

CHROM. 7214

## GENERALIZATION OF THE GAS CHROMATOGRAPHIC RETENTION INDEX SYSTEM

J. NOVÁK and J. RŮŽIČKOVÁ

*Institute of Instrumental Analytical Chemistry, Czechoslovak Academy of Sciences, Brno (Czechoslovakia)*

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### SUMMARY

It is possible to express the retention index of a given substance, chromatographed on a given sorbent, in different ways by employing different series of compounds to define the reference retention scale. Thermodynamic analysis of the concept of retention index shows that the conventional Kováts retention index (*n*-paraffin scale) of a substance *i*,  $I_p(i)$ , is  $I_p(i) = 100[n(i) + G(X_i)/G(CH_2)]$ , where  $n(i)$  is the carbon number of the substance and  $G(X_i)$  and  $G(CH_2)$  are the standard molar sorption Gibbs free energies of the functional group  $X_i$  of the substance and of a  $CH_2$  group in the hydrocarbon chain of the substance. The general retention index,  $I_a(i)$ , is  $I_a(i) = 100\{n(i) + [G(X_i) - G(X_a)]/G(CH_2)\}$  where *a* signifies a reference homologous series of compounds with functional group  $X_a$ ,  $G(X_a)$  being the respective sorption Gibbs free energy. The quantities  $I_a(i)$  and  $I_p(i)$  are related to each other by the equation  $I_a(i) = I_p(i) - I_p(a) + 100 n(a)$ , where  $I_p(a)$  is the paraffin-scale retention index of a reference compound of type *a* and  $n(a)$  is its carbon number. The difference  $I_p(i) - I_a(i)$  on a given sorbent is equal to  $I_p(X_a)$ , i.e., it is not a characteristic of the compound *i*. For measurements on different sorbents, differences in retention index on sorbents A and B are given by the equation  $I_a^A(i) - I_a^B(i) = I_p^A(i) - I_p^B(i) - [I_p^A(a) - I_p^B(a)]$ .

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### INTRODUCTION

It is about 15 years since the Kováts retention index system was introduced in gas chromatography<sup>1</sup>, and the experience obtained with this system has shown that it is a most suitable means of expressing chromatographic retention data. It follows from the nature of the retention index system that it can be applied to characterize both the solute substance and the stationary phase. Both modes of application have been dealt with in a number of papers. As the retention index system provides for the efficient elimination of errors due to variations in the experimental conditions, retention indices are the most suitable form of retention data for comparative purposes.

There are instances in which the advantages of the conventional retention index system cannot be utilized to their full extent. In the chromatography of polar

compounds on high-polarity stationary phases, the use of paraffins as reference compounds gives rise to certain difficulties; relatively low solubilities of hydrocarbons in polar liquids and the tendency of the former to be adsorbed on polar liquid surfaces can make the results dubious. In order to remedy this shortcoming, it was suggested recently<sup>2</sup> that a series of polar compounds could be employed instead of *n*-paraffins to determine the retention index scale. In this context, straight-chain primary alcohols<sup>2</sup>, methyl *n*-alkyl ketones<sup>3</sup> and *n*-propyl *n*-alkyl ethers<sup>4</sup> have been suggested. In fact, various reference compounds other than *n*-paraffins have already been used in order to define the respective retention index scales; a number of examples can be found in the literature<sup>5-10</sup>.

The use of reference compounds that are chemically similar to those under analysis can extend the area of applicability of the retention index system and improve significantly the reliability of retention indices measured in systems in which the use of *n*-paraffins as reference compounds is unsuitable. This paper is intended to promote the above approach by showing a general relationship between retention indices based on different retention scales.

