

## Note

### Use of Kováts retention indices for characterization of solutes in linear temperature-programmed capillary gas-liquid chromatography

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(Received September 17th, 1985)

Kováts retention indices<sup>1</sup> are generally considered to be the most practical parameter to characterize the retention of compounds in gas chromatography<sup>2</sup>. These indices are defined after the isothermal retention time of the compounds of interest and of the *n*-alkanes eluted immediately before and after them:

$$I = 100z + 100 \frac{\log(t'_{R,i}/t'_{R,z})}{\log(t'_{R,z+1}/t'_{R,z})} \quad (1)$$

In linear temperature-programmed gas chromatography (LTPGC) the retention time of *n*-alkanes increases linearly with the number of carbon atoms, so Van den Dool and Kratz<sup>3</sup> proposed to calculate the retention indices by a linear interpolation:

$$I_{\text{prog}} = 100z + 100 \frac{T_{R,i} - T_{R,z}}{T_{R,z+1} - T_{R,z}} \quad (2)$$

where  $T_{R,i}$  is the retention temperature of compound *i*. Since the isothermal retention indices do vary, albeit slowly, with temperature, there has been much attention devoted to the derivation of a reliable relationship between the programmed retention indices and the isothermal indices measured at some "equivalent temperature".

Van den Dool and Kratz<sup>3</sup> found a good agreement between programmed indices and the isothermal indices measured at the retention temperature (equivalent temperature equal to retention temperature). Guiochon<sup>4</sup> has shown that there is a better agreement if the equivalent temperature is taken as  $T_R$  minus 20°C. Giddings<sup>5</sup> suggested that the equivalent temperature is equal to  $0.92T_R$ . Lee and Taylor<sup>6</sup> found

that the equivalent temperature is better approximated by the harmonic mean between the retention temperature and the initial temperature of the programmed run:  $T = 2T_R \cdot T_0 / (T_R + T_0)$ .

Golovnya and Uraletz<sup>7</sup> preferred to calculate the programmed indices as the arithmetic average between the isothermal indices at the retention temperature and at the initial temperature of the run. Other authors<sup>8,9</sup> have used polynomial dependence between retention temperature in LTPGC and the number of carbon atoms of the *n*-alkanes involved.

Kratzsch<sup>10</sup> and Anders *et al.*<sup>11</sup> have used iterative processes to recalculate retention times and decrease the differences found between isothermal and temperature programmed retention indices. They have not taken the thermal variation of the isothermal indices into account, however.

Unfortunately none of these approaches has been entirely successful and it is generally considered that the agreement between retention indices measured in LTPGC and those derived from isothermal data is not satisfactory for identification purposes<sup>12</sup>. The aim of this work is to present an alternative approach to the use of isothermal retention indices for the identification of compounds separated by LTPGC.

#### THEORETICAL

We shall make the following, simplifying assumptions:

(i) Linear temperature programming begins when the sample is injected. There is no isothermal period at the beginning of the run.

(ii) All compounds considered are eluted in LTPGC conditions. This precludes applicability of the method to early eluting compounds, with retention temperature below  $1.09T_0$  (ref. 5).

(iii) The isothermal retention indices vary linearly with temperature ( $dI/dT = \text{constant}$ ).

(iv) The experimental conditions, and especially the initial temperature and carrier gas flow-rate, are kept constant.

Under these conditions it is observed that the retention indices of *n*-alkanes (which are, by definition, equal to one hundred times the number of their carbon atoms) are not linearly related to their retention temperatures in LTPGC (*cf.* Fig. 1). The slope of each segment on this figure depends both on the program rate ( $a = dT/dt$ ) and on the number of carbon atoms of the alkane considered. It must be observed, however, that for a starting temperature of 40°C, only the compounds which are eluted at a temperature above  $(273 + 40)/0.92 = 340$  K or 67°C can be considered as eluted in actual temperature programming conditions<sup>5,13</sup>. This is not the case of *n*-heptane in most of the experiments reported in Fig. 1 (except for  $a = 0.8$  and 1°C/min), nor even of *n*-octane in the two first runs ( $a = 0.1$  and 0.2°C/min). This explains in part the non-linear behavior of the plots on Fig. 1<sup>13</sup>.

If the assumption of Van den Dool and Kratz<sup>3</sup> is correct and the programmed temperature index is equal to the isothermal index at the elution temperature,  $T_{R,i}$ , we can relate that temperature to the known value of the index at some reference temperature and the coefficient of thermal variation of the index. As a first approximation, it has been shown that the index of most compounds increases linearly with temperature:

