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## CONTRIBUTION TO THE THEORY OF THE RETENTION INDEX SYSTEM

## III. RETENTION INDEX AND MOLECULAR STRUCTURE. CALCULATION OF RETENTION INDICES OF PARAFFIN HYDROCARBONS ON THE BASIS OF THEIR MOLECULAR STRUCTURE

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SUMMARY

While studying the correlation between retention index and molecular structure, we developed an approximation method by which the retention index of a substance can be determined on the basis of its molecular structure. The results obtained which only serve as a modest demonstration of the method indicate the great possibilities of the calculation procedure.

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## INTRODUCTION

Of the methods used in gas chromatography (GC) for presenting retention data, the retention index system of Kováts<sup>1</sup> probably will become a widely used method of general applicability. This has induced most researchers working in the field in recent years to deal with the retention index system and related problems more thoroughly. In spite of the remarkable results achieved, a number of questions remain unanswered. One of the most important problems is to elucidate the relationship between retention index and molecular structure.

Having achieved remarkable results in studying this relationship are a number of workers<sup>2-70</sup>, such as Schomburg<sup>2-6</sup>, Rohrschneider<sup>7-11</sup>, Chovin and Lebbe<sup>12-14</sup>, Guiochon *et al.*<sup>15, 16</sup>, Janák *et al.*<sup>17, 18</sup>, Tourres and Loewenguth<sup>19-21</sup>, Walraven<sup>22</sup>, Keulemans *et al.*<sup>23, 24</sup>, Evans and Smith<sup>25-27</sup>, Groenendijk and Kemenade<sup>30, 31</sup>, Kwa and Boelhauer<sup>34-36</sup>, Matukuma<sup>37</sup>, Piringner<sup>38</sup>, Altenburg<sup>39</sup>, Landa *et al.*<sup>42, 43, 59</sup>, Tóth<sup>50</sup>, Allen and Haken<sup>58, 60</sup>, to mention only some besides Kováts<sup>65-69</sup>. Their results have greatly helped us in elaborating our method.

Determination of the relationship between retention index and molecular structure by calculation is so complicated that we have confined ourselves to dealing with

saturated aliphatic hydrocarbons and to studying their behaviour on squalane stationary phase.

#### THEORY

It is well known that in elaborating the retention index system Kováts has given the retention indices of normal hydrocarbons on any stationary phase and at any temperature by definition as:

$$I_{nP_z} = 100z \quad (1)$$

where

$I_{nP_z}$  = the retention index of a normal paraffin hydrocarbon of carbon atom number  $z$  (index units) on any stationary phase and at any temperature,

$z$  = carbon atom number.

This definition partly determined the way of solving the problem as we had to adhere to this definition throughout the procedure. We reduced the retention index to separate additive components such as:

- |  |   |  |
|--|---|--|
| (a) atomic index contribution ( $I_a$ )      | } | molecular index contribution ( $I_m$ ) |
| (b) bond index contribution ( $I_b$ )        |   |  |
| (c) interaction index contribution ( $I_t$ ) |   |  |

On account of the additivity of index contributions, the retention index is:

$$\begin{aligned} I_{\text{substance}}^{\text{stationary phase}}(T) &= I_a + I_b + I_t^{\text{stationary phase}}(T) = \\ &= I_m + I_t^{\text{stationary phase}}(T) \end{aligned} \quad (2)$$

Atomic index contribution is the sum of the index values of the atoms given in index units (i.u.), similarly as molecular weight is the sum of atomic weights. Bond index contribution is the sum of the retention index values of the bonds between the atoms, whereas the interaction index contribution expresses the interactions between the substance studied and the stationary phase in index units.

Whereas molecular index contribution (atomic and bond) is independent of the stationary phase and temperature and is only determined by the material quality of the substance under study, the interaction index contribution depends on the stationary phase and temperature of the column. It should be noted that the dependence of the retention index on the stationary phase and column temperature is due to the interaction index contribution.