#### THERMODYNAMIC INTERPRETATION OF THE CONCEPT OF RETENTION INDEX

##### *Regularities in the retention versus carbon number dependences for homologous series of compounds*

In GLC, the standard molar Gibbs free energy of sorption, referred to the transfer of pure solute between the states of unit fugacity (gaseous phase) and infinite dilution in the sorbent (stationary phase) is given by<sup>11,12</sup>

$$\Delta G_{sp} = RT \ln (RT\rho_s/KM_s) \quad (1)$$

where *R* is the perfect gas constant, *T* is the absolute temperature of the column, *M<sub>s</sub>* and *ρ<sub>s</sub>* are the molecular weight and density of the stationary liquid, respectively, and *K* is the chromatographic partition coefficient defined by

$$K = (V_R - V_m)/V_s \quad (2)$$

where *V<sub>R</sub>* is the overall solute retention volume as measured at the mean pressure and temperature of the column, *V<sub>m</sub>* is the gas hold-up of the column and *V<sub>s</sub>* is the volume of the stationary phase contained in the column, as measured at temperature *T*. For the sake of brevity,  $\Delta G_{sp}$  will henceforth be represented simply by *G*.

The relationship between the constitution of solute compounds and their chromatographic retention can be considered very efficiently by assuming that the sorption Gibbs free energy found for a given solute in a given sorption system is composed additively of the sorption Gibbs free energies of the individual groups constituting the solute molecule. Thus, in view of this assumption, the *G* value of a straight-chain monofunctional compound CH<sub>3</sub>(CH<sub>2</sub>)<sub>*N*</sub>X is given by

$$G = NG(\text{CH}_2) + G(\text{CH}_3) + G(\text{X}) \quad (3)$$

where  $N$  represents the number of methylene groups. The combination of eqns. 1 and 3 gives

$$\ln K = -N \frac{G(\text{CH}_2)}{RT} - \left[ \frac{G(\text{CH}_3)}{RT} + \frac{G(\text{X})}{RT} + \ln \frac{M_s}{RT\varrho_s} \right] \quad (4)$$

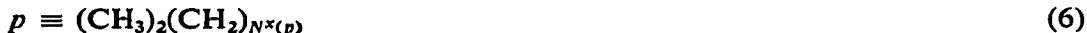
Actually, this is analogous to Martin's approach<sup>13</sup>, which was used in order to derive the rule of additivity of  $\Delta R_M$  values.

When considering a homologous series of compounds, the only variable in eqn. 4 is  $N$ , so that a plot of  $\ln K$  versus  $N$  is a straight line with a slope equal to  $-G(\text{CH}_2)/RT$ . The actual  $G(\text{CH}_2)$  values are almost always negative in GC systems, resulting in positive slopes for the  $\ln K$  versus  $N$  plots. It is commonly found that if the above plots are constructed for different homologous series, employing the same stationary phase at a given temperature, the resulting lines are virtually parallel. This result is an indication that the  $G(\text{CH}_2)$  contributions are more or less independent of the kind of functional group present. Actually, this favourable property of  $G(\text{CH}_2)$  is one of the main factors that constitute the universality of the retention index system, especially as regards the correlations between retention indices based on different reference scales, discussed below.

In practice, the logarithm of retention is plotted against total carbon number ( $n$ ) rather than against the number of methylene groups. However, as the values of  $G(\text{CH}_3)$  and  $G(\text{CH}_2)$  are not exactly the same, the intercept of the line obtained from the points for higher homologues and extrapolated to  $n = 0$  does not correspond accurately to  $- \{ [G(\text{X})/2.303 RT] + \log (M_s/RT\varrho_s) \}$ . A more exact procedure appears to be to plot the logarithm of retention against the number of methylene groups,  $N$ , which gives an intercept defined by  $- \{ [G(\text{CH}_3)/2.303 RT] + [G(\text{X})/2.303 RT] + \log (M_s/RT\varrho_s) \}$  upon extrapolation to  $N = 0$ .

It is frequently observed that the first and sometimes also the second member of a homologous series do not fit the line determined by the higher homologues. This effect is probably due to the fact that the properties of the methyl and/or methylene groups situated in the close vicinity of the functional group are altered by the latter.