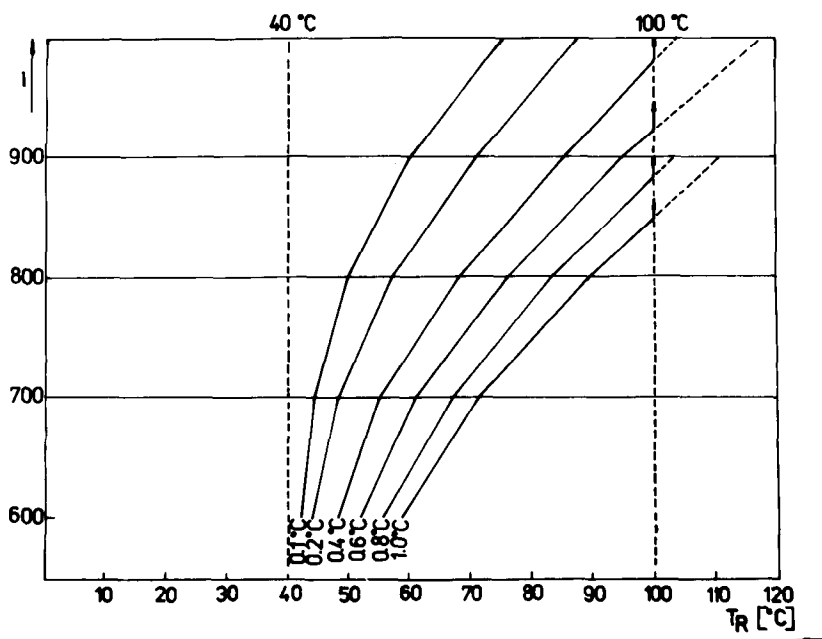


Fig. 1. Plot of retention indices of *n*-alkanes versus their elution temperature. Column B, squalane. The temperature gradient is indicated on each line.

$$I(T_{R,i}) = I(T_1) + (T_{R,i} - T_1)i \quad (3)$$

with:

$$i = \frac{dI}{dT} \quad (4)$$

For most branched, cyclic and aromatic hydrocarbons  $dI/dT$  is between 0 and 0.3 unit/°C (cf. data below).

If now we equal eqns. 2 and 3 and solve for  $T_{R,i}$ , we obtain:

$$T_{R,i} = \frac{[I(T_1) - 100 \cdot z - i \cdot T_1] (T_{R,z+1} - T_{R,z}) + 100 \cdot T_{R,z}}{100 - i(T_{R,z+1} - T_{R,z})} \quad (5)$$

Deviations between experimental values of  $T_{R,i}$  and those calculated from eqn. 5 are easy to determine. They are a measure of the validity of the assumptions that (i) the elution actually takes place in programmed-temperature conditions and that (ii) the programmed-temperature index is closely approximated by the isothermal index at the retention temperature. Other assumptions such as the one suggested by Giddings<sup>5</sup> can be checked by replacing  $100 - i(T_{R,z+1} - T_{R,z})$  in the denominator of the right-hand side of eqn. 5 by  $100 - 0.92 \cdot i(T_{R,z+1} - T_{R,z})$ .

The difference between our approach and the one taken originally by Van den Dool and Kratz<sup>3</sup> is illustrated in Fig. 2. In the first case<sup>3</sup>, one can derive the retention

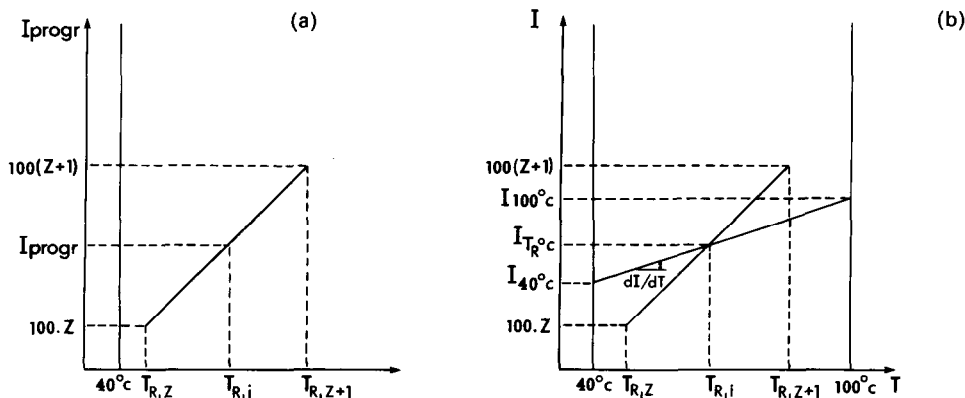


Fig. 2. Comparison between the methods described by Van den Dool and Kratz<sup>3</sup> (a) and by this work (b) for the determination of the retention temperature. This diagram illustrates how the temperature dependence of the isothermal retention indices is taken into account for the determination of the retention temperature.