To calculate the atomic index contribution, the index values of carbon and hydrogen atoms had to be defined. The index value of hydrogen atom was defined by us as 0.10 and that of carbon atom as 1.21 i.u. on the basis of iterative calculations on normal hydrocarbons.

The bond index contributions were more difficult to define. In the case of hydrocarbons only two atom types (carbon and hydrogen) but a number of bond types had to be considered. The great number of bond types results in the great variety of compounds with different behaviour, even if the atomic index values are the same.

The following notations we have introduced for the exact description of the bond variations of saturated compounds of C-C bonds.

(1) C-C saturated bonds were denoted by C.

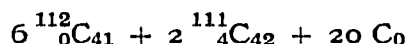
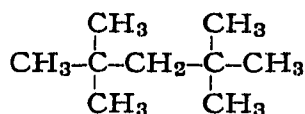
(2) Attached to the symbol C as a subscript on the right-hand side the orders (primary, secondary, tertiary and quaternary) of the two carbon atoms between which the bond is formed are given, *e.g.* C<sub>21</sub> stands for a saturated bond between a primary and secondary carbon atom. The higher order always stands in the first place.

(3) The orders of the carbon atoms next to the higher order carbon of the bond in question are given as a superscript on the left-hand side in increasing order, *e.g.* <sup>112</sup>C<sub>41</sub> stands for a C-C saturated bond between a quaternary and primary carbon atom, and the quaternary carbon atom is bound to one secondary and two other primary carbon atoms.

(4) As a subscript on the left-hand side, the order(s) of the carbon atom(s) attached to the lower order carbon atom of the bond is(are) given *e.g.* <sup>111</sup>C<sub>43</sub> denotes a saturated bond between a quaternary and a tertiary carbon atom, all the neighbouring carbon atoms being primary. If only hydrogen atoms are bound to the carbon atom, the index on the left-hand side is 0, *e.g.* <sup>13</sup>C<sub>31</sub> denotes a bond between a primary and tertiary carbon atom. The tertiary carbon is bound to a primary and to a secondary carbon, whereas the primary is bound only to hydrogens.

(5) C<sub>0</sub> denotes a bond between hydrogen and carbon atom in any case.

In this way the bonds of all the saturated hydrocarbons can be coded very easily. The bond code of 2,2,4,4-tetramethylpentane is as follows:



As a further step, the values (i.u.) of bonds occurring in normal hydrocarbons were determined by iteration. The values calculated this way are summarised in Table I.

After calculating the values (i.u.) of bonds and atoms occurring in normal hydrocarbons, the interaction values of these compounds could be calculated, as by subtracting the molecular index contribution from the value of the retention index, the interaction index contribution is obtained. Let us consider some simple cases.

The atomic index contribution of methane is 1.61 i.u. ( $1 \cdot 1.21 + 4 \cdot 0.10 = 1.61$ ). Subtracting this from the retention index of methane (100.00 i.u.) 98.39 i.u. remain for the bond and interaction index contribution. Taking into consideration that methane contains 4 equivalent C<sub>0</sub> bonds ( $4 \cdot 5.96 = 23.84$  i.u.), we obtain for the interaction index contribution  $98.39 - 23.84 = 74.55$  i.u.

For ethane the atomic index contribution is 3.02 i.u. ( $2 \cdot 1.21 + 6 \cdot 0.10$ ). In ethane there are 6 C<sub>0</sub> and 1 <sup>0</sup>C<sub>11</sub> bonds, the bond index contribution of which is

TABLE I

BOND INDEX CONTRIBUTIONS OF SOME BOND TYPES OCCURRING IN NORMAL HYDROCARBONS

Bond code	Bond index contribution (i.u.)
C <sub>0</sub>	5.96
<sup>0</sup> C <sub>0 11</sub>	12.12
<sup>1</sup> C <sub>0 21</sub>	12.12
<sup>2</sup> C <sub>0 21</sub>	11.00
<sup>1</sup> C <sub>1 23</sub>	14.36
<sup>2</sup> C <sub>1 22</sub>	13.24
<sup>2</sup> C <sub>2 22</sub>	12.12

47.88 (6·5.96 + 1·12.12). Thus the interaction index contribution of ethane is 200.00 — 50.90 = 149.10 = 2·74.55 i.u.