*Conventional retention index.* The Kováts retention index is actually a hundred multiple of the number of carbon atoms ( $100 n^*$ ) of an  $n$ -paraffin that has the same retention as the compound in question. Let the compound and the  $n$ -paraffin ( $i$  and  $p$ , respectively) have the following structures:



The  $N^*(p)$  and the corresponding  $n^*(p)$  values can obviously be represented by real numbers, *i.e.*, paraffin  $p$  is generally a hypothetical compound. In the context of the above-mentioned definition of the Kováts retention index, the equation  $K(i) = K(p)$  holds, provided that both components are chromatographed on the same stationary phase under identical conditions, which implies that also

$$G(i) = G(p) \quad (7)$$

By again applying the assumption of the additivity of the partial  $G$  values, eqn. 3 is obtained for component  $i$  and

$$G(p) = 2G(\text{CH}_3) + N^x(p)G(\text{CH}_2) \quad (8)$$

is obtained for component  $p$ . Hence, with respect to eqn. 7, we can write

$$N^x(p) = N(i) - \frac{G(\text{CH}_3)}{G(\text{CH}_2)} + \frac{G(X_i)}{G(\text{CH}_2)} \quad (9)$$

The Kováts retention index has been defined in terms of carbon number rather than the number of methylene groups. As  $N(i) = n(i) - 1$  and  $N^x(p) = n^x(p) - 2$ , eqn. 9 can be rewritten as

$$n^x(p) = n(i) + 1 - \frac{G(\text{CH}_3)}{G(\text{CH}_2)} + \frac{G(X_i)}{G(\text{CH}_2)} \quad (10)$$

where  $n(i)$  and  $n^x(p)$  represent the carbon numbers of compound  $i$  and of the reference (hypothetical) paraffin, respectively. When supposing that  $G(\text{CH}_3)$  and  $G(\text{CH}_2)$  are approximately equal, we can eventually write for the Kováts retention index of substance  $i$ ,  $I_p(i)$ , the equation

$$I_p(i) = 100 \{n(i) + [G(X_i)/G(\text{CH}_2)]\} \quad (11)$$

where the subscript  $p$  indicates that the retention index is referred to an  $n$ -paraffin scale. The effect of this approximation is obviously less the higher is the carbon number,  $n(i)$ . Eqn. 11 is well suited to illustrate the thermodynamic meaning of the so-called homomorphy factor<sup>14</sup>,  $H$ , which is defined as follows:

$$H(i) = I_p(i) - 100 n(i) = 100 G(X_i)/G(\text{CH}_2) \quad (12)$$

Eqn. 4 reveals that  $G(\text{CH}_2)$  is given simply by

$$G(\text{CH}_2) = -RT \ln [K(i_{n+1})/K(i_n)] \quad (13)$$

where  $i_{n+1}$  and  $i_n$  denote two successive homologues of the given series. Hence  $G(X_i)$  can be written as

$$G(X_i) = -RT \left[ \frac{I_p(i)}{100} - n(i) \right] \ln \frac{K(i_{n+1})}{K(i_n)} \quad (14)$$

**General retention index.** Consider two species of straight-chain monofunctional compounds,  $a$  and  $b$ , which are to be used as reference substances for defining two different retention scales, specified as follows:

$$a \equiv \text{CH}_3(\text{CH}_2)_{N^x(a)}X_a \quad (15)$$

$$b \equiv \text{CH}_3(\text{CH}_2)_{N^x(b)}X_b \quad (16)$$

the analyzed substance being

$$i \equiv \text{CH}_3(\text{CH}_2)_{N(i)}\text{X}_i \quad (17)$$

In an analogous manner to the situation expressed by eqn. 7, the two kinds of retention index of substance  $i$  are determined by the equalities

$$G(i) = G(a) = G(b) \quad (18)$$

When again employing the above additivity rule for the  $G$  values, we can write

$$N^*(a) = N(i) + \frac{G(\text{X}_i)}{G(\text{CH}_2)} - \frac{G(\text{X}_a)}{G(\text{CH}_2)} \quad (19)$$

and

$$N^*(b) = N(i) + \frac{G(\text{X}_i)}{G(\text{CH}_2)} - \frac{G(\text{X}_b)}{G(\text{CH}_2)} \quad (20)$$

