

CHROM. 13.764

Note

Conversion of linear retention indices into logarithmic retention indices

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(First received December 13th, 1980; revised manuscript received March 3rd, 1981)

In contrast to logarithmic retention indices (I), there is no need of logarithmic calculation or of determination of the elution time of the non-sorbing gas for estimating the values of linear retention indices (I_A). The latter yield fine correlations between structure, temperature dependence of retention and differences in retention on different stationary phases^{1,2}. Moreover, Saha and Mitra¹ and Soják and Vigdergauz² have demonstrated that, under identical experimental conditions, I_A values can be measured more accurately than I values; the standard deviations of I_A values on polar phases are significantly smaller than those of I values².

The major draw-back with the I_A system, is that, unlike the I system, it does not reflect the thermodynamics of the processes involved in elution during gas chromatography. However, this can be eliminated if accurate I values can be determined directly and easily through I_A values. The mathematical relationship between I_A and I given by Vigdergauz and Martynov³ has the form:

$$J = \frac{\frac{\delta I}{\sigma^{100}} - 1}{\sigma - 1} \quad (1)$$

where

$$\sigma = \frac{t'_{Rn+1}}{t'_{Rn}} = \frac{t'_{Rn}}{t'_{Rn-1}} = \frac{t_{Rn+1} - t_{Rn}}{t_{Rn} - t_{Rn-1}}$$

$$J = \frac{t_{Rx} - t_{Rn}}{t_{Rn+1} t_{Rn}} + n = \frac{I_A}{100}$$

and

$$\delta I = I - 100n$$

The adjusted and non-adjusted retention times of normal paraffins with carbon number n and of sample component x are denoted by t'_{Rn} , t_{Rn} and t'_{Rx} , t_{Rx} respectively.

Eqn. 1 has been found to be incorrect. In this paper a simple graphical method followed by a modified mathematical relation is proposed for the of I values directly from I_A values, predetermined from experimental unadjusted retention data.

EXPERIMENTAL

Retentions were determined at $50 \pm 0.01^\circ\text{C}$ on a stainless-steel capillary column (100 m \times 0.25 mm I.D.) coated dynamically with 10% w/v squalane in *n*-hexane. A device for high accuracy measurement of retention time was used⁴. The carrier gas was nitrogen at 2.5 atm. Sample components were injected as a 0.1- μl mixture with a splitting ratio of 1:400. The retention data used in the calculations of I_A values were averages from three injections. The same values of retention data, were used for the calculation of experimental I values.

RESULTS AND DISCUSSION

Mathematical relation between the two indices

The logarithm of σ is defined as the slope of a plot of the adjusted retention values of normal paraffins on the log scale against carbon number¹. Since σ is related both to the adjusted and non-adjusted retentions of paraffins between which a component elutes, it may be used as a basis of correlation of I_A and I . The modified mathematical relation which results has the form

$$\frac{I_A - 100n}{100} = \frac{\sigma^{\frac{I-100n}{100}} - 1}{\sigma - 1} \quad (2)$$

where I_A and I are defined as the arithmetic index or linear retention index⁵ and as the Kováts' retention index or logarithmic retention index⁶ respectively.

The validity of eqn. 2 can easily be tested by assuming the values of I_A and I to be 600 for *n*-hexane and the carbon number of the lower paraffin to be 5 ($n = 5$). Linear and logarithmic retention indices of various types of hydrocarbons have been determined and are shown in Table I. The values determined from non-adjusted retention did not match those determined from adjusted retention of normal paraffins. This deviation is due to the very small retention of methane, used as a non-retentive peak in the FID system. Thus the σ value of 2.66 determined from non-adjusted retention (see Table I) may be used for the interconversion of the two index systems. Furthermore, the actual instrumental dead time was calculated to be 481.5 sec using this σ value. When a dead time of 481.5 sec was used for adjusting the retention times of paraffins, the pre-calculated σ values of 2.73 and 2.70 became 2.66. Thus it was supposed that methane is retained for 9 sec (490.5–481.5) on the liquid phase of the capillary column. Therefore it is quite likely that the I values calculated through the I_A values may be more accurate (see Table I).

Graphical methods of conversion of I_A into I values

In order to determine I values from the predetermined I_A values, graphical methods were developed as follows.

TABLE I
COMPARISON OF THE TWO RETENTION INDICES OF HYDROCARBON COMPONENTS ON SQUALANE

Compound	Retention time (sec)	Linear retention index, I_A	Logarithmic retention index, I		
			Experimental*	Graphical**	Analytical***
Methane	490.5	—	—	—	—
<i>n</i> -Pentane	645.5	500.00	500.00	500.00	500.00
2,3-Pentadiene	700.6	520.48	530.00	530.00	530.00
4-Methylpentene-2 (<i>cis</i>)	763.5	543.80	555.95	556.0	555.85
4 Methylpentene-2 (<i>trans</i>)	782.8	550.80	562.59	563.0	562.52
Hexene-1	845.5	574.21	581.92	582.0	582.07
<i>n</i> -Hexane	915.0	600.00	600.00	600.00	600.00
2,2-Dimethylpentane	1037.2	616.81	625.60	625.0	625.15
Benzene	1108.8	625.67	638.02	638.0	637.56
Cyclohexane	1279.0	650.10	662.61	662.0	661.80
2-Methylhexane	1310.0	654.45	666.60	666.0	665.83
3-Methylhexene-3 (<i>cis</i>)	1470.0	676.40	684.55	684.0	684.68
1,2-Dimethylcyclopentane (<i>trans</i>)	1514.4	682.50	689.06	688.0	688.26
Heptene-3 (<i>cis</i>)	1535.7	685.42	691.12	690.0	690.26
<i>n</i> -Heptane	1631.6	700.00	700.00	700.00	700.00

* Calculated from Kováts' equation using experimental data from methane injection.

