

CONSIDERATIONS ON THE RETENTION INDEX CONCEPT

I. RETENTION INDEX AND COLUMN TEMPERATURE

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In the last few years, the retention index concept of Kováts¹⁻³ has been more and more in use. A fairly large number of papers have appeared on this subject in the various scientific journals and review papers^{4,5} have summarized the most important information. In addition, an increasing number of retention index data are being published, the most notable being the compilation of the Data Subcommittee of the English Gas Chromatography Discussion Group⁶ and REYNOLDS' book⁷.

Most of the publications on this subject have dealt with the utilization of the retention index concept for the identification of unknown components, and the correlation between molecular structure and the index value.

The purpose of the present paper is different. Our aim is to investigate the temperature dependency of the retention index and the utilization of index *vs.* temperature plots for the evaluation of the proper column temperature when analyzing multicomponent samples. In essence, we are discussing in more detail and in more general terms some observations already mentioned, to some extent, by other authors, *e.g.* CHOVIN AND LEBBE⁸, BLAUSTEIN *et al.*⁹ and BRICTEUX AND DUYCKAERTS¹⁰.

Our examples mainly concern hydrocarbons as sample components and squalane as the liquid phase. The basic reason for this is that we were unable to find any published data on liquid phases other than squalane on which we could rely. The values of the Data Subcommittee⁶ for squalane show a remarkable accuracy. Unfortunately, their data on polar liquid phases are less accurate and since only values at three temperatures are given, we could not properly evaluate the randomness of the data. However, theoretically, we see no reason why our treatment could not be extended to polar samples and to liquid phases other than squalane.

GENERAL DISCUSSION

The retention index concept expresses the retention characteristics of a substance in a uniform scale determined by the retention of the normal paraffins. It is known that the logarithm of the net (or adjusted) retention volumes (or times) of members of a homologous series are generally proportional to the number of carbon atoms in the molecule. The retention index concept is utilizing this plot for normal paraffins and the retention index value of a substance is simply the number of carbon atoms (conveniently multiplied by 100) of a hypothetical normal paraffin which would have identical retention characteristics.

Mathematically, the retention index (I) can be expressed by the following equation:

$$I = 100 \frac{\log X_n - \log X_{C_z}}{\log X_{C_{z+1}} - \log X_{C_z}} + 100z \quad (1)$$

where X is the net retention volume (V_N), the adjusted retention volume (V_R') or time (t_R'): C_z and C_{z+1} refer to normal paraffins with z and $z + 1$ carbon numbers respectively and n refers to the substance of interest.

Equation 1 can be modified in the following way:

$$I = 100 \frac{\log r_{n/C_z}}{\log r_{C_{z+1}/C_z}} + 100z \quad (2)$$

where r_{n/C_z} and r_{C_{z+1}/C_z} are the respective relative retentions of substance n and a normal paraffin with $z + 1$ carbon atoms, utilizing a normal paraffin with z carbon atoms as the reference substance.

Let us now consider the influence of column temperature on the value of the retention index.

It is known⁸ that the relative retention of two peaks is related to column temperature (T , °K) by the following equation:

$$\log r = a + \frac{b}{T} \quad (3)$$

Equation 2 contains two relative retention values, both being temperature dependent. By substituting eqn. 3 into eqn. 2, we can write that

$$I \propto \frac{aT + b}{cT + d} \quad (4)$$

where a , b , c and d are constants. Theoretically, this equation covers four possibilities.

In the first case, $a = c = 0$, in other words neither relative retention is temperature dependent. As a consequence, the retention index remains unchanged when changing the column temperature.

In the second case, $b = d = 0$ while in the third case, $aT + b = cT + d$. This means that both relative retentions are temperature dependent but their relative change is identical and thus, the value of the retention index will still remain constant. As will be shown later, on squalane liquid phase, the relative retention of two consecutive n -paraffins is definitely temperature dependent (according to eqn. 3). Similarly, among the hydrocarbons investigated, we did not find any in which constancy of the retention index with temperature could be observed although some approached this case.

