

CHREV. 127

## EVALUATION OF PROCEDURES FOR THE ESTIMATION OF DEAD TIME

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### 1. INTRODUCTION

The presentation of gas chromatographic data in a precise manner is important for comparative inter-laboratory studies and therefore several methods of presentation have been introduced. Irrespective of the retention scheme used, a knowledge of the column dead time,  $t_m$ , is necessary because retention times are dependent on this dead time, which is a function of the flow-rate used and the void volume of the experimental apparatus. Therefore the retention times of components must be corrected by subtracting the dead time from them, giving the adjusted retention time,  $t'_R$ .

Adjusted retention times (which are still dependent on several variables, such as flow-rate, pressure drop, liquid phase and column temperature) are then used in a variety of ways to obtain a method of presentation that is dependent only on the column temperature and the stationary phase used.

### 2. METHODS OF PRESENTATION OF RETENTION DATA

Several methods of presentation have been introduced, but the most widely used are relative retention data<sup>1</sup> and the retention index system introduced by Kováts<sup>2</sup>.

Relative retention is presented as a volume or time relative to that of some standard compound, while Kováts retention indices are calculated by numerical

interpolation, by means of the following general equation proposed by Kováts<sup>2</sup>:

$$I = 100 \left( n + \frac{\log t'_r - \log t'_n}{\log t'_{n+1} - \log t'_n} \right) \quad (1)$$

where  $t'_R$  is the corrected retention time of the substance,  $t'_n$  and  $t'_{n+1}$  are the corrected retention times of two  $n$ -alkanes ( $t'_n < t'_r < t'_{n+1}$ ),  $I$  is the retention index and  $n$  is the carbon number of the first alkane used.

Kováts retention indices can also be calculated by graphical interpolation within the linear relationship between  $\log t'_R$  and the number of carbon atoms<sup>3</sup>,  $n_c$ , according to

$$\log t'_R = aI + b \quad (2)$$

where  $a$  and  $b$  are constants and Kováts retention indices for  $n$ -alkanes are defined as  $100Z$  for every temperature and every liquid phase ( $Z$  is the carbon number of the  $n$ -alkane).

However, as can be seen from eqns. 1 and 2, the corrected retention time and thus the column dead times, must be known.

### 3. MEASUREMENT OF COLUMN DEAD TIME

Dead times are determined experimentally by the injection of air, methane or some other substance that is not significantly retarded by the column<sup>4</sup>. A flame-ionization detector does not ordinarily produce a signal with air and the use of methane introduces a slight error as it is retarded to some extent. Hilmi<sup>4</sup> found that when the carrier gas is presaturated with a low-volatility organic solvent, negative air peaks can be readily detected with a hydrogen flame-ionization detector. By measuring the retention time of the air peak and making allowance for the vapour pressure of the solvent, the column dead time can be determined. The method, which suffers from considerable experimental difficulties, requires large injections of air (of the order of 1 cm<sup>3</sup>) and has not found wide acceptance.

### 4. CALCULATION OF COLUMN DEAD TIME

The inability of the flame-ionization detector to produce an air peak and the questionable accuracy of methane retention as a measure of the dead time have led to the development of several methods for calculating the dead time.

#### A. Classical methods

Of the many classical methods reported, the most widely used include the following.

(1) Linearization of a logarithmic plot for homologous  $n$ -alkanes by graphical trial and error, as reported by Evans and Smith<sup>5</sup>. This method was time consuming and was soon superseded by mathematical treatment of the alkane lines.

(2) The use of a linear relationship derived by Peterson and Hirsch<sup>6</sup>, which

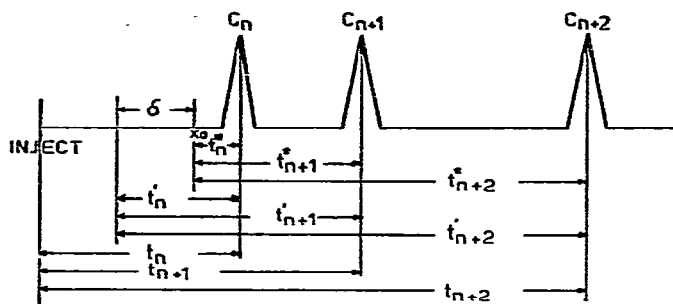


Fig. 1. Schematic chromatogram.  $t$  = uncorrected retention time;  $t^*$  = retention time relative to origin  $x_0$ ;  $t'$  = corrected retention time.

requires three evenly spaced homologues. This method is illustrated in Fig. 1, where three consecutive alkane peaks are used. An arbitrary reference origin ( $x_0$ ) is used and distances are determined from this origin. If the origin corresponds to the true column dead time, then  $\delta = 0$ . However, in the general case the distance to a given peak is not measured from the true carrier gas but from the origin. In this case the following equation is established:

$$t'_n = t_n^* + \delta \quad (3)$$

The linear relationship between retention time and carbon number is now shown by eqns. 4-6:

$$\log(t_n^* + \delta) \propto n \quad (4)$$

when the three adjacent homologues are used,

$$\frac{t_{n+1}^* + \delta}{t_n^* + \delta} = \frac{t_{n+2}^* + \delta}{t_{n+1}^* + \delta} \quad (5)$$

or

$$\delta = \frac{t_{n+1}^{*2} - t_n^* t_{n+2}^*}{t_{n+2}^* + t_n^* - 2t_{n+1}^*} \quad (6)$$

Thus, one can measure from any arbitrary point ( $x_0$ ) to the peaks of three homologues and record the distances as  $t_n^*$ ,  $t_{n+1}^*$  and  $t_{n+2}^*$ , and solve for  $\delta$  and measure from this arbitrary origin to the point which should correspond to the column dead time,  $t_m$ . If  $\delta$  is positive,  $t_m$  precedes  $x_0$ ; if  $\delta$  is negative,  $t_m$  follows  $x_0$ .

Peterson and Hirsch<sup>6</sup> further modified their method by suggesting the use of the second peak as the origin of reference. In this case,  $t_{n+1}^* = 0$ . Then, the distance measured between the peaks of homologues 2 and 1 multiplied by that between homologues 2 and 3, divided by their sum ( $t_n^*$  is a negative number in this formulation), is the distance from homologue 2 to  $t_m$ .

(3) The method of Peterson and Hirsch<sup>6</sup> was modified by Gold<sup>7</sup> who described, a method that did not require the restriction of using equally spaced homologues. The

method is based on the fact that as  $\log(t - t_m)$  is proportional to the carbon number,  $n$ , then

$$n = m \log(t - t_m) + k \quad (7)$$

If the difference between the carbon numbers of the first homologues is given by  $\Delta n_{1,2} = n_2 - n_1$ , then

$$\Delta n_{1,2} = m[\log(t_2 - t_m) - \log(t_1 - t_m)] \quad (8)$$

where  $t_1$  and  $t_2$  are uncorrected retention times of the first and second peaks. Then,

$$m = \frac{\Delta n_{1,2}}{\log(t_2 - t_m) / (t_1 - t_m)} \quad (9)$$

Eqn. 8 can be solved for  $t_m$  by taking exponentials, giving

$$t_m = \frac{t_2 - e^{(\Delta n_{1,2}/m)} t_1}{1 - e^{(\Delta n_{1,2}/m)}} \quad (10)$$

Eqns. 9 and 10 are simultaneous and can be solved by the method of successive approximations, but such a method is extremely tedious.