The interaction index contribution of any normal hydrocarbon can be calculated as follows:

$$I_i(nP_z) = z \cdot 74.55 = 15z \cdot 4.97 \text{ i.u.} \quad (3)$$

where 4.97 = Kováts constant<sup>70</sup>.

Starting from the general concept of the index system, each compound (*x*) can be considered as a normal hydrocarbon with carbon atom number:

$$z(x) = \frac{I_x}{100}$$

On this basis, eqn. 3 could be generalised to say that the interaction index contribution of any compound can be calculated by means of the following relationship:

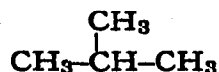
$$I_{i, \text{substance}}^{\text{stationary phase}}(T) = 0.15 \cdot 4.97 \cdot I_{\text{substance}}^{\text{stationary phase}}(T) \quad (4)$$

where

*I* = the retention index of the substance on the given stationary phase and constant column temperature (i.u.) and

*T* = column temperature (°C).

Next we have extended our studies to some simple branched-chain hydrocarbons. As an example, let us examine 2-methylpropane:



The molecule contains 10  $C_0$  and 3  $^{11}_0C_{31}$  bonds. The index contribution of the latter can be calculated accurately. Calculating the interaction index contribution by eqn. 4,  $I_{i,2\text{-methylpropane}}^{\text{squalane}}(50^\circ) = 272.63$  i.u., the contribution of the  $^{11}_0C_{31}$  bond can be calculated using the following relationship:

$$\begin{aligned} {}^{11}_0C_{31} &= \frac{I_{2\text{-methylpropane}}^{\text{squalane}}(50^\circ) - 272.63 - 59.60 - 5.84}{3} \\ &= \frac{365.70 - 338.07}{3} = \frac{27.63}{3} = 9.21 \text{ i.u.} \end{aligned} \quad (5)$$

The contribution of the  $^{11}_0C_{41}$  bond in 2,2-dimethylpropane can be calculated similarly. There are 4 equivalent  $^{11}_0C_{41}$  bonds in the molecule, in addition to the  $C_0$  bonds:

$$\begin{aligned} {}^{11}_0C_{41} &= \frac{I_{2,2\text{-dimethylpropane}}^{\text{squalane}}(50^\circ) - 306.92 - 71.52 - 7.25}{4} \\ &= \frac{411.70 - 385.69}{4} = \frac{26.01}{4} = 6.50 \text{ i.u.} \end{aligned} \quad (6)$$

It is to be noted here that not all the bond contributions can be calculated this way, as in many cases the available system of equations is underdetermined. This is quite understandable as each molecule has a peculiar bond order, which involves a peculiar interaction within the molecule. If the molecules did not possess this, a number of molecules would have identical index values, which is not the case in reality, as the index values of even isomers differ markedly.

With branched-chain hydrocarbons the situation is more involved due to the presence of tertiary and quaternary carbon atoms which greatly affect interactions within the molecule. It can be stated by calculation that there are four variations of the C-C bond between a primary and a secondary carbon atom, 10 variations of the bond between two secondary carbon atoms, 10 of that between a tertiary and a primary carbon atom, and even more of further bond types, which are summarised in Table II. Not all of these possibilities occur in reality and therefore not all their

TABLE II

COMBINATION POSSIBILITIES OF CARBON-CARBON SATURATED BONDS

<i>Symbol of the bond</i>	<i>Number of variations</i>
$C_{11}$	1
$C_{21}$	4
$C_{22}$	10
$C_{31}$	10
$C_{32}$	40
$C_{33}$	55
$C_{41}$	20
$C_{42}$	80
$C_{43}$	200
$C_{44}$	210