In the fourth case $aT + b \neq cT + d$. This means that the retention index will be temperature dependent. Generally, a plot of I vs. T from eqn. 4 yields a curve. However, as will be shown later, we have found that for squalane liquid phase and for

the hydrocarbons investigated (within the given temperature range), this curve can actually be replaced by a straight line approximating the relationship:

$$I \approx a'T + b' \quad (5)$$

The possibility of drawing such straight line plots has two important applications. These plots permit an easy and convenient way of determining the retention index value at any temperature within the range investigated, generally with a ± 1 index unit accuracy. Besides this, the family of these plots permits the evaluation of the proper column temperature for the analysis of multicomponent mixtures, and demonstrates the change in elution sequence of the sample components.

EXAMPLES

The validity of the relationships discussed, and their utilization in practice will be illustrated by a number of examples. The data used are partly from our own measurements, and partly from that published by the Data Subcommittee⁶. Our own measurements were obtained on 100 (Table I) and 150 ft. (Table II) long, 0.020 in. I.D. support-coated open tubular columns prepared with squalane liquid phase, at different temperatures, using helium as the carrier gas, at an average linear gas velocity of about 20 cm/sec. Tables I and II summarize the results obtained.

TABLE I
FIRST SERIES OF MEASUREMENTS

	<i>n</i> -Pentane	<i>n</i> -Hexane	<i>n</i> -Heptane	<i>n</i> -Octane	Benzene
<i>Temperature: 60°C</i>					
Retention time (t_R), sec	251.6	409.8	809.0	1816.5	543.3
Adjusted retention time (t_R'), sec	103.9	262.2	661.4	1668.8	395.6
Partition ratio (k)	0.70	1.78	4.48	11.31	2.68
Retention index (I)	500	600	700	800	644
<i>Temperature: 77°C</i>					
Retention time (t_R), sec	232.7	337.8	582.3	1149.2	433.5
Adjusted retention time (t_R'), sec	79.9	185.4	430.0	996.8	281.1
Partition ratio (k)	0.52	1.22	2.82	6.54	1.85
Retention index (I)	500	600	700	800	649
<i>Temperature: 82°C</i>					
Retention time (t_R), sec	230.3	320.1	523.1	985.0	396.8
Adjusted retention time (t_R'), sec	70.0	159.4	362.6	824.3	236.2
Partition ratio (k)	0.44	0.99	2.26	5.13	1.47
Retention index (I)	500	600	700	800	648
<i>Temperature: 90°C</i>					
Retention time (t_R), sec	217.3	291.7	455.9	818.5	360.2
Adjusted retention time (t_R'), sec	61.4	135.8	300.0	662.5	204.3
Partition ratio (k)	0.39	0.87	1.92	4.25	1.31
Retention index (I)	500	600	700	800	651

TABLE II
SECOND SERIES OF MEASUREMENTS

	<i>n</i> -Heptane	Methyl- cyclo- hexane	2,5- Dimethyl- hexane	2,4- Dimethyl- hexane	2,2,5- Trimethyl- pentane	<i>n</i> -Octane
<i>Temperature: 45°C</i>						
Retention time (t_R), sec	1810.4	2244.6	2340.5	2412.7	2513.8	4565.2
Adjusted retention time (t_R'), sec	1578.9	2013.1	2109.0	2181.3	2282.4	4333.7
Partition ratio (k)	6.82	8.70	9.11	9.42	9.86	18.72
<i>Temperature: 74°C</i>						
Retention time (t_R), sec	766.3	937.8	924.6	948.7	997.8	1517.5
Adjusted retention time (t_R'), sec	548.0	719.5	706.3	730.4	779.5	1299.2
Partition ratio (k)	2.51	3.30	3.24	3.35	3.57	5.95
<i>Temperature: 95°C</i>						
Retention time (t_R), sec	538.6	642.5	621.3	632.1	664.7	902.4
Adjusted retention time (t_R'), sec	309.4	413.4	392.1	403.0	435.6	673.2
Partition ratio (k)	1.35	1.80	1.71	1.76	1.90	2.94

Relative retention of two consecutive n-paraffins on squalane

Table III summarizes the relative retention data of two consecutive normal paraffins on squalane liquid phase. As seen, the values measured at one temperature differ only in the third decimal place while there is a distinct difference in the values measured at different temperatures.