Gold<sup>7</sup> also suggested a graphical procedure by using the relationship shown in eqn. 9 for  $\Delta n_{1,3}$ , which leads to two equations for  $m$ . Various values of  $t_m$  are assumed and plotted against the resulting value of  $m$  for each of the two equations. The common solution is the point at which the two lines intersect. The method has little to recommend it and offers little improvement over the trial and error procedure of Evans and Smith<sup>5</sup>. The method of Gold has been adapted for use on a Hewlett-Packard HP65 programmable pocket calculator by Ebel and Kaiser<sup>8</sup>.

(4) Hafferkamp<sup>9</sup> and Hansen and Andresen<sup>10</sup> have proposed a method that uses equally spaced homologues as proposed by Petersen and Hirsch<sup>6</sup>. However, they eliminated the need for choosing an arbitrary origin. The method simply uses the uncorrected retention times to give a direct calculation of  $t_m$ , as shown in the equation

$$t_m = \frac{t_{n+2} \cdot t_n - t_{n+1}^2}{t_{n+2} + t_n - 2t_{n+1}} \quad (11)$$

Reference to eqn. 6 shows the comparison between this method and that proposed earlier by Peterson and Hirsch<sup>6</sup>.

(5) Recently, a further method similar to that of Gold has been described<sup>11</sup>, in which the retention times of three successive homologues are used to estimate  $t_m$ . The relationship shown in eqn. 12 can be expressed in the form of eqn. 13.

$$\log(t_n - t_m) = an + b \quad (12)$$

$$t_n - t_m = e^{(an+b)} \quad (13)$$

Hence, for two successive homologues  $n = n$  and  $n = n + 1$ , the expressions shown in eqns. 14–19 are derived.

$$t_n = t_m + e^{(an+b)} \quad (14)$$

and

$$t_{n+1} = t_m + e^{[a(n+1)+b]} \quad (15)$$

Therefore,

$$\Delta t_{n,n+1} = t_{n+1} - t_n = e^{(an+b)} (e^a - 1) \quad (16)$$

Similarly, for the pair  $n = n + 1$  and  $n = n + 2$

$$t_{n+2} = t_m + e^{a(n+2)+b} \quad (17)$$

Hence,

$$\Delta t_{n+1,n+2} = t_{n+2} - t_{n+1} = e^{a(n+1)+b} (e^a - 1) \quad (18)$$

and

$$\frac{\Delta t_{n+1,n+2}}{\Delta t_{n,n+1}} = e^a \quad (19)$$

Therefore, by using the differences in retention times for three consecutive homologues,  $a$  can be evaluated from the equation

$$a = \log \left( \frac{\Delta t_{n+1,n+2}}{\Delta t_{n,n+1}} \right) \quad (20)$$

Having evaluated  $a$ ,  $b$  is evaluated using eqn. 16 (or 17), which is rewritten as

$$b = \log \left( \frac{\Delta t_{n,n+1}}{e^a - 1} \right) - an \quad (21)$$

Then  $t_m$  is calculated from

$$t_m = t_n - e^{(an+b)} \quad (22)$$

For all pairs of homologues employed a consistent result confirms the validity.

The method does not provide any advantage in accuracy over that of Hansen and Andresen<sup>10</sup> and involves more effort in calculation.

### *B. Statistical and iterative methods*

The previous classical methods were limited in accuracy as only three alkanes could be used or a graphical trial and error was needed. Therefore, several more sophisticated methods have been developed.

(1) The method of Grobler and Balizs<sup>12</sup>, which uses two successive linear regressions. Although the derivation of the expressions used is not given in the paper, the following derivation gives the required equations (eqns. 23–35).

Restating eqn. 2, we have

$$\log t'_R = bZ_i + c \quad (23)$$

Thus

$$\log (t_R - t_m) = bZ_i + c \quad (24)$$

$$t_R - t_m = e^{bZ_i + c} \quad (25)$$

$$t_{R+1} - t_m = e^{bZ_{i+1} + c} \quad (26)$$

But  $Z_{i+1} = Z_i + 1$ . Therefore, the previous equation becomes

$$t_{R+1} - t_m = e^{b(Z_i+1) + c} \quad (27)$$

Subtraction of eqn. 25 from eqn. 27 gives

$$(t_{R+1} - t_m) - (t_R - t_m) \quad (28)$$

which

$$= e^{b(Z_i+1) + c} - e^{bZ_i + c} \quad (29)$$

$$= e^{bZ_i} e^b e^c - e^{bZ_i} e^c \quad (30)$$

$$= e^c e^{bZ_i} e^{(b-1)} \quad (31)$$

Therefore,

$$t_{R+1} - t_R = A e^{bZ_i} \quad (32)$$

where

$$A = e^c e^{(b-1)} \quad (33)$$

Taking logarithms, we obtain

$$\log(t_{R+1} - t_R) = \log A + bZ_i \quad (34)$$

Therefore, a linear regression on eqn. 34 of  $\log(t_{R+1} - t_R)$  against  $Z_i$  will give  $b$  as the slope. We then obtain

$$b = \frac{(n-1) \sum_{i=Z_1}^{Z_n} Z_i \log [t_{R(i+1)} - t_{R(i)}] - \sum_{i=Z_1}^{Z_n-1} Z_i \sum_{i=Z_1}^{Z_n-1} \log [t_{R(i+1)} - t_{R(i)}]}{(n-1) \sum_{i=Z_1}^{Z_n-1} Z_i^2 - \left( \sum_{i=Z_1}^{Z_n-1} Z_i \right)^2} \quad (35)$$

This is eqn. 1 in the paper by Grobler and Baliz<sup>12</sup> (it should be noted that there is a mistake in that paper; the  $n$  in the numeration should be  $n-1$  as in eqn. 35 above).

Now, from eqn. 2,

$$t_R = t_m + e^{bz} e^c \quad (36)$$

$$t_R = t_m + Aq^z \quad (37)$$

where

$$A = e^c \text{ and } q = e^b \quad (38)$$

We can perform another linear regression on  $t_R$  against  $q^z$  and  $t_m$  will be the intercept. Therefore, we obtain

$$t_m = \frac{\sum_{i=Z_1}^{Z_n} q^{Z_i} \sum_{i=Z_1}^{Z_n} t_{R(i)} q^{Z_i} - \sum_{i=Z_1}^{Z_n} q^{2Z_i} \sum_{i=Z_1}^{Z_n} t_{R(i)}}{\left( \sum_{i=Z_1}^{Z_n-1} q^{2Z_i} \right)^2 - n \sum_{i=Z_1}^{Z_n-1} q^{2Z_i}} \quad (39)$$

This is eqn. 4 in the paper by Grobler and Baliz<sup>12</sup>.

Finally,  $c$  can be found from a linear regression on eqn. 39 of  $\log t'_R$  against  $Z_i$ . This gives

$$c = \frac{\sum_{i=Z_1}^{Z_n} \log t'_{R(i)} - b \sum_{i=Z_1}^{Z_n} Z_i}{n} \quad (40)$$

This is eqn. 5 in the paper by Grobler and Baliz<sup>12</sup>.

