

## NON-LINEARITY OF THE PLOT OF LOG (ADJUSTED RETENTION TIME) VERSUS CARBON NUMBER FOR *n*-ALKANES IN SERIES-COUPLED GAS CHROMATOGRAPHIC COLUMNS

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### SUMMARY

The validity of the fundamental relationship of the Kováts retention index concept, namely the linear dependence of  $\log t'_R$  on the carbon number of *n*-alkanes, was studied for a system of two series-coupled columns without intermediate trapping. Non-linearity of the  $\log t'_R$  versus carbon number plot for the system was deduced from basic equations and confirmed experimentally. It was shown that the discrepancy from the Kováts concept in such a system will be especially large if the slopes of the *n*-alkane plots for the two individual columns differ significantly.

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### INTRODUCTION AND THEORY

Multi-dimensional gas chromatography (GC) is increasingly used for the separation of very complex mixtures (for reviews, see refs. 1-6; for the theoretical background, see refs. 7 and 8). The use of Kováts retention indices in series-coupled systems for the characterization of the separated compounds has been described<sup>9-15</sup>. It is based on different concepts: (i) determination of two independent sets of retention index data by intermediate trapping<sup>9</sup> in order to create a defined starting point for the separation on the second column or determination of the indices on the second column after separating the compounds of interest on the first column in a temperature-programmed mode and with intermediate trapping<sup>10,11</sup>; (ii) determination of the retention index data on each column without intermediate trapping by calculating retention time differences<sup>12</sup>; (iii) determination of retention indices with the coupled system without intermediate trapping<sup>13-15</sup>.

Retention indices determined according to concepts (i) and (ii) are valid for a particular column. In contrast, the retention indices determined according to concept (iii) are not related on a single column. They are "system indices" which reflect the interplay of two retention characteristics (different retention systems or different separation conditions). A feature of series-coupled columns run without intermediate trapping is the opportunity to adjust the polarity and selectivity by changing the temperatures and/or the flow-rates<sup>16</sup>.

In this work the validity of the fundamental relationship of the Kováts retention index concept, namely the linear dependence of  $\log t'_R$  on the carbon number of  $n$ -alkanes<sup>17</sup>, was studied for such a series-coupled column system. The flow dependence<sup>15</sup> of the "system indices" will be not discussed here.

The linearity between  $\log t'_R$  and the carbon number,  $Z$ , is expressed by

$$\log t'_R(Z) = A + BZ \quad (1)$$

The slope  $B$  equals the logarithm of the ratio of the adjusted retention times of two neighbouring  $n$ -alkanes:

$$B = \log \left[ \frac{t'_R(Z+1)}{t'_R(Z)} \right] \quad (2)$$

The retention times in the series-coupled column system are additive:

$$t_{R(S)} = t_{R(1)} + t_{R(2)} \quad (3)$$

$$t'_{R(S)} = t'_{R(1)} + t'_{R(2)} \quad (4)$$

$$t_{M(S)} = t_{M(1)} + t_{M(2)} \quad (5)$$

where  $t_R$  is the total retention time,  $t'_R$  the adjusted retention time,  $t_m$  the dead time and the subscripts 1 and 2 refer to columns 1 and 2 and S represents the system.

Substituting  $t'_{R(S)}$  for  $t'_R$  in eqn. 1 gives

$$t'_{R(S)}(Z) = \exp[A_{(1)} + B_{(1)}Z] + \exp[A_{(2)} + B_{(2)}Z] \quad (6)$$

Using this expression for  $t'_{R(S)}$ , the slope  $B_{(S)}$  can be written as

$$B_{(S)} = \log \left\{ \frac{\exp[A_{(1)} + B_{(1)}(Z+1)] + \exp[A_{(2)} + B_{(2)}(Z+1)]}{\exp[A_{(1)} + B_{(1)}Z] + \exp[A_{(2)} + B_{(2)}Z]} \right\} \quad (7)$$

This expression implies that the slope  $B_{(S)}$  (valid for the system) varies with the carbon number of the  $n$ -alkanes used for the measurement. This means that one has to take into account a more or less curved plot of  $\log t'_{R(S)}$  versus carbon number.

A schematic plot for both the single columns and the column system (Fig. 1) illustrates the non-linearity of this dependence for the system. The plot reveals further that the discrepancy from the Kováts concept will be especially large if the slope on the first column differs very much from that on the second column.