According to CHOVIN AND LEBBE¹¹, on squalane liquid phase, the correlation between the relative retention of two consecutive normal paraffins and the column temperature can be described by eqn. 3 where $a = -0.2853$ and $b = 231.4$. In Figs. 1 A and B, we have plotted our values and also the values calculated according to CHOVIN AND LEBBE. These figures clearly demonstrate the validity of eqn. 3 for the

TABLE III

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

<i>Temperature</i> (°C)	<i>Relative retention</i>		
	<i>n</i> -Hexane	<i>n</i> -Heptane	<i>n</i> -Octane
	<i>n</i> -Pentane	<i>n</i> -Hexane	<i>n</i> -Heptane
45			2.745 ^b
60	2.524 ^a	2.523 ^a	2.523 ^a
74			2.371 ^b
77	2.320 ^a	2.319 ^a	2.318 ^a
82	2.277 ^a	2.275 ^a	2.273 ^a
90	2.212 ^a	2.209 ^a	2.208 ^a
95			2.176 ^b

^a From measurements reported in Table I.

^b From measurements reported in Table II.

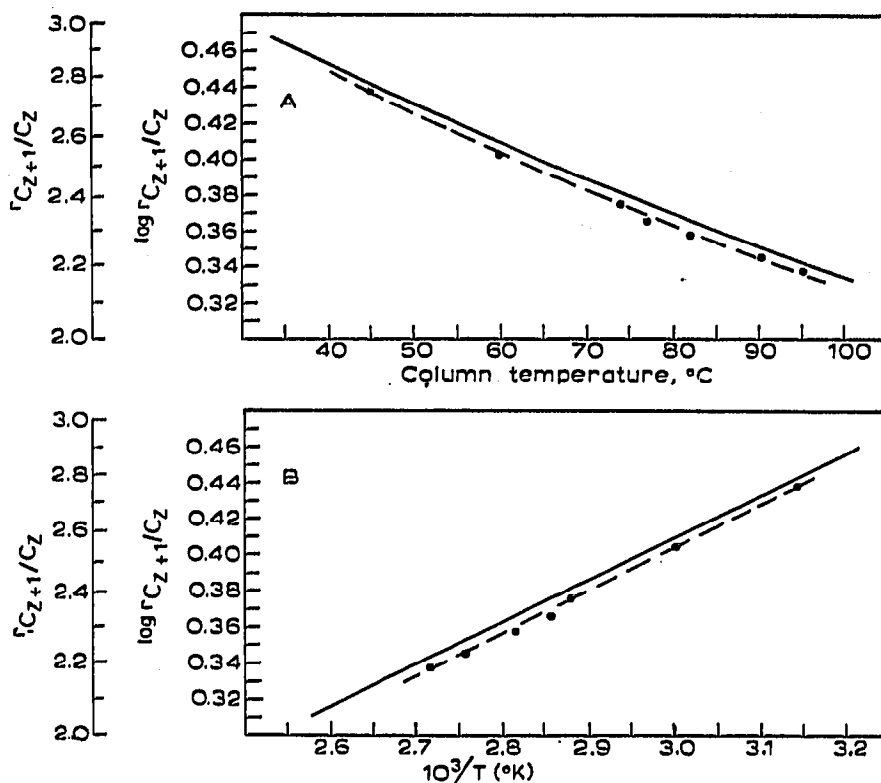


Fig. 1. The relationship between relative retention and column temperature for two consecutive normal paraffins, on squalane liquid phase. Solid line: curve according to CHOVIN AND LEBBE¹¹. Dots: our own measurements (see Table III).

n-paraffins on squalane, and that the relationship between their relative retention and column temperature approximates the following equation:

$$\log r_{C_{z+1}/C_z} \approx a'T + b' \quad (6)$$

Our curve in both plots is practically parallel to that obtained by calculating the relative retention values according to eqn. 3, using the values of CHOVIN AND LEBBE for *a* and *b*. The difference between the two curves is very small and can easily be explained by a small discrepancy in temperature measurement.

Correlation of retention index and temperature

The second question investigated in detail is the validity of eqn. 5 as an expression of the relationship between retention index and column temperature.

(a) *Squalane liquid phase.* In Fig. 2-4, we plotted the retention index values for 32 paraffins, 4 cycloparaffins and 2 aromatics, reported by the Data Subcommittee, against temperature. As seen, the linear relationship is well established for practically all the 38 substances and the deviation of the actual points from the respective straight lines is generally ± 1 index unit. This agreement is even more remarkable if one considers that the index numbers are always rounded up to the next unit and no decimals are given.