TABLE I

## LIST OF COMPOUNDS IN THE MODEL MIXTURE

| Name  | Abbreviation            |
|---|-------------------------|
| 1,1,3-Trimethylcyclopentane                             | 1,1,3-Tri-MeCyPe        |
| 1- <i>trans</i> -2- <i>cis</i> -4-Trimethylcyclopentane | 1-Tr-2-Cis-4-TriMeCyPe  |
| 1- <i>trans</i> -2- <i>cis</i> -3-Trimethylcyclopentane | 1-Tr-2-Cis-3-TriMeCyPe  |
| 1,1,2-Trimethylcyclopentane                             | 1,1,2-TriMeCyPe         |
| 1- <i>cis</i> -2- <i>trans</i> -4-Trimethylcyclopentane | 1-Cis-2-Tr-4-TriMeCyPe  |
| 1- <i>cis</i> -2- <i>cis</i> -4-Trimethylcyclopentane   | 1-Cis-2-Cis-4-TriMeCyPe |
| 1- <i>cis</i> -2- <i>trans</i> -3-Trimethylcyclopentane | 1-Cis-2-Tr-3-TriMeCyPe  |
| 1-Methyl- <i>cis</i> -3-ethylcyclopentane               | 1-MeCis-3-EtCyPe        |
| 1-Methyl- <i>trans</i> -3-ethylcyclopentane             | 1-MeTr-3-EtCyPe         |
| 1-Methyl- <i>trans</i> -2-ethylcyclopentane             | 1-MeTr-2-EtCyPe         |
| 1-Methyl-1-ethylcyclopentane                            | 1-Me-1-EtCyPe           |
| Isopropylcyclopentane                                   | iso-ProCyPe             |
| 1-Methyl- <i>cis</i> -2-ethylcyclopentane               | 1-MeCis-2-EtCyPe        |
| Propylcyclopentane                                      | n-ProCyPe               |
| 1- <i>cis</i> -2- <i>cis</i> -3-Trimethylcyclopentane   | 1-Cis-2-Cis-3-TriMeCyPe |
| 1- <i>trans</i> -4-Dimethylcyclohexane                  | 1-Tr-4-DiMeCyHex        |
| 1,1-Dimethylcyclohexane                                 | 1,1-DiMeCyHex           |
| 1- <i>cis</i> -3-Dimethylcyclohexane                    | 1-Cis-3-DiMeCyHex       |
| 1- <i>trans</i> -2-Dimethylcyclohexane                  | 1-Tr-2-DiMeCyHex        |
| 1- <i>trans</i> -3-Dimethylcyclohexane                  | 1-Tr-3-DiMeCyHex        |
| 1- <i>cis</i> -4-Dimethylcyclohexane                    | 1-Cis-4-DiMeCyGHex      |
| 1- <i>cis</i> -2-Dimethylcyclohexane                    | 1-Cis-2-DiMeCyHex       |
| Ethylcyclohexane  | EtCyHex                 |
| Ethylbenzene  | EtBe                    |
| 1,4-Dimethylbenzene                                     | <i>p</i> -Xylene        |
| 1,3-Dimethylbenzene                                     | <i>m</i> -Xylene        |
| 1,2-Dimethylbenzene                                     | <i>o</i> -Xylene        |

index from the retention temperature, as indicated in Fig. 2a. To relate the programmed-temperature and the isothermal indices, one has to assume that the isothermal index does not depend on the temperature, which is only approximative. As shown in Fig. 2b, we take directly the temperature dependence of the isothermal retention index into account. Then the difference between the predicted and the measured retention temperatures derives mainly from the effect of experimental errors, such as the reproducibility of the oven temperature, the temperature gradient inside the oven, the influence of a secondary retention mechanism due to solid-gas or liquid-gas adsorption.

The validity of this approach has been studied in the simple case of complex hydrocarbon mixtures analyzed on squalane.

## EXPERIMENTAL

A model mixture containing mostly C<sub>8</sub> cyclopentanes, cyclohexanes and aromatic hydrocarbons was prepared by catalytic hydrogenation of a C<sub>8</sub> aromatic hy-

TABLE II

KOVÁTS INDICES OF COMPOUNDS EXPERIMENTALLY FOUND ( $I_F$ ) AND PUBLISHED<sup>14</sup> ( $I_P$ ) AT 50°C ON SQUALANE AS WELL AS EXPERIMENTALLY FOUND TEMPERATURE INCREMENTS OF KOVÁTS INDICES ( $\Delta I/10^\circ\text{C}$ )

| Compound No. | Abbreviation            | $I_F$ | $I_P$ | $\Delta I/10^\circ\text{C}$ |
|--------------|-------------------------|-------|-------|-----------------------------|
| 8            | 1,1,3-TriMeCyPe         | 723.7 | 723.6 | 1.91                        |
| 13           | 1-Tr-2-Cis-4-TriMeCyPe  | 741.0 | 741.1 | 1.69                        |
| 15           | 1-Tr-2-Cis-3-TriMeCyPe  | 747.8 | 747.8 | 1.65                        |
| 17           | 1,1,2-TriMeCyPe         | 763.4 | 763.2 | 2.32                        |
| 20           | 1-Cis-2-Tr-4-TriMeCyPe  | 773.0 | 773.1 | 2.18                        |
| 21           | 1-Cis-2-Cis-4-TriMeCyPe | 774.8 | 774.6 | 2.19                        |
| 22           | 1-Cis-2-Tr-3-TriMeCyPe  | 778.8 | 778.6 | 2.21                        |
| 23           | 1-Cis-3-DiMeCyHex       | 785.1 | 784.7 | 2.42                        |
| 24           | 1-Tr-4-DiMeCyHex        | 785.6 | 784.9 | 2.20                        |
| 25           | 1,1-DiMeCyHex           | 787.1 | 787.0 | 2.91                        |
| 26           | 1-MeTr-3-EtCyPe         | 787.7 | 787.6 | 1.99                        |
| 27           | 1-MeCis-3-EtCyPe        | 790.3 | 790.3 | 1.92                        |
| 28           | 1-MeTr-2-EtCyPe         | 791.2 | 790.8 | 1.90                        |
| 29           | 1-Me-1-EtCyPe           | 794.0 | 793.6 | 2.0                         |
| 31a          | 1-Cis-2-Cis-3-TriMeCyPe | 802.3 | 802.2 | —                           |
| 31           | 1-Tr-2-DiMeCyHex        | 801.8 | 801.8 | 2.75                        |
| 32           | 1-Cis-4-DiMeCyHex       | 805.0 | 805.2 | 2.61                        |
| 33           | 1-Tr-3-DiMeCyHex        | 805.4 | 805.6 | 2.67                        |
| 34           | iso-ProCyPe             | 812.0 | 812.1 | 2.47                        |
| 35           | 1-MeCis-2-EtCyPe        | 820.7 | 821.0 | 2.33                        |
| 36           | 1-Cis-2-DiMeCyHex       | 829.0 | 829.3 | 3.07                        |
| 37           | <i>n</i> -ProCyPe       | 829.9 | 830.3 | 1.84                        |
| 38           | EtBe                    | 833.3 | 834.6 | 2.62                        |
| 39           | EtCyHex                 | 834.3 | 834.3 | 2.69                        |
| 41           | <i>p</i> -Xylene        | 848.0 | 848.3 | 2.47                        |
| 42           | <i>m</i> -Xylene        | 850.2 | 850.3 | 2.20                        |
| 43           | <i>o</i> -Xylene        | 968.4 | 968.8 | 2.85                        |