TABLE III  
BOND INDEX CONTRIBUTIONS OBTAINED BY INTERATION

Bond code	Bond index contribution (i.u.)	Bond code	Bond index contribution (i.u.)	Bond code	Bond index contribution (i.u.)
$C_0$	5.96	$^{11}_2 C_{32}$	11.80	$^{22}_{11} C_{33}$	13.01
$^0_0 C_{11}$	12.12	$^{11}_3 C_{32}$	9.58	$^{12}_{12} C_{33}$	8.23
$^1_0 C_{21}$	12.12	$^{13}_1 C_{32}$	12.00	$^{14}_{11} C_{33}$	9.00
$^2_0 C_{21}$	11.00	$^{12}_2 C_{32}$	9.65	$^{23}_{11} C_{33}$	8.50
$^1_1 C_{22}$	14.36	$^{22}_1 C_{32}$	11.44	$^{13}_{12} C_{33}$	6.77
$^2_1 C_{22}$	13.24	$^{11}_4 C_{32}$	3.61	$^{22}_{12} C_{33}$	6.06
$^3_0 C_{21}$	10.60	$^{14}_1 C_{32}$	12.00	$^{23}_{12} C_{33}$	5.73
$^2_2 C_{22}$	12.12	$^{12}_3 C_{32}$	5.69	$^{14}_{12} C_{33}^\beta$	6.58
$^4_0 C_{21}$	9.46	$^{23}_1 C_{32}$	11.80	$^{13}_{13} C_{33}^\beta$	6.17
$^3_1 C_{22}$	11.58	$^{22}_2 C_{32}$	11.28	$^{13}_{13} C_{33}^\alpha$	3.57
$^4_1 C_{22}$	13.06	$^{12}_4 C_{32}$	5.31	$^{12}_{11} C_{33}^\beta$	8.18
$^3_2 C_{22}$	9.69	$^{13}_3 C_{32}$	4.31	$^{12}_{11} C_{33}^\alpha$	8.02
$^4_2 C_{22}$	5.31	$^{14}_2 C_{32}$	8.22	$^{33}_{11} C_{33}$	6.93
$^3_3 C_{22}$	6.12	$^{22}_3 C_{32}$	6.17	$^{22}_{13} C_{33}$	4.24
$^4_3 C_{22}$	13.25	$^{24}_1 C_{32}$	9.78	$^{22}_{22} C_{33}$	5.23
$^4_4 C_{22}$	2.50	$^{33}_1 C_{32}$	9.17	$^{24}_{11} C_{33}$	7.57
$^{11}_0 C_{31}$	9.21	$^{23}_2 C_{32}$	3.64	$^{12}_{12} C_{33}^\alpha$	3.34
$^{12}_0 C_{31}$	8.93	$^{13}_2 C_{32}$	8.61	$^{12}_{12} C_{33}^\beta$	3.58
$^{13}_0 C_{31}$	11.00	$^{14}_3 C_{32}$	2.58	$^{111}_0 C_{41}$	6.50
$^{22}_0 C_{31}$	12.33	$^{24}_2 C_{32}$	4.19	$^{112}_0 C_{41}$	8.60
$^{14}_0 C_{31}$	11.50	$^{33}_2 C_{32}$	3.46	$^{113}_0 C_{41}$	7.50
$^{23}_0 C_{31}$	12.00	$^{22}_4 C_{32}$	2.13	$^{122}_0 C_{41}$	12.00
$^{24}_0 C_{31}$	12.00	$^{13}_4 C_{32}$	1.00	$^{114}_0 C_{41}$	7.75
$^{33}_0 C_{31}$	11.25	$^{34}_1 C_{32}$	6.84	$^{123}_0 C_{41}$	11.00
$^{34}_0 C_{31}$	9.13	$^{23}_3 C_{32}$	5.99	$^{222}_0 C_{41}$	9.92
$^{44}_0 C_{31}$	9.21	$^{11}_{11} C_{33}$	8.35	$^{124}_0 C_{41}$	6.75
$^{11}_1 C_{32}$	13.00	$^{12}_{11} C_{33}$	8.92	$^{133}_0 C_{41}$	5.25
$^{12}_1 C_{32}$	11.50	$^{13}_{11} C_{33}$	8.75	$^{223}_0 C_{41}$	6.99