The only two substances where relatively larger deviations from the straight line can be observed are benzene and toluene. In Fig. 5, we show the plot for benzene in

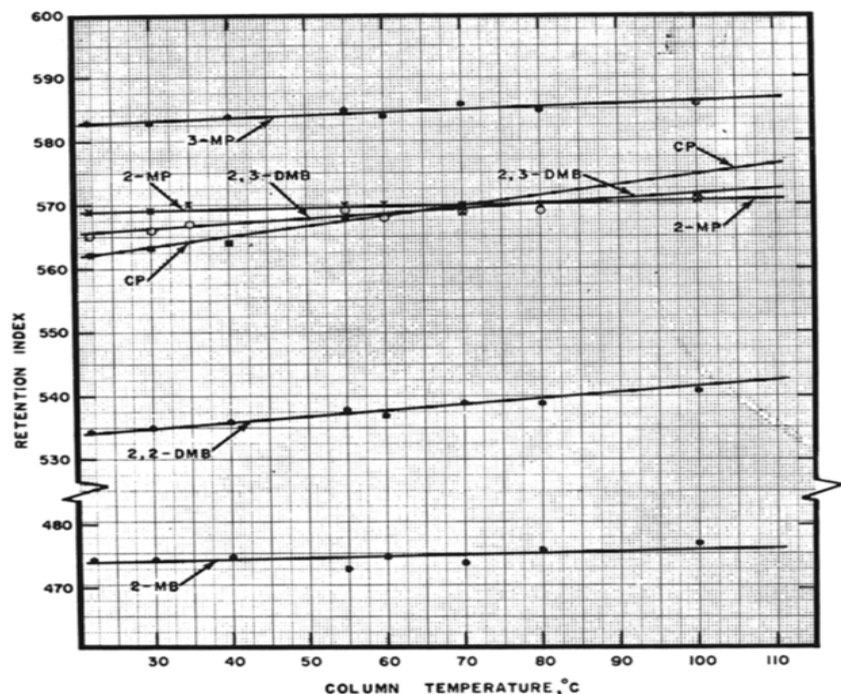


Fig. 2. Plot of retention index values of hydrocarbons obtained on squalane liquid phase against column temperature. Retention index range: 470-600. For explanation of the abbreviations, see Table IV.

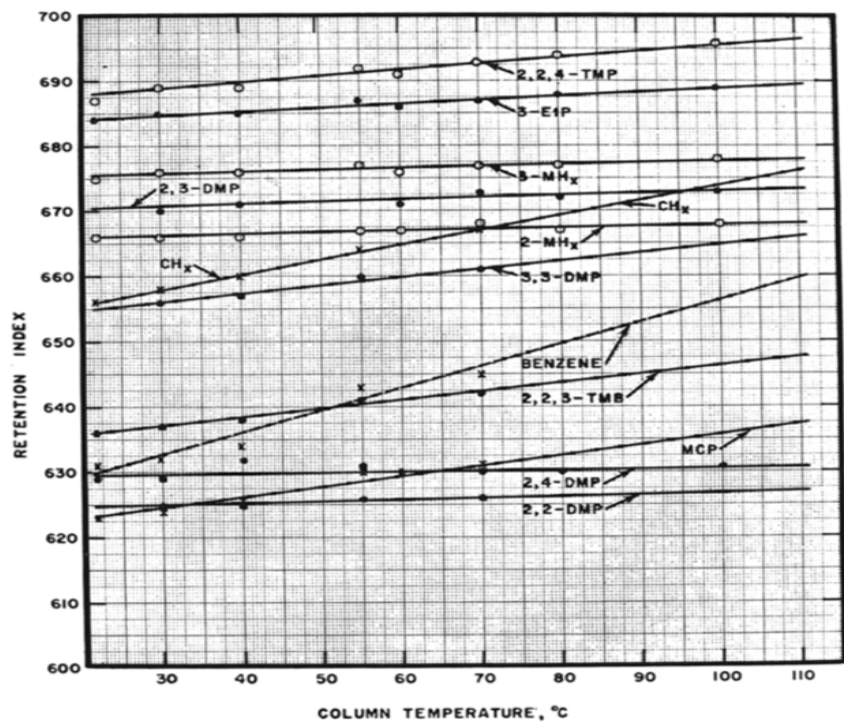


Fig. 3. Plot of retention index values of hydrocarbons obtained on squalane liquid phase against column temperature. Retention index range: 600-700. For explanation of the abbreviations, see Table IV.