Thus, eqns. 35, 39 and 40 give the dead time,  $t_m$ , and the slope,  $b$ , and intercept,  $c$ , of the plot of the logarithm of the adjusted retention times against carbon number, where:

$t_{R(i)}$  = uncorrected retention time of the  $i$ th  $n$ -alkane;

$t'_{R(i)}$  = corrected retention time of the  $i$ th  $n$ -alkane;

$Z_i$  = carbon number of the  $i$ th  $n$ -alkane;

$q$  = antilog  $b$ ;

$n$  = number of  $n$ -alkanes used.

Thus, the retention index for any compound can be calculated from the equation

$$I = 100 (\log t'_R - c)/b \quad (41)$$

(2) The method of Guardino *et al.*<sup>13</sup> requires an iteration to be carried out on  $T_m$ , while a least-squares fit is applied to  $b$  and  $c$ . The best values of  $T_m$ ,  $b$  and  $c$  are determined by minimizing the sum of squares of the difference between the known and the calculated  $I$  values. Fig. 2 shows a flow diagram, where UPLIM and LOWLIM are the upper and lower limits, respectively, of the sum of squares of the deviation,

$T_m$  is the dead time,  $INC$  is the increment in the dead time,  $IC$  is the calculated Kováts retention index,  $SUM$  is the sum of squares of the deviations,  $TR$  is the unadjusted retention times of the compounds,  $I$  is the known Kováts retention index (100Z, where  $Z$  is the carbon number) and  $PREC$  is the precision to which the answer is required.

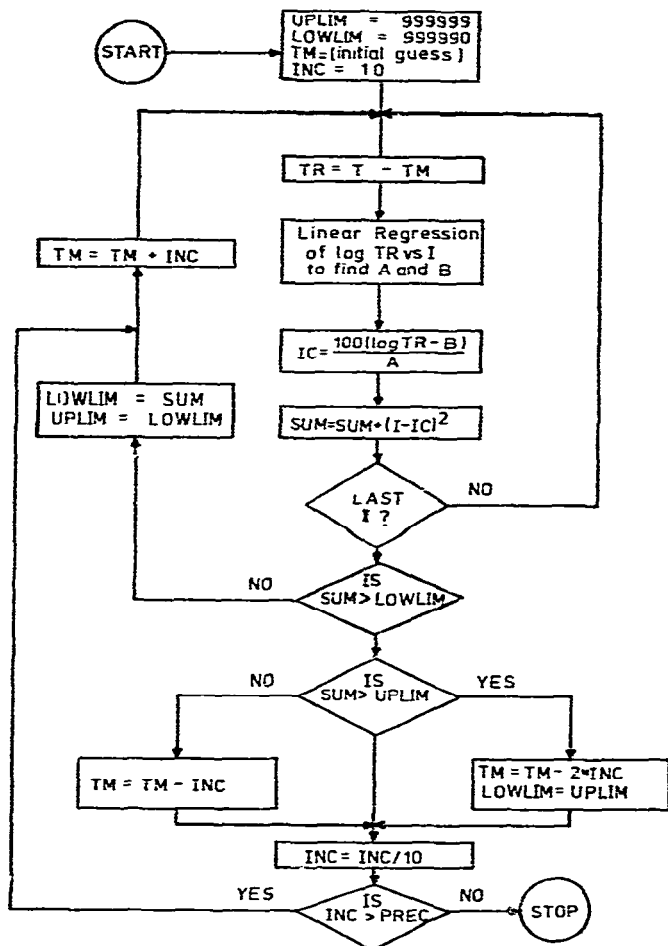


Fig. 2. Flow chart for calculation of mathematical dead time by Guardino *et al.*'s method<sup>13</sup>.

(3) The non-linear least-squares estimation of  $t_m$ ,  $b$  and  $c$  simultaneously<sup>14,15</sup> by the use of numerical minimization<sup>16</sup>. The objective function that is minimized is the sum of squares of the differences between the known and calculated  $I$  values for the series of  $n$ -alkanes.

## 5. EVALUATION OF PROCEDURES FOR THE CALCULATION OF DEAD TIME

### A. Comparison of calculated dead time with methane retention

The use of methane retention as an estimate has been criticized<sup>16,17,18</sup>. If one



accepts the linearity of the plot of the logarithm of the corrected retention times of homologous series *versus* carbon number, then methane as the first *n*-alkane homologues must have a finite corrected retention time. That is, methane provides a poor estimate of dead time, being the sum of dead time plus the retention of methane. Further, if one accepts the evidence that the use of any homologous series can provide the same estimate of dead time<sup>19</sup>, then the logical conclusion is that the retention of methanol and similar oxygenated C<sub>1</sub> compounds should be a good estimate of dead time.

The controversy surrounding the comparative merits of methane injection and mathematical dead time estimates has recently been raised by Sharples and Vernon<sup>20</sup>. They pointed out inaccuracies in mathematical dead time estimates when the method of Peterson and Hirsch<sup>6</sup> is applied to retention times for *n*-alkanes measured by a stop-watch. They have shown that when stop-watch measurement of retention is employed, the retentions of air and methane are identical for polar and non-polar phases over a wide temperature range.

The errors attributed to the method of Peterson and Hirsch<sup>6</sup> are caused in two ways. Firstly, the method is one using the analysis of three equally spaced points and therefore the centre point is weighted excessively and so small errors in retention times measurement (particularly with the second alkane) leads to gross errors in  $t_m$ . This error in the estimation procedure can be overcome by the more statistically sound approach of Grobler and Baliz<sup>12</sup>, which weights all points equally. The second source of error is that of measuring retention times. Sharples and Vernon<sup>20</sup> suggest that the reason that other workers<sup>10,18</sup> measured methane retentions in excess of the calculated dead time was because of errors in measurement of retention times. However, Smith *et al.*<sup>15</sup> found similar excess retentions of methane in a study in which a computer was used to measure the retention time of the *n*-alkanes and in which a proved method of statistical estimation of  $t_m$  was employed<sup>12</sup>.

Smith *et al.*<sup>15</sup> calculated the dead time for six alkanes (C<sub>5</sub>-C<sub>10</sub>) and over a series of 18 injections obtained a mean estimate of  $t_m$  of 54.0 sec with a standard deviation of 0.5 sec. The same number of air and methane injections gave retentions of 55.1 and 55.5 sec, respectively, both with a standard deviation of 0.7 sec. In all instances the calculated dead time was less than both the air and methane injections.

Recently, Wainwright *et al.*<sup>21</sup> used a mixture of methane and C<sub>5</sub>-C<sub>9</sub> *n*-alkanes in nitrogen to compare the mathematical dead time with methane retention. This method, in which methane and the *n*-alkanes are injected simultaneously onto the column, gives an accurate comparison under identical operating conditions. Calculated dead times and methane retention were measured on polar (OV-25) and non-polar (SE-30) columns at several temperatures and carrier gas flow-rates. In all instances the methane retention was in excess of the calculated value of  $t_m$ . The results of this study are consistent with those of Garcia Dominguez *et al.*<sup>17</sup>, who found that methane was retained on various chromatographic columns of different polarity for the temperature range 100-180°. The results are also consistent with those of an earlier study<sup>3</sup> in which it was observed that the use of methane retention time as an estimate of column dead time produced curvature in the logarithmic plot of the *n*-alkanes. The solubility of methane in liquid phases has been shown elsewhere<sup>22</sup>.