Now, consider the retention of a particular substance of type  $b$  referred to the retention scale determined by compounds of type  $a$ . In this case

$$b \equiv \text{CH}_3(\text{CH}_2)_{N(b)}\text{X}_b \quad (21)$$

$$a \equiv \text{CH}_3(\text{CH}_2)_{N^{**}(a)}\text{X}_a \quad (22)$$

The symbol  $N(b)$  in eqn. 21 has no superscript  $x$  in order to signify that  $N(b)$  values are represented by integers, whereas the two superscripts in  $N^{**}(a)$  are to stress that the latter is generally different from  $N^*(a)$ . By using exactly the same procedure as that leading to eqns. 19 and 20, we obtain

$$N^{**}(a) = N(b) + \frac{G(\text{X}_b)}{G(\text{CH}_2)} - \frac{G(\text{X}_a)}{G(\text{CH}_2)} \quad (23)$$

Subtraction of eqn. 20 from eqn. 19 and substitution for  $[G(\text{X}_b) - G(\text{X}_a)]/G(\text{CH}_2)$  from eqn. 23 gives

$$N^*(b) = N^*(a) - N^{**}(a) + N(b) \quad (24)$$

As all of the above numbers of methylene groups are less by one unit than the respective carbon numbers, eqn. 24 can be rewritten in terms of the carbon number:

$$n^*(b) = n^*(a) - n^{**}(a) + n(b) \quad (25)$$

Further, as  $100 n^*(b) = I_b(i)$ ,  $100 n^*(a) = I_a(i)$  and  $100 n^{**}(a) = I_a(b)$ , where  $I_b(i)$  and  $I_a(i)$  are the retention indices of substance  $i$  referred to the scales of compounds  $b$  and  $a$ , respectively, and  $I_a(b)$  is the retention index of a substance  $b$  with carbon number  $n(b)$ , referred to the scale of series  $b$ , eqn. 25 can be rewritten as

$$I_b(i) = I_a(i) - I_a(b) + 100 n(b) \quad (26)$$

Eqn. 26 shows that retention indices based on different reference scales can easily be interconverted; it is necessary only to know the retention index, referred to the original scale, and the carbon number of a compound pertaining to the series determining the new scale.

#### RELATIONSHIP BETWEEN THE FORMAL EXPRESSIONS OF DIFFERENT KINDS OF RETENTION INDEX

Eqn. 26 can also be derived by a treatment based on the conventional formal expressions of the retention index. One can write for the retention indices of a substance  $i$ , expressed with respect to the reference scales defined by series of compounds of types  $a$  and  $b$ , the equations

$$I_a(i) = 100 n(a) + \alpha \cdot 100 \left[ \frac{\log r(i) - \log r(a_n)}{\log r(a_{n+\alpha}) - \log r(a_n)} \right] \quad (27)$$

and

$$I_b(i) = 100 n(b) + \beta \cdot 100 \left[ \frac{\log r(i) - \log r(b_n)}{\log r(b_{n+\beta}) - \log r(b_n)} \right] \quad (28)$$

where  $n$  is the carbon number,  $\alpha$  and  $\beta$  are the differences in the carbon numbers of the higher and the lower reference homologues of types  $a$  and  $b$ , respectively, and  $r$  represents a retention quantity corrected for the column gas hold-up. Analogously, the retention indices of homologues  $b_n$  and  $b_{n+\beta}$  referred to the scale formed by compounds of type  $a$  are

$$I_a(b_n) = 100 n(a) + \alpha \cdot 100 \left[ \frac{\log r(b_n) - \log r(a_n)}{\log r(a_{n+\alpha}) - \log r(a_n)} \right] \quad (29)$$

and

$$I_a(b_{n+\beta}) = 100 n(a) + \alpha \cdot 100 \left[ \frac{\log r(b_{n+\beta}) - \log r(a_n)}{\log r(a_{n+\alpha}) - \log r(a_n)} \right] \quad (30)$$

By subtracting eqn. 29 from eqns. 27 and 30 and dividing the first difference by the second, we obtain

$$\frac{I_a(i) - I_a(b_n)}{I_a(b_{n+\beta}) - I_a(b_n)} = \frac{\log r(i) - \log r(b_n)}{\log r(b_{n+\beta}) - \log r(b_n)} \quad (31)$$