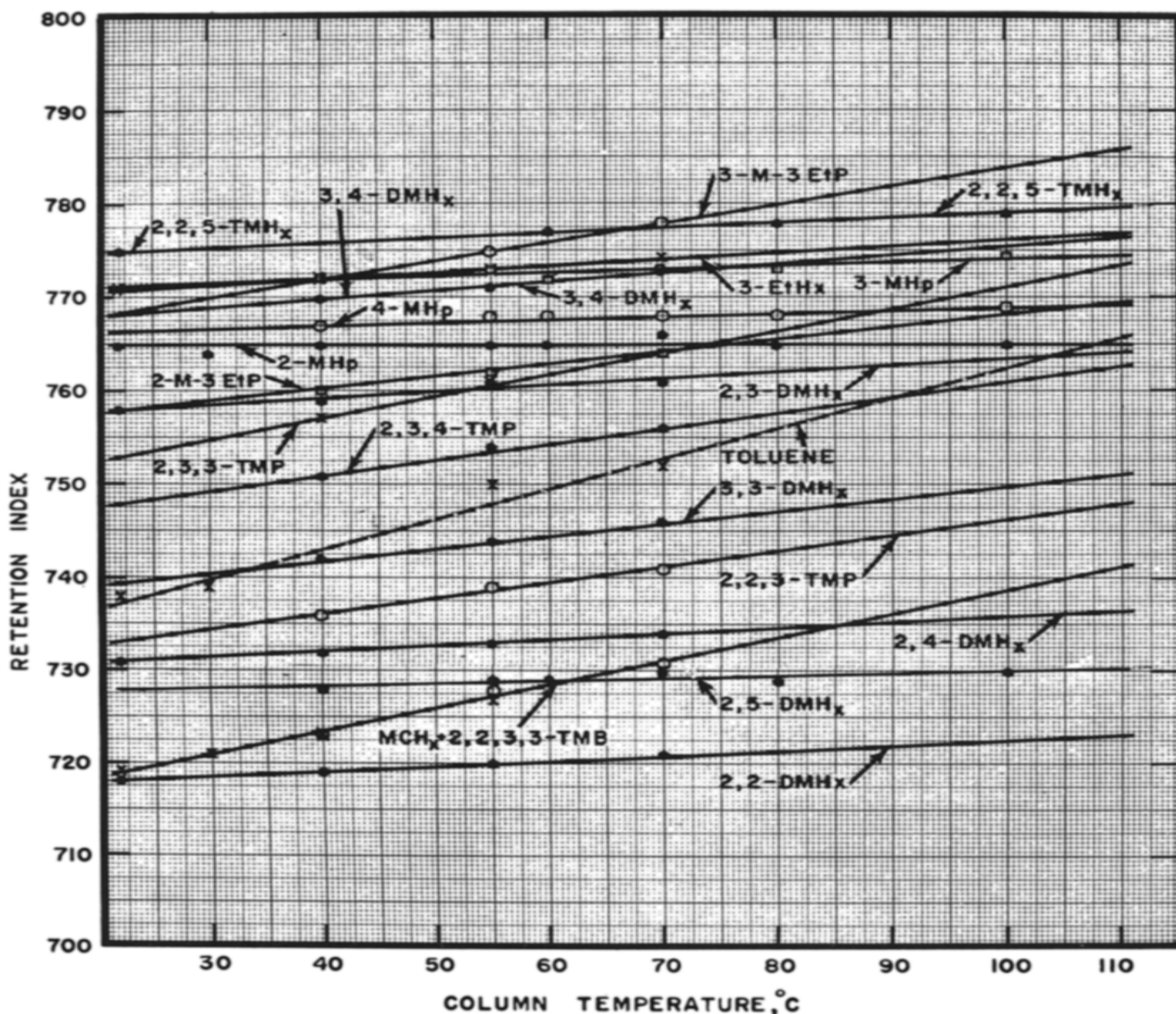


Fig. 4. Plot of retention index values of hydrocarbons obtained on squalane liquid phase against column temperature. Retention index range: 700–800. For explanation of the abbreviations, see Table IV.