### B. Comparison of methods of computing mathematical dead time

The classical methods described earlier in general use the uncorrected retention times of three equally spaced homologues to calculate the retention times. A recent paper<sup>11</sup> compared methane retention with a calculation method that uses only two alkanes. Data were presented for the uncorrected retention times of  $C_1$ - $C_4$  *n*-alkanes together with the retention times calculated by eqns. 14-19. These values are presented in Table 1 for two different column packings. The retention data for  $C_2$ - $C_4$  *n*-alkanes have been used here to calculate  $t_m$  by the method of Peterson and Hirsch<sup>6</sup>. It is evident from Table 1 that both methods of calculation give essentially the same dead times, all providing estimates of  $t_m$  that are less than methane retention. The error in using methane retention is highlighted with the non-polar (squalane) stationary phase, where the difference is approximately 7% compared with a value of 0.5% for dinonyl phthalate.

TABLE 1  
COMPARISON OF DIFFERENT METHODS OF ESTIMATING DEAD TIMES  
Data from ref. 11.

| <i>n</i> -Alkane | Squalane |        |         |            |             | Dinonyl phthalate |        |         |            |             |
|------------------|----------|--------|---------|------------|-------------|-------------------|--------|---------|------------|-------------|
|                  | $t_R$    | $t'_R$ | $t_m^*$ | $t_m^{**}$ | $t_m^{***}$ | $V_R$             | $V'_R$ | $V_m^*$ | $V_m^{**}$ | $V_m^{***}$ |
| $C_1$            | 21.5     | 1.5    | 20.0    | 20.2       | 19.8        | 19.05             | 0.25   | 18.95   | 18.95      | 18.64       |
| $C_2$            | 26.5     | 6.4    | 20.0    |            |             | 19.68             | 0.75   | 18.95   |            |             |
| $C_3$            | 46.5     | 26.0   | 20.1    |            |             | 21.10             | 2.15   | 18.95   |            |             |
| $C_4$            | 129.5    | 109.1  | 20.4    |            |             | 25.29             | 6.34   | 18.95   |            |             |

\* Estimated by the method of ref. 11.

\*\* Estimated by the method of ref. 6 (for  $C_2$ - $C_4$ ).

\*\*\* Estimated by the method of ref. 12 (for  $C_1$ - $C_3$ ).

Haken *et al.*<sup>14</sup> made a comparison of the different methods for calculating dead times. These results are summarised in Table 2. It is evident that the three iterative methods described above give essentially the same dead times (to the fourth significant figure). The values of  $t_m$  calculated by the classical methods of Peterson and Hirsch<sup>6</sup> and Gold<sup>7</sup> differ from the iterative methods by less than 0.2 sec in 60 sec.

TABLE 2  
COMPARISON OF DIFFERENT METHODS FOR CALCULATING DEAD TIMES<sup>14</sup>

Methods: A = non-linear regression using Simplex; B = method of Grobler and Balizs<sup>12</sup>; C = method of Guardino *et al.*<sup>13</sup>; D = method of Peterson and Hirsch<sup>6</sup>; E = method of Gold<sup>7</sup>.

| Run | Dead time (sec) |       |       |       |       |
|-----|-----------------|-------|-------|-------|-------|
|     | A               | B     | C     | D     | E     |
| 1   | 59.79           | 59.77 | 59.74 | 59.95 | 59.95 |
| 2   | 60.58           | 60.50 | 60.53 |       |       |
| 3   | 62.91           | 63.04 | 62.86 |       |       |
| 4   | 69.74           | 69.75 | 69.73 | 69.62 | 69.62 |

In a subsequent paper<sup>15</sup> a more detailed study of the iterative procedures was performed following the comments of Gassiot *et al.*<sup>23</sup>. The three methods were written in Fortran IV and run on a Cyber 72-26 digital computer to ensure maximum accuracy.

Seven series of calculation were conducted using the retention times of the following alkanes for each of the 46 sets of data: (a) C<sub>5</sub>-C<sub>7</sub>, (b) C<sub>5</sub>-C<sub>8</sub>, (c) C<sub>6</sub>-C<sub>9</sub>, (d) C<sub>7</sub>-C<sub>10</sub>, (e) C<sub>5</sub>-C<sub>9</sub>, (f) C<sub>6</sub>-C<sub>10</sub> and (g) C<sub>5</sub>-C<sub>10</sub>.

Flexible Simplex and the method of Guardino *et al.*<sup>13</sup> both use an iterative technique and thus require an objective function to be defined which is then minimized. In a previous paper<sup>14</sup> we used the objective function suggested by Guardino *et al.*<sup>13</sup> which is the sum of squares of the differences between the known and calculated Kováts retention indices as shown in the equation

$$\text{Objective function} = \Sigma(I - I_c)^2 \quad (42)$$

where  $I$  is the known and  $I_c$  is the calculated Kováts retention index.

However, as  $I$  is defined as 100 times the carbon number,  $Z$ , for  $n$ -alkanes, its value is known, and it is thus the independent variable. The objective function should, however, be based on the dependent variable, which in this instance is the retention time,  $t_R$ . This would suggest the use of the sum of squares of the differences between the experimental and calculated retention times as defined in the equation

$$\text{Objective function} = \Sigma(t_R - t_{Rc})^2 \quad (43)$$

where  $t_R$  is the experimental and  $T_{Rc}$  is the calculated retention time. However, this function weights those alkanes with longer retention times and which are the least accurate, as discussed in a previous paper<sup>14</sup>. Therefore, to overcome this difficulty and to take account of the logarithmic nature of our model (eqn. 23), an objective function based on the sum of squares of the difference between the logarithms of the experimental and calculated connected retention times was chosen, as shown in eqn. 23:

$$\text{Objective function} = \Sigma(\log t'_R - \log t'_{Rc})^2 = \Sigma \left( \log \frac{t_R - t_m}{t_{Rc} - t_m} \right)^2 \quad (44)$$

where  $t_R$  = the experimental retention time,  $t_{Rc}$  = the calculated retention time and  $t_m$  = the calculated dead time.

The difference between the objective functions shown in eqns. 43 and 44 can be seen by reducing each to a simpler form, eqns. 45 and 46 respectively:

$$\Sigma(t_R - t_{Rc})^2 = \Sigma(t'_R - e^{bZ+c})^2 \quad (45)$$

$$\Sigma \left( \log \frac{t_R - t_m}{t_{Rc} - t_m} \right)^2 = \Sigma(\log t'_R - \log e^{bZ+c})^2 = \Sigma(\log t'_R - bZ - c)^2 \quad (46)$$

Table 3 compares the three objective functions studied, where it is apparent that the objective function used by Guardino *et al.*<sup>13</sup> gives identical dead times to the Simplex method to five significant figures. When the objective work function is sub-