With regard to the formal definition of the retention index, the right-hand side of eqn. 31 is equal to  $[I_b(i) - 100 n(b)]/100\beta$ , so that

$$I_b(i) = 100 n(b) + \beta \cdot 100 \left[ \frac{I_a(i) - I_a(b_n)}{I_a(b_{n+\beta}) - I_a(b_n)} \right] \quad (32)$$

Finally, the value of the difference  $I_a(b_{n+\beta}) - I_a(b_n)$  is very close to that of  $100\beta$ , the substitution of which into eqn. 32 yields eqn. 26. Eqn. 32 has the same meaning as that quoted by Castello and D'Amato<sup>15</sup>, the difference being only in that a factor of 100 is absent from the second term of the right-hand side of Castello and D'Amato's equation.

*Different kinds of retention index on a single stationary phase*

It may seem at first sight that the differences in the retention indices of a given substance determined on a single stationary phase with the use of several different kinds of reference substance can be utilized for identification of substances, but the following treatment shows that this is not so. Because of the parallelism of the plots of  $\log r$  versus  $n$  for different homologous series, it is possible to write

$$I_a(i) = I_a(X_i) + 100 n(i) \quad (33)$$

$$I_b(i) = I_b(X_i) + 100 n(i) \quad (34)$$

and

$$I_a(i) - I_b(i) = I_a(X_i) - I_b(X_i) \quad (35)$$

However, according to eqn. 26,

$$I_a(i) - I_b(i) = I_a(b_n) - 100 n(b) \quad (36)$$

where  $I_a(b_n)$  is given by

$$I_a(b_n) = I_a(X_b) + 100 n(b) \quad (37)$$

so that

$$I_a(i) - I_b(i) = I_a(X_b) \quad (38)$$

This simple relationship reveals that the difference discussed does not characterize the substance  $i$ , but rather is a characteristic of the reference compounds of type  $b$ . Namely, no parameter referring to substance  $i$  occurs on the right-hand side of eqn. 38.

*Different kinds of retention index on different stationary phases*

Let us consider the retention indices of substance  $i$  on the  $a$  and  $b$  scales on two stationary phases, A and B. The following equations hold (*cf.* eqns. 33–35)

$$\hat{I}_a^A(i) - \hat{I}_a^B(i) = \hat{I}_a^A(X_i) - \hat{I}_a^B(X_i) \quad (39)$$

and

$$\hat{I}_b^A(i) - \hat{I}_b^B(i) = \hat{I}_b^A(X_i) - \hat{I}_b^B(X_i) \quad (40)$$

However, eqn. 26 shows that it is possible to write

$$\hat{I}_b^A(i) = 100 n(b) + \hat{I}_a^A(X_i) - \hat{I}_a^A(X_b) \quad (41)$$

and

$$\hat{I}_b^B(i) = 100 n(b) + \hat{I}_a^B(X_i) - \hat{I}_a^B(X_b) \quad (42)$$

which give, on combination with eqns. 39 and 40, the equation

$$\hat{I}_b^A(i) - I_b^B(i) = \hat{I}_a^A(i) - I_a^B(i) - [\hat{I}_a^A(b) - I_a^B(b)] \quad (43)$$

Hence, the differences in the retention indices of a given compound on two stationary phases, expressed with respect to a given scale, can easily be converted into that referred to another scale. In order to do so, it is necessary simply to know the respective difference in the retention indices, based on the original scale, of a homologue of the series used to determine the new scale.

### EXAMPLES

In order to prove the applicability of the above relationships, specific retention volumes and Kováts retention indices of a group of compounds were selected from the literature<sup>16</sup> and processed according to eqns. 26–28, 38 and 43. The results are summarized in Tables I–V. All the data refer to Apiezon J (AP) and Carbowax 1540 (CW) stationary phases at a temperature of 120°.