TABLE IV

ABBREVIATIONS USED IN FIGS. 2–4

<i>Symbol</i>	<i>Meaning</i>
D	Di-
T	Tri- or tetra-
C	Cyclo-
M	Methyl-
Et	Ethyl-
B	Butane
P	Pentane
Hx	Hexane
Hp	Heptane

more detail; some additional points according to our own measurements (Table I) have been added. CHOVIN AND LEBBE¹¹ also determined the retention index of benzene on squalane at 70°C, and found it equal to 645, the value published by the Data Subcommittee. From Fig. 5, the randomness of the data and thus, the validity of eqn. 5 can clearly be established. The same is true for toluene.

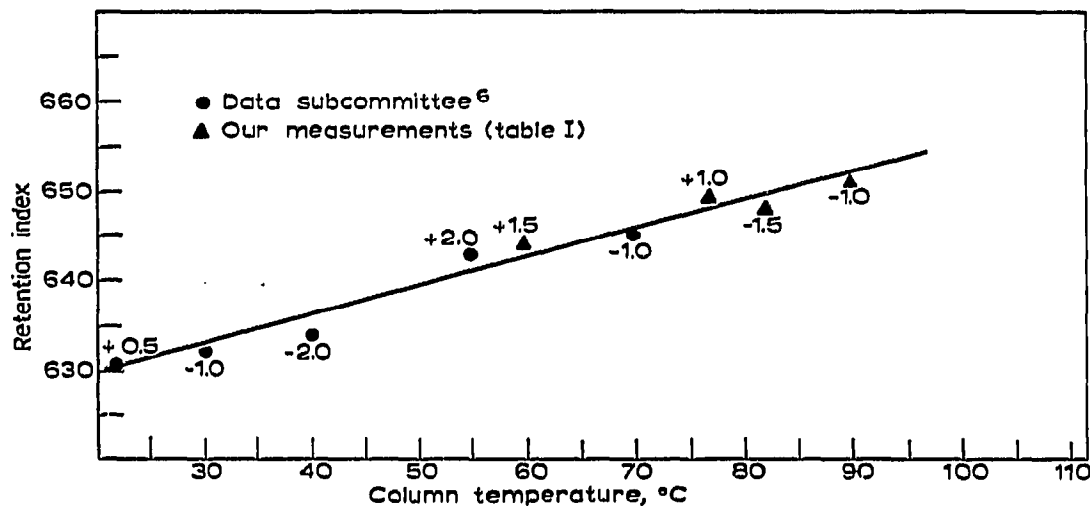


Fig. 5. Plot of retention index values of benzene obtained on squalane liquid phase against column temperature. The numbers give the deviation of the actual values (in index units) from the straight line drawn to fit these points.

In Fig. 5, we also indicate the deviation of the actual measurements from the straight line drawn to fit the points. In evaluating these data, one should keep in mind that the reproducibility of retention index measurements between various laboratories is generally considered as 2–5 units. Actually, the agreement between our data and those of the Data Subcommittee is better than the accepted reproducibility figure.

(b) *Other liquid phases.* As seen for squalane liquid phase and hydrocarbon samples, in the range investigated (22–100°), the I vs. T relationship can be considered as linear and following eqn. 5. It seems to us that for polar liquid phases, the curvature of the I vs. T plot is more evident, although this cannot be decided unequivocally. The reason for this is that there are not enough data available to evaluate the accuracy of the plot.

In Fig. 6, values for 10 substances obtained on poly(ethylene glycol) 400 are plotted; these data are from the publication of the Data Subcommittee⁶. The apparent curvature for most substances is only slight. However, since only data at three temperatures were available and their accuracy is given as ± 5 units, one cannot decide whether or not the curvature is real. A brief investigation of Fig. 6 reveals that if we took a randomness of only ± 3 units into account, we could replace all the curves except that of toluene by a straight line.

The uncertainty in the evaluation of Fig. 6 underlines even more the necessity of listing retention index values at multiple temperatures and eliminating all possible sources of error in the measurement. The principal sources of error consist of support effects and the difficulty of obtaining chemically defined pure liquid phases⁴.