drocarbon sample<sup>14</sup>. The qualitative composition of the sample is given in Table I.

This mixture was analyzed in isothermal conditions on a 180 m × 0.25 mm I.D. open-tubular glass column coated with squalane (column A), at 40, 50, 60, 69 and 82°C. Analysis of this mixture with addition of *n*-heptane, *n*-octane and *n*-nonane allowed the determination of the retention indices and their thermal coefficient (*cf.* Table II). Another squalane column, made with a 100 m × 0.25 mm I.D. stainless-steel tube (column B), was used to carry out isothermal analysis at 40, 70 and 100°C, as well as LTPGC analysis with program rates of 0.1, 0.2, 0.4, 0.6, 0.8 and 1.0°C/min.

Details about the preparation of the column are given elsewhere<sup>14</sup>.

Column A was used with a Fractovap 2350 gas chromatograph (Carlo Erba, Milan, Italy) and column B with an HP 5880A (Hewlett-Packard, Avondale, PA, U.S.A.), both equipped with flame ionization detectors and using nitrogen as carrier gas. Elution temperatures were derived from the elution time measured with a digital integrator and the known temperature program rate. Because of the relatively high vapor pressure of squalane, temperature-programmed runs had to be stopped at 100°C in order not to lose stationary phase.

Fig. 3 shows four of the chromatograms obtained with the model mixture on column A. Fig. 4 shows five chromatograms obtained with column B, in gradient elution at different program rates. It is seen that even with a mixture of hydrocarbons of relatively low polarity the elution order of some component pairs changes with temperature. Accordingly, this order changes also with program rate in LTPGC.

Also in Table II are reported values of the retention indices found in the lit-

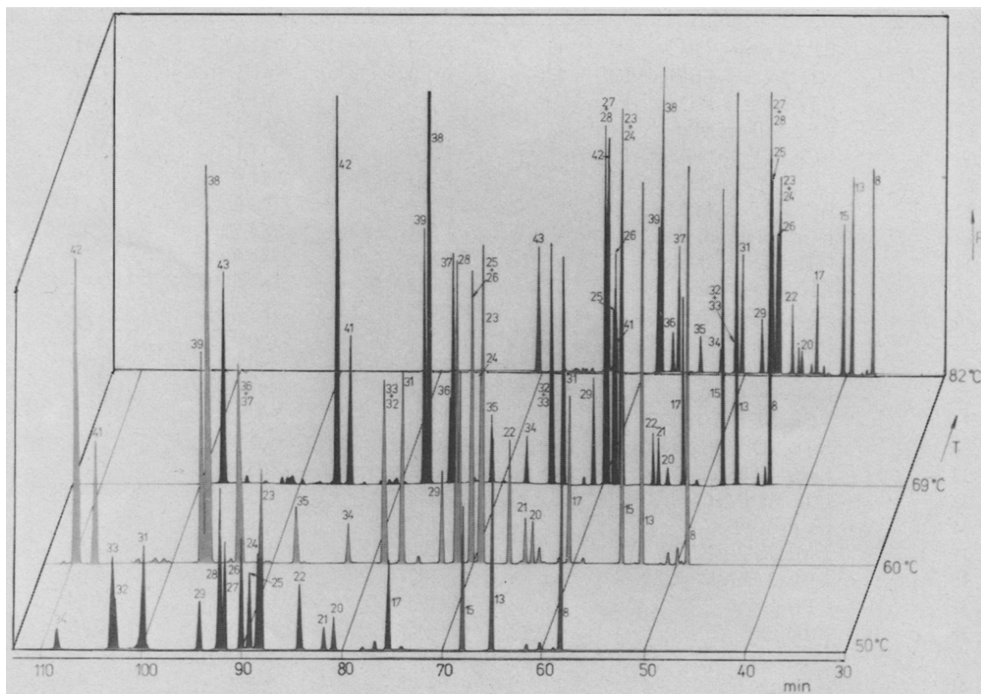


Fig. 3. Chromatograms obtained in isothermal conditions at different temperatures for a hydrocarbon mixture (*cf.* Table I). Column A, squalane. For peak identification, see compound Nos. in Table II.