TABLE I

ALCOHOL-, KETONE- AND ACETATE-SCALE RETENTION INDICES [ $I_{a1}(i)$ ,  $I_{ke}(i)$  AND  $I_{ac}(i)$ ] OF A GROUP OF COMPOUNDS ON APIEZON J AT 120°

Also comparison of direct paraffin-scale retention indices [ $I_p(i)$ ] with those calculated by eqn. 26 from  $I_{a1}(i)$ ,  $I_{ke}(i)$  and  $I_{ac}(i)$  [ $I_p^*(i)$ ,  $I_p^{**}(i)$  and  $I_p^{***}(i)$ , respectively].

Solute ( <i>i</i> )	$V_g$ (ml/g)	$I_p(i)$	$I_{a1}(i)$	$I_{ke}(i)$	$I_{ac}(i)$	$I_p^*(i)$	$I_p^{**}(i)$	$I_p^{***}(i)$
Hexane	14.0	600	375	243	245			
Octane	55.0	800	560	440	440			
1-Hexanol	73.1	841	600	480	480	840	840	841
2-Hexanone	41.3	758	520	400	395	760	760	755
Pentyl formate	50.9	788	550	430	430	790	790	790
Butyl acetate	42.5	762	525	403	400	765	763	760

TABLE II

DATA AS IN TABLE I, BUT ON CARBOWAX 1540 AT 120°

Solute ( <i>i</i> )	$V_g$ (ml/g)	$I_p(i)$	$I_{a1}(i)$	$I_{ke}(i)$	$I_{ac}(i)$	$I_p^*(i)$	$I_p^{**}(i)$	$I_p^{***}(i)$
Hexane	2.9	600	-125	-160	-115			
Decane	28.2	1000	270	290	315			
Dodecane	81.0	1200	450	495	515			
1-Hexanol	185	1361	600	655	675	1365	1365	1365
2-Hexanone	48.5	1102	365	400	415	1095	1105	1100
Pentyl formate	58.1	1137	395	435	450	1145	1140	1135
Butyl acetate	44.4	1086	350	380	400	1080	1090	1085



In Tables I and II, the  $V_g$  and  $I_p(i)$  (specific retention volumes and paraffin-scale retention indices) are literature data, whereas  $I_{a1}(i)$ ,  $I_{kc}(i)$ , and  $I_{ac}(i)$  (alcohol-, ketone- and acetate-scale retention indices) were calculated from the literature  $V_g$  data by eqn. 26, always employing those two homologues of the given reference series which bracketed the given compound  $i$ . The carbon number refers to the hydrocarbon chain supposed to be subject to  $\text{CH}_2$  incremental changes, in accordance with the specifications expressed by eqns. 5, 15 and 16.  $I_p^*(i)$ ,  $I_p^{**}(i)$ , and  $I_p^{***}(i)$  are the paraffin-scale retention indices calculated from  $I_{a1}(i)$ ,  $I_{kc}(i)$ , and  $I_{ac}(i)$ , respectively, by eqn. 26, always employing the  $I_a(b)$  and  $n(b)$  values of the homologue that eluted most closely to the substance  $i$ . The agreement with the original  $I_p(i)$  values is apparent.

The data in Table III show the effect of the choice of the new-reference-scale homologue in calculations by eqn. 26. It is evident that the calculated  $I_b(i)$  values are virtually independent of the choice of  $I_a(b)$  and  $n(b)$ , except for the first members of the homologous series.

TABLE III

ACETATE-SCALE RETENTION INDICES OF A GROUP OF COMPOUNDS ON APIEZON J AT 120°, CALCULATED FROM PARAFFIN-SCALE RETENTION INDICES BY EQN. 26 WHILE EMPLOYING DIFFERENT HOMOLOGUES OF THE REFERENCE ACETATE

Reference acetate	$I_{ac}(i)$				
	Hexane	1-Hexanol	2-Hexanone	Pentyl formate	Butyl acetate
Methyl	224	465	382	512	386
Ethyl	242	483	400	530	404
Propyl	243	484	401	531	405
Butyl	238	479	396	526	400
Pentyl	238	479	396	526	400
Hexyl	238	479	396	526	400
Heptyl	237	478	395	525	400

Table IV demonstrates that the difference  $I_a(i) - I_b(i)$  is not a characteristic of the substance  $i$ .