## EXPERIMENTAL

A Siemens Sichromat 2 gas chromatograph, equipped with a split injector and 2 flame ionization detectors was used. Column 1 (50 m  $\times$  0.32 mm I.D.) contained FS-WG-PB-1 (OV-1) (WGA) and column 2 (1.5 m  $\times$  1 mm I.D.) contained Carbowack C particles (0.16–0.2 mm). The column temperatures were  $T_1 = 100^\circ\text{C}$  and

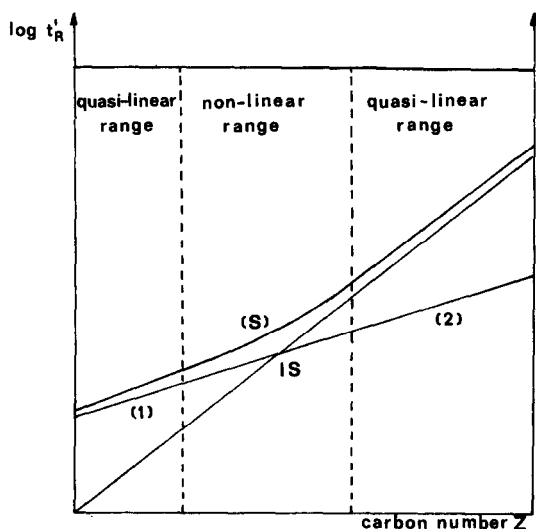


Fig. 1. Schematic graph of the  $\log t'_R$  versus carbon number plots for the system (S) and the single columns (1) and (2); IS = intersection.

$T_2 = 220^\circ\text{C}$  and the pressures (hydrogen) were  $P_I = 4.4$  bar and  $P_M = 4.0$  bar ( $I = \text{inlet}$ ;  $M = \text{mid-point}$ ).

The Live-T-Piece of the Sichromat 2 was used in a monitoring mode; thus the first detector shows which part of the sample is entering the second column. The percentage of sample going to the first detector was adjusted by changing the positive pressure difference.

## RESULTS AND DISCUSSION

In order to illustrate the phenomenon of non-linearity, two columns with very different retention characteristics have to be applied. Using two capillary columns coated with liquid stationary phases of different polarity, we could not measure such non-linearities. To meet the requirements mentioned above, an OV-1 capillary column was coupled with a graphitized carbon black micropacked column, because the slopes of the *n*-alkane plots are very different on these columns<sup>18</sup>. The slopes  $B$  were calculated according to eqn. 2.

The dead times  $t_{M(1)}$  and  $t_{M(2)}$  were evaluated from *n*-alkane retention times with a computer program described by Ebel and Kaiser<sup>19</sup>. The calculated dead times were compared with those determined by injection of methane. The dead time for the system was calculated using eqn. 5 and also compared with the retention time of methane. Eqn. 3 was applied for calculating the net retention times for the second column.

Table I shows the non-linearity of the *n*-alkane plot for the coupled system. Whereas the slopes  $B_{(1)}$  and  $B_{(2)}$  for the single columns remain constant, the slope  $B_{(S)}$  for the system increases. The slopes  $B_{(S)}$  agree well with those calculated according to eqn. 7.

In this example the intersection, IS, of the *n*-alkane plots of the single columns is in the range of the *n*-alkanes used. The non-linearity is especially large in this range,

TABLE I

SLOPES OF THE *n*-ALKANE PLOT FOR THE INDIVIDUAL COLUMNS [ $B_{(1)}$  AND  $B_{(2)}$ ] AND THE COUPLED SYSTEM [ $B_{(S)}$ ]

Results of linear regression:  $t_{M(1)} = 2.54$ ,  $A_{(1)} = -4.462$ ,  $B_{(1)} = 0.648$ ;  $t_{M(2)} = 0.15$ ,  $A_{(2)} = -6.742$ ,  $B_{(2)} = 0.917$ .

| Compound | Carbon number (Z) | $t_{R(1)}$ (meas.) min | $t_{R(2)}$ (eqn. 3) min | $t_{R(S)}$ (meas.) min | $B_{(1)}$ (eqn. 2) | $B_{(2)}$ (eqn. 2) | $B_{(S)}$ (eqn. 2) | $B_{(S)}$ (eqn. 7) |
|----------|-------------------|------------------------|-------------------------|------------------------|--------------------|--------------------|--------------------|--------------------|
| Methane  | 1                 | 2.540                  | 0.150                   | 2.695                  |                    |                    |                    |                    |
| Hexane   | 6                 | 3.103                  | 0.439                   | 3.542                  | 0.65               | 0.92               | 0.75               | 0.75               |
| Heptane  | 7                 | 3.617                  | 0.873                   | 4.490                  | 0.65               | 0.92               | 0.77               | 0.76               |
| Octane   | 8                 | 4.603                  | 1.960                   | 6.563                  | 0.65               | 0.92               | 0.78               | 0.78               |
| Nonane   | 9                 | 6.481                  | 4.675                   | 11.156                 | 0.65               | 0.92               | 0.80               | 0.80               |
| Decane   | 10                | 10.059                 | 11.461                  | 21.520                 |                    |                    |                    |                    |

as can also be seen from Fig. 1. The carbon number of the intersection can be calculated according to

$$IS = \frac{A_{(2)} - A_{(1)}}{B_{(1)} - B_{(2)}} \quad (8)$$

The correct values of the constants  $A$  and  $B$  for the single columns can be calculated by linear regression. This means that dead-time determinations based on linear regression may be not applicable or may give erroneous results. Similar effects can possibly be expected when applying mixed stationary phases in one column. On the other hand, on coupling columns with similar retention characteristics this effect is small.

The extraordinary features of a coupled system consisting of a gas-liquid and a gas-adsorption column will be described elsewhere<sup>20</sup> (utilization of both vapour pressure and geometry for separation).

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