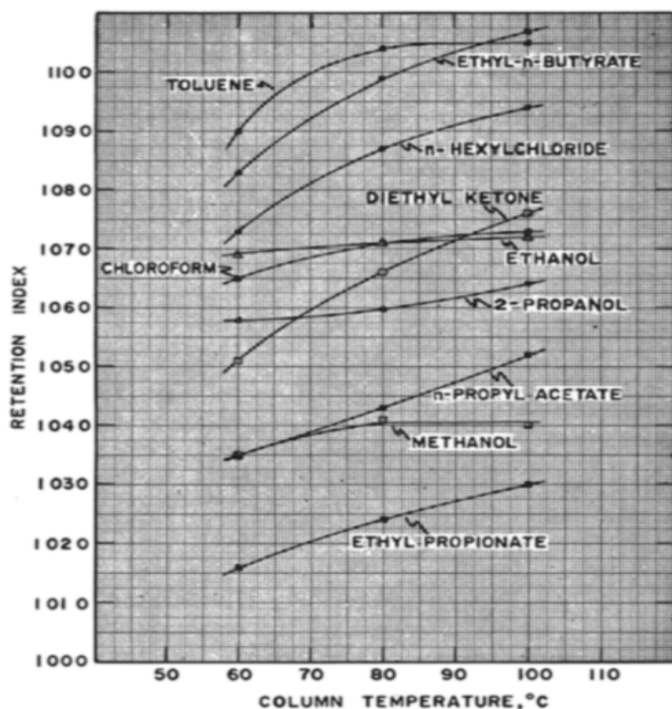


Fig. 6. Plot of retention index values of certain substances obtained on poly(ethylene glycol) 400 liquid phase against column temperature. Retention index range: 1000-1100.

The applications of retention index vs. temperature plots

Plots like those shown in Figs. 2-6 are not merely exercises in analytical geometry but actually have many practical applications.

It is evident that listing of index values at only one temperature has no practical meaning. Kováts in his original paper¹ suggested giving the retention index increments for 10° change; however, the plots shown here represent a better way to present retention index data. They permit the interpolation to any desired temperature and make the evaluation of the influence of column temperature more convenient.

The investigation of the retention index *vs.* column temperature plots also elicits certain general rules. It can be seen that on squalane liquid phase and with isoparaffin samples, the greater the substitution in the molecule the greater the influence of temperature on the retention index value. In the case of isomers with the same number of substituents (*e.g.* 2,2- and 3,3-dimethylpentane), the isomer with the substitution closer to the end of the main chain will generally have a plot with a smaller slope. It can also be seen that the retention index values of cycloparaffins and aromatics are much more temperature dependent than the retention indices of isoparaffins.

The evaluation of retention index *vs.* column temperature plots also helps in the selection of the best column temperature for the analysis of multicomponent mixtures. For example, let us consider a sample consisting of the following five components: 2,2,3-trimethylbutane (2,2,3-TMB), benzene (Bz), cyclohexane (CHx), 2-methylhexane (2-MHx), and 2,3-dimethylpentane (2,3-DMP).

Fig. 3 indicates that there are three temperatures where peak overlapping occurs: at 55° (2,2,3-TMB and Bz), at 70° (CHx and 2-MHx) and at 95° (CHx and 2,3-DMP). Thus, temperatures other than these three should be selected. It can also be seen that by proper selection of the column temperature, one can shift the relative

position of the peaks. This peak shift might be advantageous, *e.g.* if the concentration of two components represented by adjacent peaks differs greatly; it is always better to have a small peak before a large than *vice versa*.

This peak shifting is illustrated by analyzing a four-component mixture consisting of methylcyclohexane (MCHx), 2,5-dimethylhexane (2,5-DMHx), 2,4-dimethylhexane (2,4-DMHx), and 2,2,3-trimethylpentane (2,2,3-TMP). Investigation of Fig. 4 reveals that by increasing the column temperature, the MCHx-peak would change its relative position, and that there are two temperatures where peak overlapping occurs: 60° and 85°. Below 60°, MCHx emerges first; between 60 and 85° it will emerge between 2,5- and 2,4-DMHx while above 85°, it will emerge after 2,4-DMHx. This is illustrated in Fig. 7 which shows three consecutive chromatograms obtained at 45, 74 and 95° respectively*; the corresponding data are summarized in Table II.