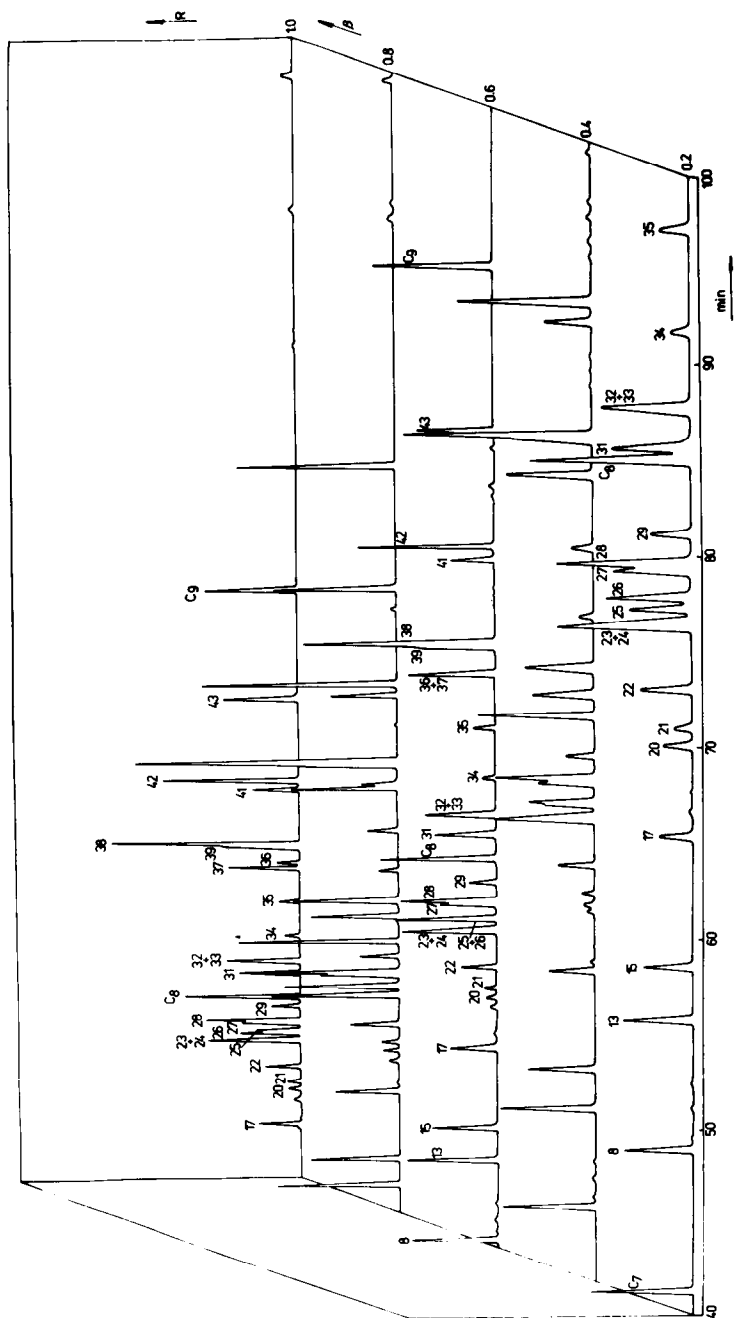


Fig. 4. Chromatograms obtained in LTPGC for a hydrocarbon mixture (*cf.*, Table II and Fig. 3). Column B, squalane. Different temperature program rates, as indicated on the right-hand-side axis. For peak identification, see compound Nos. in Table II.

erature<sup>14</sup> for the component of our model mixture. The agreement is excellent. The average difference between the two sets of experimental data is 0.03 index unit, while the standard deviation of the differences is 0.4 unit.

## RESULTS AND DISCUSSION

Eqn. 5 permits the prediction of the retention temperature in LTPGC from the retention index and its thermal coefficient (*cf.*, Table II), and from the retention temperatures of two *n*-alkanes.

An alternative graphic procedure can be used. Fig. 5 shows a plot of the retention index of 27 of the model mixture components *versus* column temperature (in isothermal conditions). Straight lines are obtained. Their slopes are equal to  $i = dI/dT$  (*cf.* eqn. 4). Fig. 5 also shows the straight lines (program lines) joining the points  $I, T_{R,z}$  for *n*-heptane, *n*-octane and *n*-nonane at various program rates (column B). If the assumption that the programmed temperature index is equal to the isothermal index at the retention temperature is valid, the retention temperature is given by the abscissa of the point at which the plot of isothermal index *versus* temperature cuts the corresponding program line. This procedure is illustrated in Fig. 6 for 1,1,2-trimethylcyclopentane. This procedure is simpler than the use of eqn. 5 (unless a modern programmable pocket calculator is available), and turns out to be as pre-