TABLE III (continued)

Bond code	Bond index contribution (i.u.)	Bond code	Bond index contribution (i.u.)	Bond code	Bond index contribution (i.u.)
$^{134}_0C_{41}$	5.45	$^{123}_1C_{42}$	12.67	$^{113}_{11}C_{43}$	15.00
$^{224}_0C_{41}$	7.16	$^{123}_2C_{42}$	4.85	$^{122}_{11}C_{43}$	14.66
$^{233}_0C_{41}$	4.94	$^{123}_3C_{42}$	11.25	$^{112}_{22}C_{43}$	15.22
$^{111}_1C_{42}$	6.20	$^{114}_2C_{42}$	3.96	$^{113}_{12}C_{43}$	12.31
$^{111}_2C_{42}$	6.00	$^{223}_1C_{42}$	13.34	$^{114}_{11}C_{43}$	14.70
$^{112}_1C_{42}$	10.00	$^{222}_2C_{42}$	2.00	$^{111}_{14}C_{43}$	17.00
$^{111}_3C_{42}$	6.20	$^{124}_1C_{42}$	11.72	$^{222}_{11}C_{43}$	12.72
$^{112}_2C_{42}$	2.32	$^{133}_1C_{42}$	9.70	$^{122}_{12}C_{43}$	13.58
$^{113}_1C_{42}$	5.15	$^{112}_4C_{42}$	8.45	$^{123}_{11}C_{43}$	15.15
$^{122}_1C_{42}$	13.34	$^{113}_3C_{42}$	22.34	$^{111}_{23}C_{43}$	12.43
$^{111}_4C_{42}$	6.58	$^{111}_{11}C_{43}$	11.90	$^{112}_{13}C_{43}$	15.08
$^{112}_3C_{42}$	8.60	$^{111}_{12}C_{43}$	11.78	$^{111}_{11}C_{44}$	19.48
$^{113}_2C_{42}$	2.63	$^{112}_{11}C_{43}$	15.00	$^{112}_{11}C_{44}$	25.50
$^{222}_1C_{42}$	13.35	$^{111}_{13}C_{43}$	14.00	$^{113}_{11}C_{44}$	25.35
$^{114}_1C_{42}$	13.21	$^{111}_{22}C_{43}$	13.90	$^{122}_{11}C_{44}$	26.56
$^{122}_2C_{42}$	10.55	$^{112}_{12}C_{43}$	13.81	$^{112}_{112}C_{44}$	31.83

bond contributions need to be calculated, e.g. the bond between two quaternary carbon atoms to which quaternary carbon atoms are attached does not occur due to steric hindrance. As there are very few cases similar to those of 2-methylpropane and 2,2-dimethylpropane in which the bond contributions can be calculated accurately, the index values necessary for our calculations were determined by iteration.

The bond contributions determined by iteration, by which the saturated aliphatic hydrocarbons from  $C_1$ - $C_{10}$  were studied, are summarised in Table III.

Next the temperature dependence of the interaction index contribution was studied. As the temperature dependence of the retention index is due to the temperature dependence of the interaction index contribution, the following relationship which is similar in form to the Antoine-type equations can be written.

$$I_{i, \text{substance}}^{\text{stationary phase}}(T) = (A - I_m) + \frac{B}{T + C} \quad (7)$$

where  $A$ ,  $B$  and  $C$  are constants which only depend on the nature of the substance studied and stationary phase under fixed conditions, within the relatively narrow

TABLE IV

DEPENDENCE ON COLUMN TEMPERATURE OF THE INTERACTION INDEX CONTRIBUTION OF 3-METHYL-3-ETHYLPENTANE ON SQUALANE STATIONARY PHASE

Column temperature (°C)	Interaction index contribution (i.u.)
30.0	159.5
50.0	160.1
70.0	160.7
90.0	161.0
110.0	161.6

temperature interval used in gas chromatography, where the differences of molar heats of evaporation can be assumed to be constants in practice.