TABLE 3

COMPARISON OF DEAD TIMES CALCULATED BY THE ITERATIVE METHODS USING DIFFERENT OBJECTIVE FUNCTIONS<sup>15</sup>

| Run | $(I - I_c)^2$                    |                  |                               | $(t_{Rc} - t_R)^2$ |                               | $\ln\left(\frac{t_R - t_m}{I_{Rc} - t_m}\right)$ |                               |
|-----|----------------------------------|------------------|-------------------------------|--------------------|-------------------------------|--|-------------------------------|
|     | Grobler and Balizs <sup>12</sup> | Flexible Simplex | Guardino et al. <sup>13</sup> | Flexible Simplex   | Guardino et al. <sup>13</sup> | Flexible Simplex                                 | Guardino et al. <sup>13</sup> |
| 1   | 53.735                           | 53.772           | 53.772                        | 54.351             | 53.936                        | 53.769   | 53.735                        |
| 2   | 55.001                           | 55.067           | 55.067                        | 55.277             | 55.117                        | 55.067   | 55.001                        |
| 3   | 54.664                           | 54.480           | 55.480                        | 54.386             | 54.494                        | 54.478   | 54.664                        |
| 4   | 54.982                           | 55.008           | 55.008                        | 55.136             | 55.037                        | 55.007   | 54.982                        |
| 5   | 54.677                           | 54.626           | 54.626                        | 54.692             | 54.650                        | 54.625   | 54.677                        |
| 6   | 54.282                           | 54.255           | 54.255                        | 54.036             | 54.200                        | 54.255   | 54.282                        |
| 7   | 53.626                           | 53.814           | 53.814                        | 54.295             | 53.916                        | 53.812   | 53.626                        |
| 8   | 53.784                           | 53.924           | 53.924                        | 53.994             | 53.918                        | 53.923   | 53.784                        |
| 9   | 54.259                           | 54.181           | 54.180                        | 53.880             | 54.110                        | 54.180   | 54.259                        |
| 10  | 54.228                           | 54.250           | 54.250                        | 54.259             | 54.247                        | 54.250   | 54.228                        |
| 11  | 54.147                           | 53.969           | 53.969                        | 53.916             | 53.916                        | 53.968   | 54.147                        |
| 12  | 53.547                           | 53.670           | 53.670                        | 53.934             | 53.723                        | 53.670   | 53.547                        |
| 13  | 53.836                           | 53.837           | 53.837                        | 54.201             | 53.936                        | 53.835   | 53.836                        |
| 14  | 53.234                           | 53.404           | 53.404                        | 53.916             | 53.512                        | 53.402   | 53.234                        |
| 15  | 53.958                           | 53.904           | 53.904                        | 53.716             | 53.864                        | 53.903   | 53.958                        |
| 16  | 53.546                           | 53.573           | 53.573                        | 53.376             | 53.504                        | 53.546   | 53.546                        |
| 17  | 53.911                           | 53.834           | 53.834                        | 53.725             | 53.813                        | 53.833   | 53.911                        |
| 18  | 53.889                           | 53.871           | 53.871                        | 53.885             | 53.881                        | 53.871   | 53.889                        |

stituted in both methods, it is evident that the method of Guardino *et al.* gives identical dead time estimations to those of Grobler and Balizs<sup>12</sup>.

## 6. PROBLEMS OF ACCURACY OF MATHEMATICAL DEAD TIME ESTIMATION

Haken *et al.*<sup>14</sup> reported inaccuracies in the estimation of  $t_m$  using the method of Grobler and Balizs.<sup>12</sup> When determining  $I$  values on a 12 ft.  $\times$   $1/4$  in. column packed with 10% squalane and operating at 120°, it became apparent that small differences (of the order of 2 sec) in uncorrected retention times of  $C_7$ - $C_{10}$  alkanes led to large differences (up to 10 sec) in  $t_m$  values. Typical results are given in Table 4.

The principle of the calculation of mathematical dead time involves the extrapolation of the least-squares line through the logarithms of the corrected retention

TABLE 4

VARIATION OF DEAD TIMES FOR RUNS USING  $C_7$ - $C_{10}$  *n*-ALKANES<sup>14</sup>

| Run | Uncorrected retention time (sec) |       |       |          | Calculated dead time (sec) |
|-----|----------------------------------|-------|-------|----------|----------------------------|
|     | $C_7$                            | $C_8$ | $C_9$ | $C_{10}$ |                            |
| 1   | 182                              | 291   | 497   | 887      | 59.77                      |
| 2   | 182                              | 291   | 497   | 889      | 60.50                      |
| 3   | 182.5                            | 290   | 495.5 | 884      | 63.04                      |
| 4   | 184                              | 290   | 494.5 | 888.5    | 69.75                      |

TABLE 5  
EFFECT OF SMALL PERTURBATIONS IN RETENTION TIMES<sup>16</sup>

| <i>n</i> -Alkane | Experimental data    |                      | Perturbed data   |                      |                  |
|------------------|----------------------|----------------------|------------------|----------------------|------------------|
|                  | Retention time (sec) | Retention time (sec) | Difference (sec) | Retention time (sec) | Difference (sec) |
| C <sub>5</sub>   | 86                   | 84                   | -2               | 88                   | +2               |
| C <sub>6</sub>   | 110                  | 109                  | -1               | 111                  | +1               |
| C <sub>7</sub>   | 156                  | 157                  | +1               | 155                  | -1               |
| C <sub>8</sub>   | 245                  | 247                  | +2               | 243                  | -2               |
| Dead time (sec)  | 60.13                | 55.60                | -4.53            | 64.18                | +4.05            |
| C <sub>7</sub>   | 182                  | 180                  | -2               | 184                  | +2               |
| C <sub>8</sub>   | 291                  | 290                  | -1               | 292                  | +1               |
| C <sub>9</sub>   | 497                  | 498                  | +1               | 496                  | -1               |
| C <sub>10</sub>  | 887                  | 889                  | +2               | 885                  | -2               |
| Dead time (sec)  | 59.79                | 55.60                | -4.19            | 63.98                | +4.17            |

times to zero carbon number. Therefore, small changes in the slope of this line will lead to large variations in calculated values of  $t_m$  and hence to large variations in  $I$ -values<sup>18</sup>. In order to quantify the effect of small systematic changes in retention times of the *n*-alkanes, small perturbations (of the order of 1 or 2 sec) were made to uncorrected retention data for two sets of alkanes, C<sub>5</sub>-C<sub>8</sub> and C<sub>7</sub>-C<sub>10</sub>. These results are presented in Table 5. It is obvious from these results that small changes in the alkane retention times lead to large changes in the dead time value.

Of the several stationary phases investigated, squalane was the only one to give significant differences in dead time values. Table 6 presents typical values of dead time for an OV-7 column that was coupled to the squalane column via a splitter. The results show that although the retention times of the alkanes show variations of similar magnitude on both columns, the differences in dead time for OV-7 are significantly lower. The mean dead time for squalane over a large number of determinations was approximately 60 sec and the value for OV-7 was approximately 67 sec. The greater inaccuracy in the dead time determination for squalane appeared to be associated with the relatively long retention times of the C<sub>7</sub>-C<sub>10</sub> alkanes. Therefore, C<sub>5</sub>-C<sub>8</sub> alkanes were used and Table 7 lists the dead time values calculated over a 6-h period of Kováts retention index calculations. It can be seen that the variation in dead time is not significant.

