

## CONSIDERATIONS ON THE RETENTION INDEX CONCEPT

## II. RETENTION INDICES AND RELATIVE RETENTION

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In our previous paper<sup>1</sup>, the retention index of a single component at different temperatures was considered. In the present discussion, the relationship between the difference of retention indices of two adjacent peaks and their relative retention ( $\alpha$ )\* is investigated. It should be mentioned that STRICKLER AND KOVÁTS<sup>2</sup> already gave a generalized treatment for relating the difference of the retention indices of two adjacent peaks to resolution, plate number, and other fundamental parameters where the evaluation is carried out by using multiple graphs. We feel that the present simplified treatment can be utilized easier in practice.

If two adjacent peaks are characterized—in order of their elution—by subscripts  $m$  and  $n$ , and we assume that both fall within the two respective normal paraffins having  $z+1$  and  $z$  carbon atoms, the retention indices of the two peaks can be expressed in the following way:

$$I_n = 100 \frac{\log t_{R'(n)} - \log t_{R'(C_z)}}{\log r_{C_{z+1}/C_z}} + 100z \quad (1a)$$

$$I_m = 100 \frac{\log t_{R'(m)} - \log t_{R'(C_z)}}{\log r_{C_{z+1}/C_z}} + 100z \quad (1b)$$

where by definition:

$$t_{R'(C_{z+1})} > t_{R'(n)} > t_{R'(m)} > t_{R'(C_z)} \quad (2)$$

Subtracting eqn. 1a from eqn. 1b:

$$I_n - I_m = 100 \frac{\log t_{R'(n)} - \log t_{R'(m)}}{\log r_{C_{z+1}/C_z}} \quad (3)$$

Since the symbol  $\Delta I$  is already characterized as the difference of the retention indices of a *single* component on *two* liquid phases (and at the same temperature), we propose to use the symbol  $i$  in order to express the difference of the retention indices of *two* components on *one* liquid phase (and at the same temperature)\*\*.

\* The relative retention of two adjacent peaks is generally characterized by the symbol  $\alpha$ , while for retention values given relative to one standard, the symbol  $r$  is used. This is the reason why we are using here the symbol  $\alpha$  while in the general equation of the retention index (standard: the normal paraffin with  $z$  carbon atoms), the relative retention is defined by the symbol  $r$ .

\*\* STRICKLER AND KOVÁTS have been using the symbol  $\delta I$  for this expression. However, in most papers, the symbol  $\delta I$  is applied to express the increment in the retention index of one substance for 10° (or other specified temperature range) change. In order to avoid any confusion, we rather suggest this new symbol.

The numerator of the fraction of eqn. 3 can be written as  $\log (t_{R'}^{(n)}/t_{R'}^{(m)})$ . On the other hand,  $t_{R'}^{(n)}/t_{R'}^{(m)}$  is the relative retention of the two adjacent peaks. Therefore, eqn. 3 may be written in the following way:

$$i = 100 \frac{\log \alpha_{n/m}}{\log r_{C_{z+1}/C_z}} \quad (4)$$

For given temperature and liquid phase,  $r_{C_{z+1}/C_z}$  is constant and independent of  $z$ . Thus, the difference of the retention indices of two adjacent peaks is directly related to the logarithm of the relative retention of the two peaks:

$$i = \text{const.} \times \log \alpha_{n/m} \quad (5)$$

The relationship described by eqn. 5 has important implications. Since it is easy to determine the relative retention of two consecutive paraffins at any temperature (the values are listed in Table I for squalane) one can calculate from the difference of the two retention indices the relative retention of the two adjacent peaks to be separated.

A further advantage of this relationship is that at low values of relative retention (which is the range of difficult chromatographic separations),  $i$  is a very sensitive measure of changes in the value of  $\alpha$ . The reason for this is the known mathematical rule that for small values of  $p$ ,  $\log (1+p) \propto p$ . This means that e.g. a change from 1.05 to 1.10 in the value of  $\alpha$  will result in a 100% change in the value of  $i$ . This will be demonstrated below, in Fig. 1.