TABLE IV

DIFFERENCES BETWEEN DIFFERENT KINDS OF RETENTION INDEX OF A GIVEN COMPOUND ON A GIVEN STATIONARY PHASE

Solute ( $i$ )	$I_{ac}(i) - I_{a1}(i)$		$I_p(i) - I_{a1}(i)$	
	AP	CW	AP	CW
Hexane	70	210	225	725
1-Hexanol	80	275	241	761
2-Hexanone	75	250	238	737
Pentyl formate	80	255	238	742
Butyl acetate	75	250	237	736

TABLE V

DIFFERENCES BETWEEN THE SAME KINDS OF RETENTION INDEX OF A GIVEN COMPOUND ON DIFFERENT STATIONARY PHASES

$$I_p^{CW}(\text{butyl acetate}) - I_p^{AP}(\text{butyl acetate}) = 324.$$

Solute (i)	$I_p^{CW}(i) - I_p^{AP}(i)$	$I_{ac}^{CW}(i) - I_{ac}^{AP}(i)$
1-Methanol	545	260
1-Ethanol	515	225
1-Propanol	511	195
1-Butanol	514	180
1-Pentanol	518	185
1-Hexanol	520	195
1-Heptanol	523	195
1-Octanol	530	—
Acetone	382	65
2-Butanone	364	35
2-Pentanone	345	15
2-Hexanone	344	20
2-Heptanone	343	20
2-Octanone	349	20
2-Nonanone	345	18
Methyl formate	384	90
Ethyl formate	364	50
Propyl formate	353	20
Butyl formate	—	—
Pentyl formate	349	20
Hexyl formate	344	25

Finally, the data in Table V represent a verification of eqn. 43; the applicability of the latter can be checked with the use of the paraffin-scale retention index difference of butyl acetate on Carbowax and Apiezon [ $I_a^A(b) - I_a^B(b)$ ]. Some deviations are again shown by the first and second members of the homologous series.

## REFERENCES

- 1 E. Kováts, *Helv. Chim. Acta*, 41 (1958) 1915.
- 2 A. Gröbler, *J. Chromatogr. Sci.*, 10 (1972) 128.
- 3 R. G. Ackman, *J. Chromatogr. Sci.*, 10 (1972) 535.
- 4 S. J. Hawkes, *J. Chromatogr. Sci.*, 10 (1972) 536.
- 5 T. K. Miwa, K. L. Mikolajczak, F. R. Earle and I. A. Wolff, *Anal. Chem.*, 32 (1960) 1739.
- 6 F. P. Woodford and C. M. van Gent, *J. Lipid Res.*, 1 (1960) 188.
- 7 R. G. Ackman, *J. Amer. Oil Chem. Soc.*, 40 (1963) 558.
- 8 W. J. A. Vandenhoevel and E. C. Horning, *Biochim. Biophys. Acta*, 64 (1962) 416.
- 9 F. H. Dymond and K. D. Kilburn, in A. B. Littlewood (Editor), *Gas Chromatography 1966*, Institute of Petroleum, London, 1967, p. 353.
- 10 G. Castello, G. D'Amato and E. Biagini, *J. Chromatogr.*, 41 (1969) 313.
- 11 D. A. Leathard and B. C. Shurlock, *Identification Techniques in Gas Chromatography*, Wiley, New York, London, 1970, p. 8.
- 12 J. Novák, J. Růžičková, S. Wičar and J. Janák, *Anal. Chem.*, 45 (1973) 1365.
- 13 A. J. P. Martin, *Biochem. Soc. Symp.*, 3 (1949) 4.
- 14 P. A. T. Swoboda, in C. M. van Swaay (Editor), *Gas Chromatography 1962*, Butterworths, London, 1962, p. 273.
- 15 G. Castello and G. D'Amato, *J. Chromatogr.*, 79 (1973) 33.
- 16 W. O. Reynolds, *Gas Chromatographic Retention Data*, Preston Technical Abstracts Company, Evanston, Ill., 1966.