TABLE 6  
RETENTION AND DEAD-TIME MEASUREMENTS MADE ON SQUALANE AND OV-7 COLUMNS FOR C<sub>7</sub>-C<sub>10</sub> *n*-ALKANES<sup>16</sup>

| Column   | Uncorrected retention time (sec) |                |                |                 | Dead time (sec) |
|----------|----------------------------------|----------------|----------------|-----------------|-----------------|
|          | C <sub>7</sub>                   | C <sub>8</sub> | C <sub>9</sub> | C <sub>10</sub> |                 |
| Squalane | 182                              | 291            | 497            | 887             | 59.77           |
|          | 184                              | 290            | 494.5          | 888.5           | 69.75           |
| OV-17    | 113.5                            | 150.5          | 216.5          | 335.5           | 66.93           |
|          | 113                              | 150            | 215            | 332.5           | 65.52           |

TABLE 7  
EFFECT ON MATHEMATICAL DEAD TIME WHEN C<sub>5</sub>-C<sub>8</sub> n-ALKANES ARE USED<sup>14</sup>

| Uncorrected retention time (sec) |                |                |                | Dead time (sec) |
|----------------------------------|----------------|----------------|----------------|-----------------|
| C <sub>5</sub>                   | C <sub>6</sub> | C <sub>7</sub> | C <sub>8</sub> |                 |
| 85                               | 108            | 152            | 236.5          | 59.92           |
| 85.5                             | 109            | 153            | 239            | 59.88           |
| 85.5                             | 108.5          | 153            | 238.5          | 60.70           |
| 86.0                             | 110            | 156.5          | 246            | 60.21           |
| 86                               | 110            | 156            | 244.5          | 59.93           |
| 86                               | 110            | 156            | 245            | 60.10           |

It is apparent from the results in Tables 6 and 7 that significant differences in dead time result from using alkanes that have long retention times. Longer retention times obviously mean a greater extrapolation and a larger error. Therefore, it is desirable to use low-molecular-weight alkanes, provided that the retention times can be measured with sufficient accuracy.

Recently, Sharples and Vernon<sup>20</sup> have shown similar inaccuracies in mathematical dead times calculated by the method of Peterson and Hirsch<sup>6</sup>. The hypothetical system having small variations in uncorrected retention times of three consecutive n-alkanes is illustrated in Table 8. It can be seen that a small error in the measurement of the retention time of the second alkane can produce an error of 3.5 sec in the estimation of a dead time of 30 sec. This calculation points to the weakness of the method of Peterson and Hirsch when crude methods of measuring retention times are used.

TABLE 8  
HYPOTHETICAL SYSTEM HAVING A 30.0-sec DEAD TIME SHOWING THE EFFECTS OF SMALL ERRORS IN A PEAK TIMING ON THE DEAD TIME AS CALCULATED BY THE METHOD OF PETERSON AND HIRSCH<sup>6</sup> (REF. 20)

| n-Alkane                     | <i>t<sub>R</sub></i><br>(sec) | Error<br>(sec) | <i>t<sub>R</sub></i><br>(sec) | Error<br>(sec) | <i>t<sub>R</sub></i><br>(sec) | Error<br>(sec) | <i>t<sub>R</sub></i><br>(sec) | Error<br>(sec) |
|------------------------------|-------------------------------|----------------|-------------------------------|----------------|-------------------------------|----------------|-------------------------------|----------------|
| C <sub>8</sub>               | 87.0                          | 0              | 87.0                          | 0              | 87.0                          | 0              | 86.0                          | -1             |
| C <sub>8+1</sub>             | 127.5                         | 0              | 128.0                         | +0.5           | 126.2                         | -1.3           | 128.0                         | +0.5           |
| C <sub>5+2</sub>             | 196.8                         | 0              | 196.8                         | 0              | 198.6                         | +1.8           | 195.3                         | -1.5           |
| <i>t<sub>m</sub></i> (calc.) | 30.0                          |                | 26.5                          |                | 40.7                          |                | 16.3                          |                |

Guberska<sup>18,24</sup> has made several studies of the determination of dead time. In his second study<sup>18</sup> he found that the retention time of methane is greater than the dead time calculated by the method of Hansen and Andresen<sup>10</sup>. However, he found that the precision of estimating *t<sub>m</sub>* by the same method<sup>10</sup> was less than the measurement of methane retention, particularly at high temperatures. He therefore devised a scheme to estimate *t<sub>m</sub>* using the retention time of methane.

Assuming that the retention time of methane in the stationary phase is dependent on the amount of the stationary phase, without regard to the type of phase, and

using experimentally obtained retention data, Guberska<sup>18</sup> developed the following empirical equation to determine dead time from the total retention time of methane:

$$t_m = t_{\text{CH}_4} - \left( \frac{t_{\text{CH}_4} M}{163} \right) \quad (47)$$

where  $M$  (wt.-%) is the amount of stationary phase in the column packing.

Table 9 compares the results of dead time determination using the Hansen and Andresen method (column 4) with dead time results (column 5) calculated according to eqn. 47 from the total retention time of methane (column 3). The absolute errors of dead time determination using eqn. 47 in relation to the dead time obtained with the Hansen and Andresen method (column 7), and the corresponding percentage errors (column 9), are also given.

In order to verify the proposed eqn. 47, results found in the literature for the dead time and retention time of methane (rows 1 and 2; columns 3 and 4), which were obtained under different conditions than those used in this work, were also used in comparison.

It can be seen from the error comparison (columns 6-9) that the values of  $\bar{t}'_m$  calculated by eqn. 47 are much closer to  $\bar{t}_m$  than to  $\bar{t}_{\text{CH}_4}$ .

The method of Guberska<sup>18</sup>, whilst having no fundamental basis does make some attempt to correct methane retention to take into account the fact the methane is retained on stationary phases. However, the assumption that the correction term is independent of the type of stationary phase is unlikely to be valid. Further work on this type of modification of methane retention as an estimate of  $t_m$  should take into account both the polarity of the stationary phase and its amount.

## 7. CALCULATION OF ADJUSTED RETENTION TIME WITHOUT ESTIMATION OF DEAD TIME

In two recent papers, Sevcik<sup>25</sup> and Sevcik and Löwentap<sup>26</sup> have described the accurate calculation of adjusted retention time by using the ratio,  $A$ , of the time differences for neighbouring  $n$ -alkanes in a homologous series. It is claimed that the procedures used to indicate the time of injection have a marked effect on gross retention times and this causes errors in  $t_m$ , either measured or calculated, even if the gas chromatographic conditions remain unchanged.

The concept of the calculation of adjusted retention time is based on the fact that the adjusted retention time is related only to the path of the compound through the column and not to contributions caused by the gas chromatograph or recording system. The adjusted retention time is therefore related to a non-retarded substance for which  $I = 0$ .

