T_0} \quad (17)$$

where  $I(\text{TPGC})$  is the retention index in temperature-programmed gas chromatography;  $T_r$  is the retention temperature (°K); and  $T_0$  the initial temperature (°K).

However, it cannot be used alone for identifying a substance. For this purpose, eqn. 17 has to be combined with VAN DEN DOOL AND KRATZ'S equation<sup>23</sup>:

$$I(\text{TPGC}) = 100 \left[ \frac{T_r(x) - T_r(z)}{T_r(z+1) - T_r(z)} + z \right] \quad (18)$$

where  $(x)$  is the unknown substance;  $(z)$  and  $(z+1)$  are normal hydrocarbons having

TABLE IV

## CALCULATED CONSTANTS IN EQN. I

Comparison of computed data with data taken from the literature<sup>10</sup>, at a column temperature of 67° with squalane as stationary phase.

Compound	Constant		Retention index		Deviation (i.u.)
	A	B	Measured (i.u.)	Calculated (i.u.)	
Carbon dioxide	$1.47654 \cdot 10^2$	$7.13029 \cdot 10^2$	152.30	152.44	0.14
Acetylene	$1.55803 \cdot 10^2$	9.07109	156.00	156.14	0.14
Ethene	$1.77590 \cdot 10^2$	8.17898	177.80	174.82	-2.98
Propene	$2.85376 \cdot 10^2$	$-1.57647 \cdot 10^2$	287.70	287.37	-0.33
Carbonyl sulphide	$2.79000 \cdot 10^2$	$-8.23299 \cdot 10^2$	304.20	303.88	-0.32
Chloromethane	$2.44108 \cdot 10^2$	$-7.16126 \cdot 10^1$	327.30	327.51	0.21
Cyclopropane	$3.33354 \cdot 10^2$	$-2.32509 \cdot 10^2$	346.00	345.79	-0.21
Vinyl chloride	$3.48819 \cdot 10^2$	$-3.47534 \cdot 10^2$	364.10	364.36	0.26
1-Butene	$3.83214 \cdot 10^2$	$-5.88109 \cdot 10^2$	385.10	384.99	-0.11
2,2-Dimethylpropane	$4.14468 \cdot 10^2$	$-9.22814 \cdot 10^1$	413.30	413.10	-0.20
Chloroethane	$4.24531 \cdot 10^2$	$-2.03512 \cdot 10^2$	415.50	416.08	0.58
1,2-Butadiene	$4.30400 \cdot 10^2$	$-1.83105 \cdot 10^{-4}$	430.30	430.40	0.10
Isoprene	$4.92483 \cdot 10^2$	$-4.23648 \cdot 10^2$	500.80	498.70	-2.10
3-Methyl-1,2-butadiene	$5.13131 \cdot 10^2$	$2.95575 \cdot 10^2$	511.10	510.95	-0.15
2,2-Dimethylbutane	$7.02474 \cdot 10^2$	$-3.20692 \cdot 10^2$	538.80	538.52	-0.28
Cyclopentene	$3.96162 \cdot 10^2$	$-1.59111 \cdot 10^2$	553.40	552.62	-0.78
2-Methyl-1,3-cis-pentadiene	$5.97103 \cdot 10^2$	$-5.50842 \cdot 10^2$	601.80	601.44	-0.36
2,3-Dimethyl-1,3-butadiene	$6.08247 \cdot 10^2$	$-2.54419 \cdot 10^2$	612.80	611.52	-1.28
2,3-Dimethyl-2-butene	$6.29340 \cdot 10^2$	$-3.84202 \cdot 10^2$	626.70	626.30	-0.40
4-Methyl-1,3-pentadiene	$6.16931 \cdot 10^2$	$-3.18265 \cdot 10^2$	630.50	629.65	-0.85
Benzene	$-4.87639 \cdot 10^2$	$-5.15291 \cdot 10^6$	644.60	644.16	-0.44
Dibromomethane	$7.80074 \cdot 10^2$	$-4.47162 \cdot 10^1$	665.60	665.81	0.21
Cyclohexane	$8.75371 \cdot 10^2$	$-1.87019 \cdot 10^2$	667.90	668.02	0.12
Cyclohexene	$7.92205 \cdot 10^2$	$-5.78449 \cdot 10^1$	676.90	676.89	-0.01
Toluene	$8.51647 \cdot 10^2$	$-4.13136 \cdot 10^1$	751.20	751.38	0.18
Cycloheptane	$8.68768 \cdot 10^2$	$-1.47785 \cdot 10^1$	800.00	801.08	1.08
Ethylbenzene	$4.22899 \cdot 10^2$	$-6.16335 \cdot 10^2$	841.20	840.94	-0.26
p-Xylene	$6.54064 \cdot 10^2$	$-1.46510 \cdot 10^2$	855.40	854.83	-0.57
m-Xylene	$5.94175 \cdot 10^2$	$-2.56077 \cdot 10^2$	857.50	857.07	-0.43
Styrene	$6.23500 \cdot 10^2$	$-1.94872 \cdot 10^2$	868.80	868.31	-0.49
o-Xylene					

$z$  and  $z+1$  carbon atoms, respectively; and  $z$  is the number of carbon atoms.

In gas chromatography in general and especially in the analytical chemistry of hydrocarbons, the total overlap of peaks must be taken into account.

In the case of the total overlap of two peaks at a given column temperature ( $T$ ), the following equality can be written:

$$I_1(T) = I_2(T) \quad (19)$$

The temperature-dependence of the retention indices of the two peaks that gives total overlap is given by:

$$A_1 + \frac{B_1}{T + C_1} = A_2 + \frac{B_2}{T + C_2} \quad (20)$$

This equation, after the necessary transformations, becomes:

$$T^2 + T \left[ (C_1 + C_2) + \left( \frac{B_1 - B_2}{A_1 - A_2} \right) \right] + \left[ C_1 C_2 + \left( \frac{B_1 C_2 - B_2 C_1}{A_1 - A_2} \right) \right] = 0 \quad (21)$$

If eqn. 21 has a real solution under gas chromatographic conditions for the given stationary phase, the two peaks totally overlap.

This procedure is demonstrated below on an example.

The constants of the two substances were as follows. For 3-methyl-2-ethyl-1-butene:  $A_2 = 650.00$ ;  $B_2 = -1980.00$ ; and  $C_2 = -520.16$ . For cyclohexane:  $A_1 = 1064.00$ ;  $B_1 = -712800.00$ ; and  $C_1 = 1459.84$ . The stationary phase was squalane. Thus,  $(A_1 - A_2) = 414.0$ ;  $(C_1 + C_2) = 939.7$ ;  $(B_1 - B_2) = -710820.0$ ;  $C_1 C_2 = -759350.4$ ;  $B_1 C_2 = 370770048.0$ ; and  $B_2 C_1 = -2890483.2$ .

Substituting these data into eqn. 21, then:

$$T^2 - 777.3 T + 143211.2 = 0 \quad (22)$$

Taking  $T_1 = 477.2^\circ\text{K}$  ( $204.2^\circ\text{C}$ ) as the first case: no solution occurs because the temperature limit of the squalane stationary phase is  $125.0^\circ\text{C}$ . In the second case, if  $T_2 = 300.1^\circ\text{K}$  ( $27.1^\circ\text{C}$ ), there is good solution.

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