Since in practice, retention index values are always rounded off to the nearest whole number, calculation from  $i$  will give only approximate values. However, they are fairly close to the actual values and since such calculations are only used to establish the proper analytical conditions, the resulting slight discrepancies have no serious effect.

The relationship between  $i$  and  $\alpha$  also permits further calculations.

According to DESTY *et al.*<sup>3</sup>, the number of effective plates ( $N$ ) is calculated from the adjusted retention time ( $t_{R'}$ ) and the peak width at base ( $w_b$ ) or the peak width at half height ( $w_h$ ):

$$N = 16 \left( \frac{t_{R'}}{w_b} \right)^2 = 5.54 \left( \frac{t_{R'}}{w_h} \right)^2 \quad (6)$$

The effective plate number is identical to the separation factor of PURNELL<sup>4</sup> and is related to the relative retention ( $\alpha$ ) and resolution ( $R$ ) according to eqn. 7:

$$N = 16R^2 \left( \frac{\alpha}{\alpha - 1} \right)^2 \quad (7)$$

With a given value of  $\alpha$ , eqn. 7 permits the calculation of the number of effective plates necessary ( $N_{ne}$ ) to achieve a desired resolution.

Expressing  $\alpha$  from eqn. 7 and substituting it into eqn. 5, we obtain:

$$i = \text{const.} \times \log \frac{\sqrt{N_{ne}}}{\sqrt{N_{ne}} - 4R} \quad (8)$$

Thus, the difference in the retention indices is related to the desired resolution and the effective plate number necessary to obtain that resolution.

In addition, the known relationships of the effective plate number to the number of theoretical plates, HETP and column length permit the calculation of these values starting from the difference of the retention indices.

One further remark is necessary in this treatise. In the previous paper<sup>1</sup>, we demonstrated the use of retention index *vs.* temperature plots. For parallel or intersecting plots of *I vs. T* for two substances, it is possible to select two temperatures ( $T_2 > T_1$ ) where  $i_{T_1} = i_{T_2}$ . In these two cases, the number of effective plates necessary to achieve a desired resolution will be the same. One should, however, realize that at the higher temperature, the partition ratio (*k*) for the substances will be smaller than at the lower temperature. Thus, while the same number of effective plates are needed at either temperature for the same resolution, more theoretical plates (*i.e.* a longer column) will be needed at the higher temperature. This is due to the known relationship between the number of effective (*N*) and theoretical (*n*) plates, the value of HETP (*h*) and the column length (*L*):

$$n = \frac{L}{h} = N \left( \frac{k+1}{k} \right)^2 \quad (9)$$

#### EXAMPLES

For the illustration of the relationship of the difference in the retention indices (*i*) with the relative retention of two adjacent peaks ( $\alpha$ ) and other values, we are using the data reported in the previous paper<sup>1</sup>.

#### *Relationship between i and $\alpha$*

In the previous paper<sup>1</sup>, the relative retention values of two consecutive *n*-paraffins on squalane as liquid phase at different temperatures were listed and their logarithm plotted against temperature. Table I repeats these values at seven temperatures.

In Fig. 1A values for  $\log \alpha$  at 40, 60, 80 and 100°, calculated from eqn. 4, are plotted against *i*. In Fig. 1B we have plotted the values of *i* against the corresponding value of  $\alpha$ . It can be seen, that the latter plots have only a very slight curvature. Actually, each plot could be approximated by taking three points ( $\alpha = 1.00$ ,  $\alpha = 1.05$  and  $\alpha = 1.20$ ) and connecting them with a straight line. In Fig. 1B, this approximated plot is shown for 40° with a broken line.