The method is best illustrated by reference to Fig. 3. The adjusted retention time of any peak in a chromatogram can be expressed as the sum of the time differences between neighbouring peaks. Assuming that  $t'_{n+1}$ ,  $t'_{n-1}$  and  $t_{n+1}$ ,  $t_n$ ,  $t_{n-1}$  are the adjusted retention times and gross retention times of  $n$ -alkanes with carbon numbers  $n+1$ ,  $n$  and  $n-1$ , respectively, then

$$A_{n+1} = t'_{n+1} - t'_n = t_{n+1} - t_n \quad (48)$$

$$A_n = t'_n - t'_{n-1} = t_n - t_{n-1} \quad (49)$$

TABLE 9  
 COMPARISON OF DEAD TIMES OBTAINED BY THE METHODS OF HANSEN AND ANDRESEN<sup>10</sup> AND GUBERSKA<sup>16</sup> USING THE  
 RETENTION TIME OF METHANE<sup>10</sup>

| Column                                 | Column temperature (°C) | $t_{CH_4}(n)$ (min) | $t_m(n)$ (min) | $t_m$ (min) | $t_{CH_4} - t_m$ (min) | $t_m - t_m$ (min) | $f_m$                        |                         |
|--|-------------------------|---------------------|----------------|-------------|------------------------|-------------------|------------------------------|-------------------------|
|  |                         |                     |                |             |                        |                   | $(t_{CH_4} - t_m) \cdot 100$ | $(t_m - t_m) \cdot 100$ |
| 10% Squalane (length 2 m)              | 50                      | 5.70 (4)            | 5.40 (4)       | 5.35        | +0.30                  | -0.05             | +5.55                        | -0.9                    |
|  | 130                     | 11.10 (2)           | 10.60 (2)      | 10.40       | +0.50                  | -0.20             | +4.59                        | -1.83                   |
| 10% Carbowax 20M (length 3 m)          | 140, 154,               | 12.78 (4)           | 11.23 (4)      | 11.05       | +1.55                  | -0.18             | +13.80                       | -1.60                   |
|  | 160, 174                |                     |                |             |                        |                   |                              |                         |
| 20% DC-200 silicone oil (length 2.7 m) | 140, 154,               | 12.69 (5)           | 11.35 (5)      | 11.13       | +1.33                  | -0.23             | +11.60                       | -2.02                   |
|  | 160, 174,               | 12.78 (3)           | 11.22 (3)      | 11.21       | +1.56                  | -0.01             | +14.00                       | -0.09                   |
|  | 140 → 234               |                     |                |             |                        |                   |                              |                         |
|  | 140                     | 12.69 (10)          | 10.81 (10)     | 11.13       | +1.88                  | +0.32             | +17.40                       | +2.96                   |
|  | 140 → 234               | 12.47 (10)          | 10.85 (10)     | 10.94       | +1.62                  | +0.09             | +14.70                       | +0.83                   |
|  | at 4°/min               |                     |                |             |                        |                   |                              |                         |



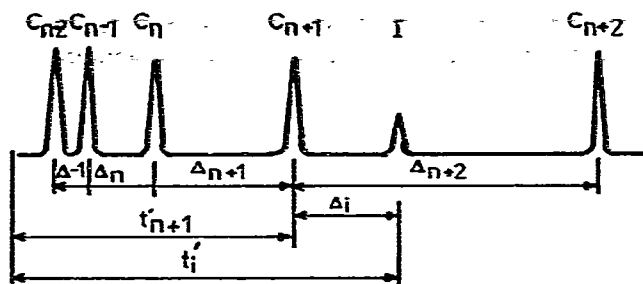


Fig. 3. Schematic chromatogram.  $t'$  = adjusted retention time;  $\Delta_n$  = time difference between the  $n$ -alkanes in row;  $\Delta_i$  = time difference between the peaks not in row<sup>25</sup>.

The adjusted retention time,  $t'_{n+1}$ , can then be expressed by

$$t'_{n+1} = \Delta_1 + \Delta_2 + \Delta_3 + \dots + \Delta_n + \Delta_{n+1} \quad (50)$$

where  $\Delta_1$  is the time difference between the elution of a substance with  $I = 0$  and one with  $I = 100$ , etc.

From eqn. 50, the adjusted retention time can be calculated if all of the time differences are known. Then,

$$t_i = \sum_0^I \Delta_x \quad (51)$$

Experimentally, it was found that the ratio of neighbouring time differences,  $\Delta_{n \pm x}$  in a homologous series is constant. Therefore,

$$\Delta_{n+x} = A \Delta_{n+x-1} \quad (52)$$

Hence a graph of the logarithm of the time difference,  $\log \Delta_x$ , versus  $I_x$  is a straight line. Assuming eqn. 52 is valid for all members of the homologous series from  $I = 1$ , we can calculate the time differences,  $\Delta_x$ , between all peaks until we reach the start of separation where  $I = 0$ . It therefore follows that

$$\Delta_1 = \Delta_n A^{-(n-1)} \quad (53)$$

$$\Delta_2 = \Delta_n A^{-(n-2)} \quad (54)$$

$$\Delta_3 = \Delta_n A^{-(n-3)} \quad (55)$$

$$\Delta_n = \Delta_n A^{-(n-n)} = \Delta_n \quad (56)$$

$$\Delta_{n+1} = \Delta_n A^{-[n-(n+1)]} = \Delta_n A \quad (57)$$

$$\Delta_{n+2} = \Delta_n A^2 \quad (58)$$

$$\Delta_{n+x} = \Delta_n A^x \quad (59)$$

By summing these time differences, the equation for the adjusted retention time of the peak due to a molecule containing  $n$  carbon atoms can be written as

$$t'_n = \Delta_n [A^{-(n-1)} + A^{-(n-2)} + \dots + 1] \quad (60)$$

or

$$t'_n = \Delta_n \left[ \frac{A^{n+1} - A}{A^{n+1} - A^n} \right] \quad (61)$$

which is expressed for ease of calculation as

$$t'_n = \Delta_n \left[ \frac{1 - \left(\frac{1}{A}\right)^n}{1 - \left(\frac{1}{A}\right)} \right] \quad (62)$$

The validity of the method was determined by injection of a mixture of  $C_7$ - $C_{12}$   $n$ -alkanes and the results are presented in Table 10. It is interesting that this method, which is not related to factors other than retention in the column, predicts a finite retention for methane.

TABLE 10  
CALCULATION OF ADJUSTED RETENTION TIME USING A MIXTURE OF  $n$ -ALKANES<sup>25</sup>

| $C_n$ | $I$  | $\Delta$ | $A^*$  | $\log \Delta$ | $\log A$ | $t'$   |
|-------|------|----------|--------|---------------|----------|--------|
| 12    | 1200 |          |        |               |          | 656.78 |
|       |      | 336.5    |        | 2.5270        |          |        |
| 11    | 1100 |          | 2.0644 |               | 0.3148   | 320.10 |
|       |      | 163.0    |        | 2.2122        |          |        |
| 10    | 1000 |          | 2.0375 |               | 0.3091   | 155.95 |
|       |      | 80.0     |        | 1.9031        |          |        |
| 9     | 900  |          | 2.0513 |               | 0.3120   | 75.95  |
|       |      | 39.0     |        | 1.5911        |          |        |
| 8     | 800  |          | 2.0526 |               | 0.3123   | 36.95  |
|       |      | 19.0     |        | 1.2788        |          |        |
| 7     | 700  |          |        |               |          | 17.95  |
|       |      | 9.26     |        | 0.96675       |          |        |
| 6     | 600  |          |        |               |          | 8.69   |
|       |      | 4.52     |        | 0.65470       |          |        |
| 5     | 500  |          |        |               |          | 4.17   |
|       |      | 2.20     |        | 0.34265       |          |        |
| 4     | 400  |          |        |               |          | 1.97   |
|       |      | 1.07     |        | 0.03060       |          |        |
| 3     | 300  |          |        |               |          | 0.89   |
|       |      | 0.52     |        | -0.28145      |          |        |
| 2     | 200  |          |        |               |          | -0.37  |
|       |      | 0.25     |        | -0.59350      |          |        |
| 1     | 100  |          |        |               |          | 0.12   |
|       |      | 0.12     |        | -0.90555      |          |        |
| 0     | 0    |          |        |               |          | 0      |

\*  $\bar{A} = 2.0514$ .