The constants  $A$ ,  $B$  and  $C$  can be calculated using equations<sup>36-38, 71</sup> on the basis of index values ( $I_1$ ,  $I_2$  and  $I_3$ ) measured at three different temperatures ( $T_1$ ,  $T_2$  and  $T_3$ ) under isothermal conditions.

In Table IV some data are given which represent the temperature dependence of the interaction value in the case of 3-methyl-3-ethylpentane and squalane as stationary phase.

It should be noted that the temperature coefficients of the interaction index contribution of the normal hydrocarbons equals zero due to the definition of the retention index by KOVÁTS.

The dependence of the interaction index contribution on the nature of the stationary phase can be studied on the basis of ROHRSCHEIDER's work<sup>9</sup>, for at constant temperature

$$\Delta I = I^p - I^s = I_t^p - I_t^s \quad (8)$$

where  $p$  = polar stationary phase;  $s$  = squalane stationary phase, since when differences are produced, the molecular index contributions, which do not depend on the stationary phase, fall out.

#### EXPERIMENTAL

The purpose of our experiments has been the completion of available literature data, as most data necessary to study the retention index and molecular structure can be found in the literature.

The measurements were made on Carlo Erba Fractovap Model D, GV and GI-452. TCD and FID detectors, various types of packed and capillary columns and a Speedomax recorder with a sensitivity of 2.5 mV/full scale, and chart speed of 1.27 cm/min were used. Hydrogen, argon and nitrogen were used as carrier gases and hydrogen, oxygen or in some cases air were used as auxiliary gases. Experiments were done in each case under isothermal conditions. A semi-automatic device or a Hamilton syringe was used for sample introduction. In Table V the data of a squalane column are summarised along with the corresponding optimum gas chromatographic conditions.



TABLE V

DATA OF OPTIMUM GC CONDITIONS IN CASE OF A STANDARD SQUALANE COLUMN

Detector: FID  
 Sensitivity:  $8 \times 100$   
 Sample:  $0.3 \mu\text{l}$  introduced by a Hamilton syringe  
 Column: aluminium spiral of 3.0 m length and 2.0 mm I.D.  
 Packing: 10.0 wt% squalane on 60/80 mesh Chromosorb W  
 Carrier gas: nitrogen  
 Inlet pressure of carrier gas: 1.80 kp/cm<sup>2</sup>  
 Auxiliary gases:  
     hydrogen, inlet pressure: 1.25 kp/cm<sup>2</sup>  
     oxygen, inlet pressure: 1.75 kp/cm<sup>2</sup>  
 Column temperature: 50.0, 70.0, 90.0 and  $110.0 \pm 0.1^\circ$   
 Temperature of evaporator:  $200.0 \pm 1.0^\circ$   
 Recorder: Speedomax G., 2.5 mV/full scale, 1.0 sec  
 Chart speed: 5.08 cm/min