TABLE I

RELATIVE RETENTION OF TWO CONSECUTIVE *n*-PARAFFINS AT DIFFERENT TEMPERATURES, ON SQUALANE LIQUID PHASE

Temperature	Relative retention	
	$r_{C_{z+1}/C_z}$	$\log r_{C_{z+1}/C_z}$
40	2.812	0.449
45	2.745	0.438
60	2.524	0.402
74	2.371	0.375
80	2.302	0.362
90	2.210	0.345
100	2.133	0.329

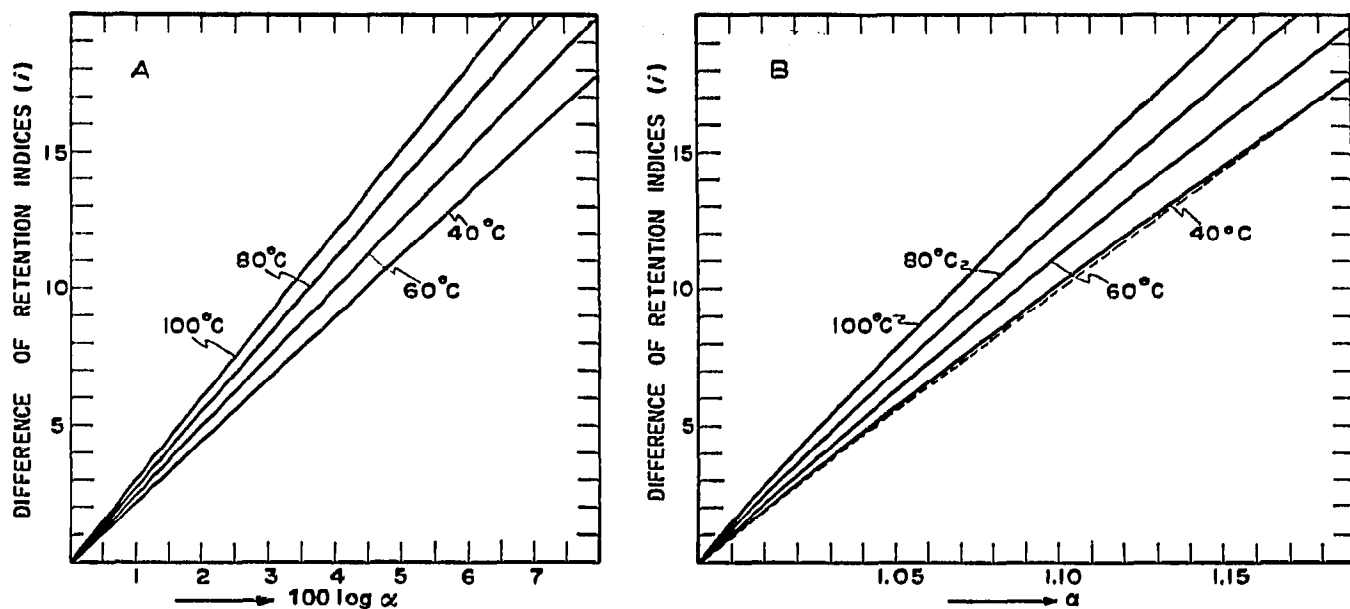


Fig. 1. (A-B). The relationship between the difference ( $i$ ) in the retention indices of two adjacent peaks and their relative retention ( $\alpha$ ), on squalane liquid phase, at four temperatures.

#### Utilization of $i$ for further calculations

The utilization of  $i$  for further calculations is demonstrated by the following case. We would like to separate 2,5-dimethylhexane (2,5-DMHx) and 2,4-dimethylhexane (2,4-DMHx) on a particular squalane column, at 45°. We know that our column has an HETP of 0.77 mm and a partition ratio ( $k$ ) of 9.42 for 2,4-DMHx. There are two questions: (a) how long need the column be in order to obtain base line resolution ( $R = 1.5$ ) between the two peaks; and (b) what kind of resolution do we obtain from a 150 ft. column?

The retention indices of the two substances are read from the graph shown in the previous article<sup>1</sup>. According to this, the respective values for 2,5-DMHx and 2,4-DMHx are 729 and 732.5; thus,  $i = 3.5$ . As given in Table I, the relative retention of two consecutive  $n$ -paraffins at 45° is 2.745. Thus:

$$\log \alpha = \frac{3.5 \times \log 2.745}{100} = 0.01314$$

and  $\alpha = 1.036$ .