The procedure described above allows the calculation of the adjusted retention times of a series of  $n$ -alkanes using the time differences between three successive  $n$ -alkanes. As the calculation is related to  $I = 0$ , the calculated adjusted retention times serve as fixed points on the time axis of the chromatogram. In relation to these points, the difference  $\Delta I$  can be measured and the adjusted retention time, and hence Kováts retention index,  $I$ , can be calculated for a substance as illustrated in Fig. 3.

In a later paper, Sevčík and Löwentap<sup>26</sup> produced further evidence for the validity of the method. They computed adjusted retention times based on four  $n$ -alkanes using four methods, as shown in Table 11. The methods of Sevčík<sup>25</sup> and Peterson and Hirsch<sup>6</sup> for  $C_5$ - $C_7$   $n$ -alkanes give excellent agreement. However, the use of methane for an estimate of  $t_m$  gives low values of  $t'$ , as expected. The use of  $C_6$ - $C_8$   $n$ -alkanes when calculating  $t_m$  gives higher values of adjusted retention times. This result is not unexpected, as Haken *et al.*<sup>14</sup> have shown that the choice of  $n$ -alkanes having high retention times can lead to errors in the estimation of  $t_m$ .

TABLE 11

RETENTION TIMES AND THEIR ESTIMATED STANDARD DEVIATIONS CALCULATED BY METHODS 1-4\* FOR FOUR  $n$ -ALKANES<sup>26</sup>

The data are mean values of five repeated measurements.

| $C_n$ | $t$ (sec)      | $t'$ (sec)     |                |                |                |
|-------|----------------|----------------|----------------|----------------|----------------|
|       |                | 1              | 2              | 3              | 4              |
| 5     | 180.54 ± 0.195 | 46.04 ± 0.207  | 48.30 ± 0.283  | 50.44 ± 0.681  | 48.03 ± 0.205  |
| 6     | 242.04 ± 0.358 | 107.56 ± 0.358 | 109.82 ± 0.477 | 111.96 ± 0.618 | 109.66 ± 0.205 |
| 7     | 381.94 ± 0.699 | 247.44 ± 0.677 | 249.70 ± 0.778 | 251.84 ± 0.850 | 249.04 ± 0.390 |
| 8     | 696.58 ± 1.915 | 562.08 ± 1.914 | 564.34 ± 2.060 | 566.48 ± 1.660 | 564.25 ± 1.324 |

\* Methods:

- 1 = methane retention as estimate of  $t_m$ ;
- 2 = method of Peterson and Hirsch<sup>6</sup> using  $C_5$ - $C_7$   $n$ -alkanes;
- 3 = method of Peterson and Hirsch<sup>6</sup> using  $C_6$ - $C_8$   $n$ -alkanes;
- 4 = method of Sevčík<sup>25</sup> for adjusted retention times.

## 8. CONCLUSIONS AND RECOMMENDATIONS

The method used for estimation of mathematical dead time is dependent on the method of measurement of uncorrected retention times and the precision required in the calculated retention indices. Many laboratories now have minicomputers and microprocessors for data acquisition. These instruments can be used to determine  $t_m$  most accurately by using at least four  $n$ -alkanes and the calculation method of Grobler and Balizs<sup>12</sup>.

However, if stop-watch timing of peaks or measurement of chart distances is used, thereby involving off-line calculations, the methods using three consecutive  $n$ -alkanes can be employed. These involve the direct calculation method first described by Peterson and Hirsch<sup>6</sup> or the inferential method of Sevčík<sup>25</sup> and Sevčík and Löwentap<sup>26</sup>.

The use of the retention of methane as an estimate of  $t_m$  must be severely questioned, particularly for highly non-polar columns. Should this method be adopted,

some correction based on the amount<sup>18</sup> and nature of the stationary phase should be made.

## 9. SUMMARY

In order to determine the exact retention of compounds in gas chromatographic studies some method of determining the column dead time must be employed. This paper reviews direct measurement techniques using methane injection as well as mathematical determination of dead-time from retention data for *n*-alkanes. A critical evaluation of these procedures is made along with recommendations concerning the choice of evaluation method to be adopted by the chromatographer.

## REFERENCES

- 1 A. T. James and A. J. P. Martin, *Biochem. J.*, 50 (1952) 679.
- 2 E. Kováts, *Helv. Chim. Acta*, 41 (1958) 1915.
- 3 H. Groenendijk and A. W. C. van Kemenade, *Chromatographia*, 1 (1968) 472.
- 4 A. K. Hilmi, *J. Chromatogr.*, 17 (1965) 407.
- 5 M. B. Evans and J. F. Smith, *J. Chromatogr.*, 9 (1962) 147.
- 6 M. L. Peterson and J. Hirsch, *J. Lipids Res.*, 1 (1959) 132.
- 7 H. J. Gold, *Anal. Chem.*, 34 (1962) 174.
- 8 S. Ebel and R. E. Kaiser, *Chromatographia*, 7 (1974) 696.
- 9 M. Hafferkamp, in R. Kaiser (Editor), *Chromatographie in der Gasphase*, Teil II, Bibliographisches Institut, Mannheim, 1966, p. 93.
- 10 H. L. Hansen and K. Andresen, *J. Chromatogr.*, 34 (1968) 245.
- 11 W. K. Al-Thamir, J. H. Purnell, C. A. Wellington and R. J. Laub, *J. Chromatogr.*, 173 (1979) 388.
- 12 A. Grobler and G. Balizs, *J. Chromatogr. Sci.*, 12 (1974) 57.
- 13 X. Guardino, J. Albaigés, G. Firpo, R. Rodriguez-Viñals and M. Gassiot, *J. Chromatogr.*, 118 (1976) 13.
- 14 J. K. Haken, M. S. Wainwright and R. J. Smith, *J. Chromatogr.*, 133 (1977) 1.
- 15 R. J. Smith, J. K. Haken and M. S. Wainwright, *J. Chromatogr.*, 147 (1978) 65.
- 16 J. A. Nelder and R. Mead, *Comput. J.*, 7 (1965) 308.
- 17 J. A. Garcia Dominguez, J. Garcia Nunoz, E. Fernandez Sanchez and M. J. Moleva, *J. Chromatogr. Sci.*, 15 (1977) 520.
- 18 J. Guberska, *Chem. Anal. (Warsaw)*, 19 (1974) 161.
- 19 J. R. Ashes, S. C. Mills and J. K. Haken, *J. Chromatogr.*, 166 (1978) 391.
- 20 W. E. Sharples and F. Vernon, *J. Chromatogr.*, 161 (1978) 83.
- 21 M. S. Wainwright, J. K. Haken and D. Srisukh, *J. Chromatogr.*, 179 (1979) 160.
- 22 V. A. Ezrets and M. S. Vigdergauz, *Chromatographia*, 9 (1976) 205.
- 23 M. Gassiot, X. Guardino, J. Albaigés, G. Firpo and R. Rodriguez-Viñals, *J. Chromatogr.*, 147 (1978) 540.
- 24 J. Guberska, *Chem. Anal. (Warsaw)*, 18 (1973) 1059.
- 25 J. Ševčík, *J. Chromatogr.*, 135 (1977) 183.
- 26 J. Ševčík and M. S. H. Löwentap, *J. Chromatogr.*, 147 (1978) 75.