** Calculated from linear retention index data using graphs in Fig. 1.

*** Calculated from linear retention index data using $t'_H/t'_P = 2.73$; $t'_{HP}/t'_H = 2.70$; $(t_{HP} - t_H)/(t_H - t_P) = 2.66$, where t'_P , t'_H , t'_{HP} and t_P , t_H , t_{HP} are the adjusted and non-adjusted retention times of *n*-pentane, *n*-hexane and *n*-heptane, respectively; and $\sigma = 2.66$.

The value of σ was determined from the non-adjusted retention data of three consecutive normal paraffins. By assigning any arbitrary adjusted retention value to the lower normal paraffin, e.g., unity ($t'_{Rn-1} = 1.0$), the adjusted retention value of the next higher normal paraffin will be increased by a factor of σ ($t'_{Rn} = \sigma$).

The adjusted retention values of any two consecutive paraffins (in this case 1 and 2.66) were now plotted against ($I_A - 100n$) on linear graph paper (Fig. 1A) and against ($I - 100n$) on semi-log graph paper (Fig. 1B). From the ($I_A - 100n$) value of a component (e.g., 50.1 for cyclohexane), the corresponding adjusted retention time (1.84) is determined (see Fig. 1A) and subsequently this value is used in Fig. 1B to determine the respective ($I - 100n$) or I values (i.e., 62 or 662 for cyclohexane). The I values can also be calculated from Kováts' formula⁶, once the adjusted values of the components have been determined.

It is worth noting that, from the same two graphs, I values of components eluting between the higher or lower paraffins can also be calculated because the value of σ , once determined, remains constant.

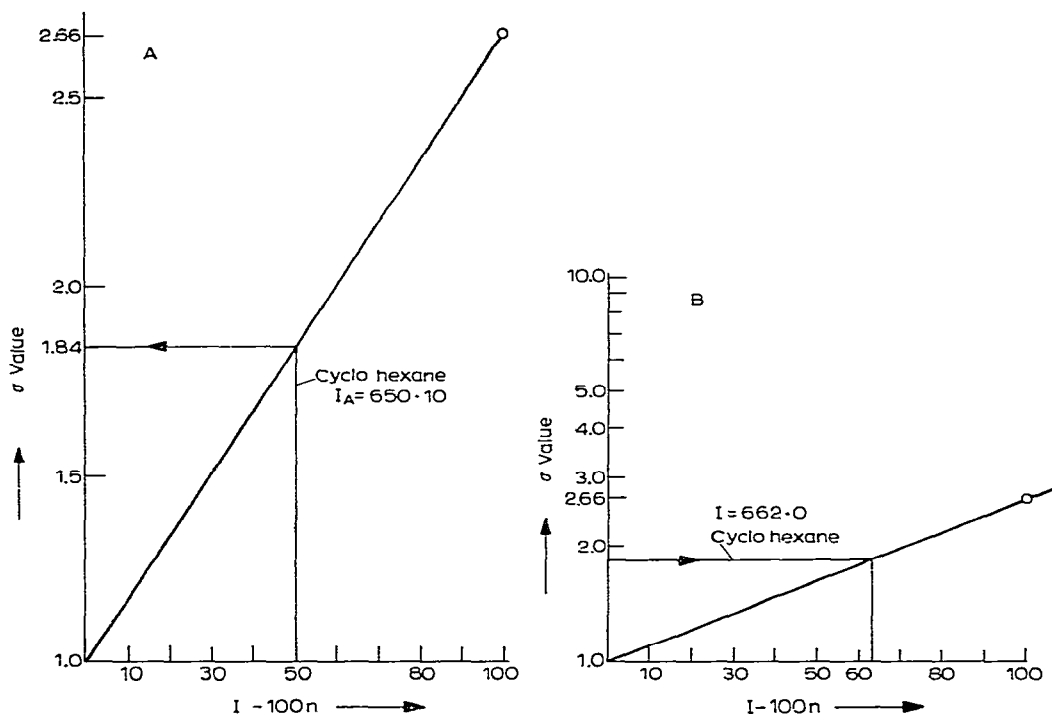


Fig. 1. Graphical conversion of linear retention indices into logarithmic retention indices: A. linear plot; B. logarithmic plot.

From a comparison of all three logarithmic retention index values (Table I), it is seen that the experimental value, using methane injection, deviates from the mathematical and graphical values which are similar. Therefore I values determined through I_A values seem to be more accurate than those determined directly from experiment, using methane injection.

ACKNOWLEDGEMENT

The author thanks Drs. S. Varma and K. M. Verma of FPDIL, Sindri, for their interest and the Laboratory of Instrumental Analysis, Technical University, Eindhoven, The Netherlands, for facilities to carry out the capillary chromatography.

REFERENCES

- 1 N. C. Saha and G. D. Mitra, *Technology, India*, 8 (1971) 3.
- 2 L. Soják and M. S. Vigdergauz, *J. Chromatogr.*, 148 (1978) 159.
- 3 M. S. Vigdergauz and A. A. Martynov, *Chromatographia*, 4 (1971) 463.
- 4 J. A. Rijks and C. A. Cramers, *Chromatographia*, 7 (1974) 99.
- 5 A. G. Douglas, *J. Chromatogr. Sci.*, 7 (1969) 581.
- 6 E. Kovats, *Helv. Chim. Acta*, 41 (1958) 1915.