From eqn. 7, we can calculate the number of effective plates necessary for  $\alpha = 1.036$  and  $R = 1.5$ . It results in 29,820 effective plates.

The correlation between the number of effective plates ( $N$ ) and theoretical plates ( $n$ ) was described in eqn. 9. In our case,  $k = 9.42$ ; therefore  $n = 36,470$ . Having an HETP of 0.77 mm, this corresponds to a column length of 28.1 meter (92.1 ft.).

Combination of eqns. 7 and 9 results in the following equation for resolution:

$$R = \left( \frac{\alpha - 1}{\alpha} \right) \left( \frac{k}{k + 1} \right) \frac{\sqrt{n}}{4} \quad (10)$$

If HETP = 0.77 mm, a 150 ft. (45.72 m) long column will have a total of 59,380 theoretical plates. Substituting  $\alpha = 1.036$ ,  $k = 9.42$ , and  $n = 59,380$  into eqn. 10, we obtain that  $R = 1.91$ .

The correctness of this calculation can be checked by evaluating an actual chromatogram obtained at 45°, on a support-coated open tubular column prepared with a squalane liquid phase. Such a chromatogram is shown in Fig. 2\*. Table II summarizes the values for the 2,5-DMHx and 2,4-DMHx peaks. As seen, we actually observed a relative retention of  $\alpha = 1.034$  and obtained a resolution of  $R = 1.84$ , while the previously calculated values were  $\alpha = 1.036$  and  $R = 1.91$ . This agreement is very good.

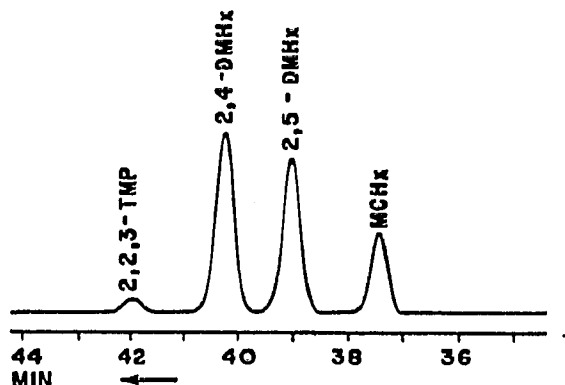


Fig. 2. Chromatogram of a mixture of methylcyclohexane (MCHx), 2,5-dimethylhexane (2,5-DMHx), 2,4-dimethylhexane (2,4-DMHx) and 2,2,3-trimethylpentane (2,2,3-TMP), at 45°C. Column: 150 ft.  $\times$  0.020 in. I.D. support-coated open tubular with squalane liquid phase ( $\beta = 70$ ). Carrier gas (He) average velocity: 19.75 cm/sec.

TABLE II  
DATA FOR THE CHROMATOGRAM SHOWN IN FIG. 2

	2,5-DMHx	2,4-DMHx
Retention time ( $t_R$ ), sec	2 340.5	2 412.7
Adjusted retention time ( $t_R'$ ), sec	2 109.0	2 181.3
Partition ratio ( $k$ )	9.11	9.42
Retention index ( $I$ ), calculated	729	732
Peak width at base ( $w_b$ ), sec	38.7	39.7
Relative retention ( $\alpha$ )		1.034
Number of theoretical plates ( $n$ )	58 525	59 090
Number of effective plates ( $N$ )	47 525	48 295
HETP, mm	0.78	0.77
Peak resolution ( $R$ )		1.84

#### SUMMARY

The difference in the retention index values of two adjacent peaks can be related to the relative retention of those two peaks. This new expression permits the calculation of certain column parameters necessary to obtain a certain resolution of the two peaks.

#### REFERENCES

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- 3 D. H. DESTY, A. GOLDUP AND W. T. SWANTON, in N. BRENNER, J. E. CALLEN AND M. D. WEISS (Editors), *Gas Chromatography*, Academic Press, New York, 1962, pp. 105-135.
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\* This chromatogram is identical to Fig. 7 (a) of the previous article<sup>1</sup>.