We would also like to use the three chromatograms of Fig. 7 to demonstrate the accuracy of retention index determinations. In Table V, the values calculated from

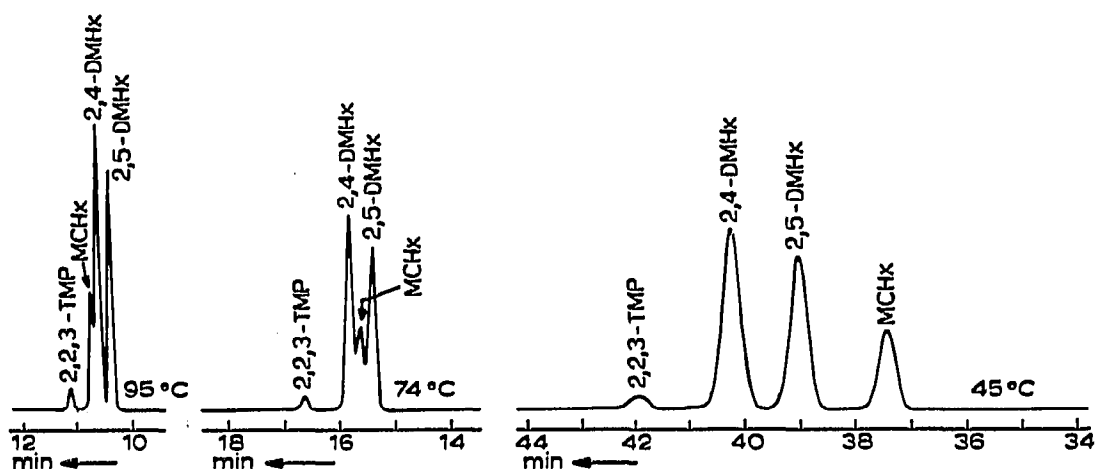


Fig. 7. Chromatograms of a four component mixture obtained at three different temperatures. Column: 150 ft. \times 0.020 in. I.D. support-coated open tubular prepared with squalane liquid phase ($\beta = 70$). Carrier gas (He) average velocity: 20 ± 1 cm/sec.

TABLE V
COMPARISON OF RETENTION INDEX VALUES

	45°C		74°C		95°C	
	Fig. 7 ^a	Fig. 4 ^b	Fig. 7 ^a	Fig. 4 ^b	Fig. 7 ^a	Fig. 4 ^b
Methylcyclohexane	724	724.5	731.5	732	737.5	737
2,5-Dimethylhexane	729	729	729.5	729	730.5	730
2,4-Dimethylhexane	732	732.5	733.5	734	734	735
2,2,3-Trimethylpentane	736.5	737	741	742	744	745

^a Our own measurements.

^b From plotting the values listed by the Data Subcommittee⁶.

* The sample analyzed for these three chromatograms also contained *n*-heptane and *n*-octane; their peaks, however, are omitted from Fig. 7.

these chromatograms are compared with values read from the plots given in Fig. 4. All values are rounded off to the nearest half. As seen, our determinations agree within one unit with the values read from the plots prepared from the values published by the Data Subcommittee.

Finally, the evaluation of retention index *vs.* temperature plots also helps in the identification of unknown mixtures. Namely, if there is any doubt in the proper assignment of a peak according to the comparison of its calculated retention index with the value read from a graph (or taken from an appropriate table), one can easily select a second temperature and investigate the possible peak shifting. For example, if during the evaluation of the chromatogram obtained at 95°C as shown in Fig. 7, one would be uncertain in assigning the second and third peaks to 2,4-DMHx and MCHx respectively, a second analysis at a temperature properly selected from the plots in Fig. 4 would immediately reveal the proper assignment.

SUMMARY

The influence of column temperature on the retention index values is discussed in general terms. It was found that on squalane liquid phase and for hydrocarbon samples, a linear relationship can be assumed between retention index and temperature while on polar liquid phases, these plots seem to show some curvature. Retention index *vs.* temperature plots permit the better utilization of published data, reveal some general rules in the temperature dependency of different substances and help in the choice of the proper analysis temperature and in the identification of unknown mixtures.

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