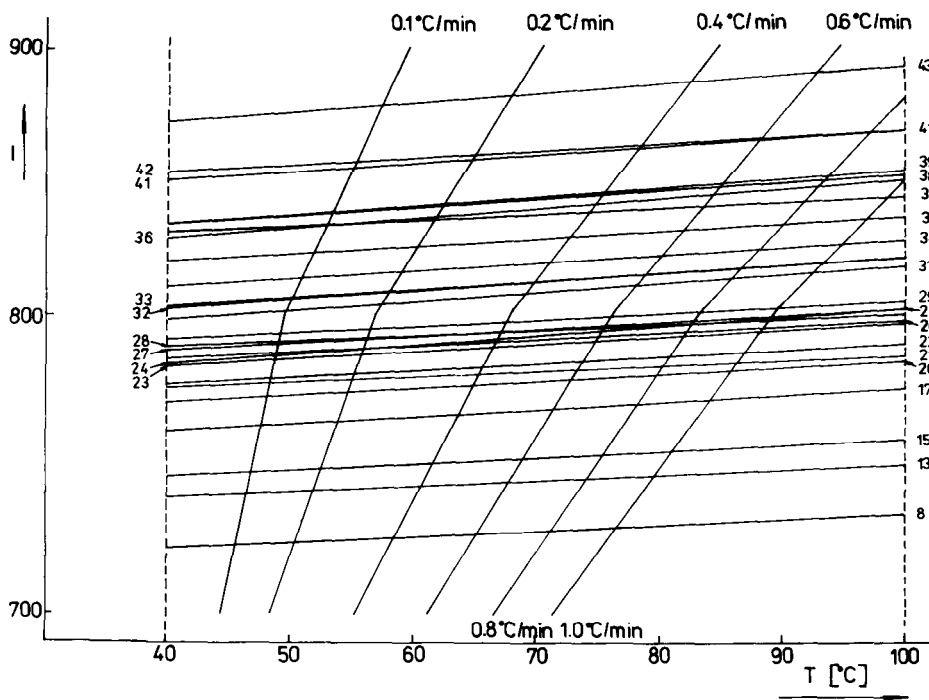


Fig. 5. Plot of isothermal retention index of hydrocarbons (*cf.* Table I) *versus* temperature and program lines of *n*-alkanes for different program rates, as indicated on these lines (*cf.* text). For compound Nos., see Table II.



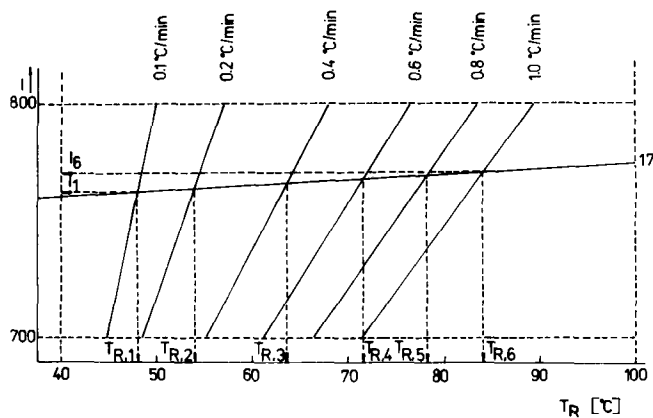


Fig. 6. Graphical procedure for the determination of the retention temperature of 1,1,2-trimethylcyclopentane (compound No. 17) at different temperature program rates.

TABLE III

KOVÁTS INDICES OF CYCLIC AND AROMATIC HYDROCARBONS AT EXPERIMENTALLY FOUND ( $I_F$ ) AND PREDICTED ( $I_{Pr}$ ) ELUTION TEMPERATURES IN LTPGC USING DIFFERENT TEMPERATURE PROGRAM RATES