TABLE VI

COMPARISON OF MEASURED AND CALCULATED RETENTION INDICES OF SOME COMPOUNDS AT  $50.0^\circ$  ON SQUALANE STATIONARY PHASE

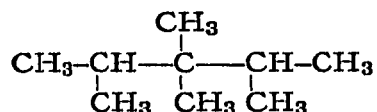
Compound	Retention Index		Deviation (i.u.)
	Measured (i.u.)	Calculated (i.u.)	
2,3-(CH <sub>3</sub> ) <sub>2</sub> C <sub>6</sub>	760.4	760.8	-0.4
2-(CH <sub>3</sub> )C <sub>7</sub>	765.1	764.8	+0.3
4-(CH <sub>3</sub> )C <sub>7</sub>	767.5	767.6	-0.1
3-(CH <sub>3</sub> )C <sub>7</sub>	772.9	773.0	-0.1
2,4-(CH <sub>3</sub> ) <sub>2</sub> C <sub>7</sub>	821.5	822.2	-0.7
2,6-(CH <sub>3</sub> ) <sub>2</sub> C <sub>7</sub>	827.2	827.5	-0.3
4-(CH <sub>3</sub> ) <sub>2</sub> C <sub>7</sub>	827.6	825.8	+1.8
2,5-(CH <sub>3</sub> ) <sub>2</sub> C <sub>7</sub>	832.9	832.9	0.0
3,5-(CH <sub>3</sub> ) <sub>2</sub> C <sub>7</sub>	833.7	833.9	-0.2
4-(C <sub>2</sub> H <sub>5</sub> )C <sub>7</sub>	857.5	861.0	-3.5
3,3-(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> C <sub>6</sub>	877.6	877.6	0.0
2,2,4-(CH <sub>3</sub> ) <sub>3</sub> -3-(C <sub>2</sub> H <sub>5</sub> )C <sub>6</sub>	901.2	899.2	+2.0
2,2,3-(CH <sub>3</sub> ) <sub>3</sub> C <sub>7</sub>	912.7	914.3	-1.6
2,2,3,3,4-(CH <sub>3</sub> ) <sub>5</sub> -C <sub>6</sub>	949.4	949.4	0.0
2,2,3,4,4-(CH <sub>3</sub> ) <sub>5</sub> -C <sub>6</sub>	918.0	918.0	0.0
2-(CH <sub>3</sub> )-C <sub>9</sub>	963.8	963.9	-0.1

The effectivity of the developed method was checked in the case of a number of compounds on a squalane stationary phase. Some of the results are presented in Table VI which also contains data found in the literature<sup>19,37</sup>.

Experiments aimed at the extension of the method developed for saturated hydrocarbons to alicyclic, unsaturated aliphatic and aromatic hydrocarbons and to compounds containing halogen atoms or hydroxyl groups are in progress.

Finally, an example will be presented to demonstrate the applicability of the method in analytical practice. A mixture of unknown composition was studied by GC on a squalane stationary phase at  $50.0^\circ$ . One of the peaks, the retention index of which was found to be 859.0 i.u., was assumed to be due to 2,3,3,4-tetramethyl-

pentane. However, the identification could not be done directly as no standard sample was available. Data similar to the index value measured was found in the literature<sup>10</sup> which had to be checked (858.9 i.u.). For checking the method just described was used. The structural formula of 2,3,3,4-tetramethylpentane is as follows:



The bonds of the compound were coded and the corresponding bond index contributions were taken from Tables I and III. These were:

20	C <sub>0</sub> bonds	20·5.96	119.20 i.u.
4	<sup>14</sup> <sub>0</sub> C <sub>31</sub> bonds	4·11.50	46.00 i.u.
2	<sup>113</sup> <sub>11</sub> C <sub>43</sub> bonds	2·15.00	30.00 i.u.
2	<sup>133</sup> <sub>0</sub> C <sub>41</sub> bonds	2·5.25	10.50 i.u.
			205.70 i.u.

Bond index contribution is 205.70 i.u. Then the atomic index contribution was calculated for C<sub>9</sub>H<sub>20</sub>.

9	C	9·1.21	10.89 i.u.
20	H	20·0.10	2.00 i.u.
			12.89 i.u.

Atomic index contribution is 12.89 i.u. Molecular index contribution is as follows:

$$I_m = 205.70 + 12.89 = 218.59 \text{ i.u.}$$

The interaction index contribution can be calculated using eqn. 4:

$$I_i = 0.15 \cdot 4.97 \cdot 859.0 = 640.38 \text{ i.u.}$$

The calculated index of 2,3,3,4-tetramethylpentane under the given conditions was:

$$I = 218.59 + 640.38 = 858.97 \text{ i.u.}$$

The measured (859.0), calculated (858.97) and literature (858.9) index data were in good agreement, and the unknown peak was due to 2,3,3,4-tetramethylpentane.

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