| Compound No. | 0.1°C/min |          | 0.2°C/min |          | 0.4°C/min |          | 0.6°C/min |          | 0.8°C/min |          | 1.0°C/min |          |
|--------------|-----------|----------|-----------|----------|-----------|----------|-----------|----------|-----------|----------|-----------|----------|
|              | $I_F$     | $I_{Pr}$ | $I_F$     | $I_{Pr}$ | $I_F$     | $I_{Pr}$ | $I_F$     | $I_{Pr}$ | $I_F$     | $I_{Pr}$ | $I_F$     | $I_{Pr}$ |
| 8            | 722.7     | 722.7    | 723.6     | 723.7    | 725.1     | 725.2    | 726.3     | 726.5    | 727.4     | 727.6    | 728.4     | 728.7    |
| 13           | 740.4     | 740.5    | 741.3     | 741.4    | 742.7     | 742.9    | 743.9     | 744.1    | 745.0     | 745.2    | 745.9     | 746.1    |
| 15           | 747.2     | 747.3    | 748.1     | 748.2    | 749.5     | 749.7    | 750.7     | 750.9    | 751.6     | 752.0    | 752.7     | 752.9    |
| 17           | 762.6     | 762.7    | 763.9     | 764.1    | 766.1     | 766.4    | 767.9     | 768.2    | 769.4     | 769.7    | 770.8     | 771.1    |
| 21           | —         | 774.3    | 775.5     | 775.7    | 777.7     | 778.0    | 779.5     | 779.7    | 781.0     | 781.3    | 782.2     | 782.6    |
| 22           | 778.2     | 778.3    | 779.6     | 779.8    | 781.9     | 782.0    | 783.7     | 783.9    | 785.2     | 785.4    | 786.5     | 786.8    |
| 23           | 784.4     | 784.4    | 786.0     | 786.1    | 788.5     | 788.7    | 790.5     | 790.7    | 792.2     | 792.4    | 793.7     | 793.9    |
| 24           | 784.6     | 784.7    | 786.1     | 786.2    | 788.4     | 788.6    | 790.2     | 790.4    | 791.7     | 791.9    | 793.1     | 793.3    |
| 25           | 786.6     | 786.7    | 788.6     | 788.8    | 791.7     | 791.9    | 794.1     | 794.4    | 796.1     | 796.5    | 797.9     | 798.4    |
| 26           | 787.4     | 787.4    | 788.7     | 788.8    | 790.8     | 791.0    | 792.5     | 792.6    | 793.8     | 794.0    | 795.0     | 795.2    |
| 27           | 790.1     | 790.1    | 791.4     | 791.5    | 793.5     | 793.6    | 795.1     | 795.2    | 796.4     | 796.6    | 797.6     | 797.8    |
| 28           | 790.6     | 790.6    | 791.9     | 792.0    | 794.0     | 794.0    | 795.6     | 795.7    | 796.9     | 797.0    | 798.0     | 798.2    |
| 29           | 793.4     | 793.5    | 794.9     | 794.9    | 797.0     | 797.1    | 798.7     | 798.8    | 800.1     | 800.3    | 801.4     | 801.6    |
| 31           | —         | 801.7    | 803.8     | 803.9    | 806.8     | 807.1    | 809.2     | 809.6    | 811.2     | 811.6    | 813.0     | 813.5    |
| 32           | 805.2     | 805.3    | 807.2     | 807.3    | 810.1     | 810.4    | 812.4     | 812.7    | 814.3     | 814.8    | 816.0     | 816.5    |
| 33           | 805.6     | 805.7    | 807.6     | 807.8    | 810.6     | 810.9    | 813.0     | 813.3    | 814.9     | 815.4    | 816.6     | 817.2    |
| 34           | 812.2     | 812.3    | 814.2     | 814.3    | 817.0     | 817.3    | 819.2     | 819.6    | 821.0     | 821.5    | 822.6     | 823.2    |
| 35           | 821.3     | 821.5    | 823.2     | 823.4    | 826.0     | 828.7    | 828.1     | 828.5    | 829.8     | 830.3    | 831.3     | 831.9    |
| 36           | 829.9     | 830.3    | 832.5     | 833.0    | 836.3     | 836.9    | 839.1     | 839.9    | 841.5     | 842.5    | 843.5     | 844.6    |
| 37           | 830.7     | 830.9    | 832.3     | 832.5    | 834.5     | 834.8    | 836.2     | 836.5    | 837.6     | 838.0    | 838.8     | 839.2    |
| 38           | 835.3     | 835.5    | 837.6     | 837.9    | 840.8     | 841.3    | 843.3     | 843.8    | 845.3     | 846.0    | 847.0     | —        |
| 39           | 835.0     | 835.8    | 837.9     | 838.4    | 841.4     | 842.0    | 844.0     | 844.6    | 846.2     | 847.0    | —         | —        |
| 41           | 849.3     | 849.6    | 851.5     | 852.0    | 854.7     | 855.3    | 857.1     | 857.7    | 859.1     | 859.9    | —         | —        |
| 42           | 851.2     | 851.5    | 853.2     | 853.6    | 856.1     | 856.6    | 858.2     | 858.7    | 860.0     | 860.7    | —         | —        |
| 43           | 970.5     | 970.9    | 973.4     | 974.0    | 977.3     | 978.1    | 980.1     | 981.0    | 982.5     | —        | —         | —        |

cise. The error is about 0.2°C, corresponding to a precision in the determination of the retention index of 0.1 unit, which is better than the reproducibility of the retention index measurement on the columns used.

A comparison between retention indices measured in LTPGC and derived by the graphic procedure is given in Table III. The largest deviation is 3.3°C, and is obtained for the compound which has the larger thermal coefficient *i*. Not surprisingly, there is a good correlation between the magnitude of the difference between calculated and observed temperature and the value of the thermal coefficient (*cf.* Table III).

Finally, in Table IV we compare the retention temperatures measured in LTPGC to those derived from eqn. 5. The largest difference is 1.1 unit, which is not large compared to the precision of the determination, if we take into account that in the case of this compound (No. 36), which is the one with the larger thermal coefficient (*ca.* 1.5), there are also larger sources of error in the determination of its

TABLE IV

ELUTION TEMPERATURES OF CYCLIC AND AROMATIC HYDROCARBONS AND C<sub>7</sub>-C<sub>9</sub> *n*-ALKANES ON SQUALANE FOUND EXPERIMENTALLY ON COLUMN A (*F*) AND PREDICTED FROM EQN. 5 ON COLUMN B (*P*) IN LTPGC USING DIFFERENT TEMPERATURE PROGRAM RATES

| Compound No.   | 0.1°C/min |          | 0.2°C/min |          | 0.4°C/min |          | 0.6°C/min |          | 0.8°C/min |          | 1.0°C/min |          |
|----------------|-----------|----------|-----------|----------|-----------|----------|-----------|----------|-----------|----------|-----------|----------|
|                | <i>F</i>  | <i>P</i> | <i>F</i>  | <i>P</i> | <i>F</i>  | <i>P</i> | <i>F</i>  | <i>P</i> | <i>F</i>  | <i>P</i> | <i>F</i>  | <i>P</i> |
| 8              | 45.3      | 45.5     | 49.8      | 50.3     | 57.6      | 58.3     | 64.3      | 65.1     | 70.1      | 71.0     | 75.3      | 76.5     |
| 13             | 46.1      | 46.5     | 51.2      | 52.0     | 59.7      | 60.5     | 66.8      | 67.7     | 73.0      | 74.0     | 78.4      | 79.5     |
| 15             | 46.4      | 46.8     | 51.8      | 52.5     | 60.5      | 61.6     | 67.8      | 69.0     | 73.1      | 75.4     | 79.6      | 80.9     |
| 17             | 47.2      | 47.8     | 53.1      | 53.9     | 62.6      | 63.8     | 70.3      | 71.5     | 76.9      | 78.2     | 82.7      | 84.1     |
| 21             | —         | 48.5     | 54.3      | 55.1     | 64.2      | 65.4     | 72.2      | 73.2     | 79.0      | 80.4     | 84.9      | 86.4     |
| 22             | 48.2      | 48.5     | 54.7      | 55.4     | 64.8      | 65.6     | 72.9      | 73.8     | 79.7      | 80.8     | 85.7      | 87.0     |
| 23             | 48.6      | 48.8     | 55.3      | 55.8     | 65.7      | 66.5     | 74.0      | 74.9     | 81.0      | 82.0     | 87.1      | 88.1     |
| 24             | 48.6      | 48.9     | 55.3      | 55.9     | 65.7      | 66.6     | 74.0      | 74.9     | 81.0      | 82.0     | 87.1      | 88.1     |
| 25             | 48.7      | 49.0     | 55.5      | 56.1     | 66.1      | 66.9     | 74.4      | 75.4     | 81.4      | 82.8     | 87.6      | 89.0     |
| 26             | 48.8      | 49.0     | 55.6      | 56.1     | 66.1      | 66.9     | 74.4      | 75.2     | 81.4      | 82.3     | 87.4      | 88.4     |
| 27             | 49.0      | 49.1     | 55.9      | 56.2     | 66.5      | 67.0     | 74.9      | 75.6     | 81.9      | 82.7     | 88.0      | 88.9     |
| 28             | 49.1      | 49.2     | 56.0      | 56.3     | 66.6      | 67.1     | 75.0      | 75.6     | 82.0      | 82.7     | 88.1      | 88.9     |
| 29             | 49.2      | 49.3     | 56.3      | 56.6     | 67.1      | 67.6     | 75.5      | 76.1     | 82.7      | 83.3     | 88.8      | 89.8     |
| 31             | —         | 49.8     | 57.2      | 57.5     | 68.3      | 69.2     | 77.0      | 78.2     | 84.3      | 85.8     | 90.6      | 92.6     |
| 32             | 50.1      | 50.2     | 57.6      | 58.1     | 68.9      | 69.8     | 77.7      | 78.9     | 85.0      | 86.6     | 91.3      | 93.4     |
| 33             | 50.1      | 50.3     | 57.6      | 58.2     | 68.9      | 69.8     | 77.7      | 78.9     | 85.0      | 86.6     | 91.3      | 93.4     |
| 34             | 50.6      | 51.0     | 58.4      | 59.1     | 70.0      | 71.2     | 78.8      | 80.3     | 86.2      | 88.1     | 92.6      | 94.8     |
| 35             | 51.4      | 52.0     | 59.5      | 60.5     | 71.4      | 82.9     | 80.4      | 82.1     | 87.9      | 89.9     | 94.4      | 96.9     |
| 36             | 52.1      | 53.1     | 60.5      | 62.0     | 72.9      | 74.9     | 82.0      | 84.5     | 89.9      | 92.9     | 96.4      | 99.7     |
| 37             | 52.2      | 53.1     | 60.7      | 61.8     | 72.9      | 74.4     | 82.0      | 83.6     | 89.7      | 91.9     | 96.2      | 98.6     |
| 38             | 52.6      | 53.5     | 61.3      | 62.5     | 73.8      | 75.5     | 83.1      | 85.1     | 90.9      | 93.4     | 97.4      | —        |
| 39             | 52.6      | 53.5     | 61.3      | 62.6     | 73.8      | 75.6     | 83.1      | 85.3     | 90.9      | 93.8     | 97.4      | —        |
| 41             | 53.9      | 55.2     | 63.1      | 64.9     | 76.1      | 78.4     | 85.6      | 88.1     | 93.6      | 97.1     | —         | —        |
| 42             | 54.2      | 55.5     | 63.4      | 65.1     | 76.5      | 78.6     | 86.1      | 88.4     | 94.1      | 97.2     | —         | —        |
| 43             | 56.1      | 57.5     | 66.1      | 68.1     | 79.8      | 82.6     | 89.8      | 92.9     | 98.0      | —        | —         | —        |
| C <sub>7</sub> | 44.1      | —        | 48.3      | —        | 55.2      | —        | 61.1      | —        | 66.5      | —        | 71.3      | —        |
| C <sub>8</sub> | 49.8      | —        | 57.1      | —        | 67.9      | —        | 76.3      | —        | 83.3      | —        | 89.3      | —        |
| C <sub>9</sub> | 59.9      | —        | 70.7      | —        | 85.0      | —        | 94.9      | —        | —         | —        | —         | —        |

retention time or temperature as it is difficult to separate it from its neighbours (Nos. 37 and 38) as can be seen in Figs. 2-4.

#### CONCLUSION

Provided the retention indices and their thermal coefficients can be measured in the temperature range in which the compounds studied are eluted in LTPGC, it is possible to predict with an acceptable precision the retention temperatures of hydrocarbons. The deviation remains of the order of the precision of the determination of the indices using efficient open tubular columns. Further work is necessary to assess the importance of the deviation with more polar compounds which have a larger thermal coefficient.

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