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CALCULATION OF THE RETENTION TIME AND PEAK WIDTH FOR THE PURPOSE OF OPTIMIZED GAS CHROMATOGRAPHIC ANALYSIS

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SUMMARY

Relationships are derived for calculating the retention time and peak width at the column outlet for any temperature programme in the column oven. The derivation of the relationships is based on the measurement of the retention times and peak widths at at least three isothermal chromatographic runs and on the determination of the time constant of the column with a given packing. The time constant is determined from measured values of retention time and peak width for a temperature programme with one temperature rise. A comparison is made of the measured and calculated retention times and peak widths for different temperature programmes.

INTRODUCTION

A major task in the determination of the optimum parameters of the gas chromatographic separation (temperature programme, programme of the carrier gas flow-rate) of a certain mixture on a given column is the calculation of the retention time and the peak width at half-height for any component of the mixture being chromatographed.

The problems of temperature programming in gas chromatographic separations have been dealt with from different viewpoints by a number of workers. Harris and Habgood[1] presented relationships for calculating the retention time with a linear temperature rise and investigated the effect of a temperature rise on the resolution of two neighbouring peaks. De Wet and Pretorius[2] studied the effect of temperature on plate height, Halász and Heine[3] and Giddings[4] investigated the effect of temperature programming on the time of analysis and Giddings[5,6], Scott[7], and others investigated the effect of temperature on the column efficiency and separability. In their consideration of the effect of temperature, the authors usually proceeded from a knowledge of the composition of the column packing and a knowledge of the individual components of the mixture being analysed.

This paper presents a method of calculating the retention time and peak width at a constant carrier gas flow-rate and with any temperature programme. The computation algorithm is derived independent of the column packing and the mixture analysed. The algorithm is based on data under isothermal conditions and the determination of the time constant of a packed column.

APPROXIMATION OF THE DEPENDENCE OF RETENTION TIME AND PEAK WIDTH ON TEMPERATURE

When measuring on a given column the retention time and peak width at half-height of the nth component of a sample mixture ($t_{R,n}$, $s_{R,n}$) at different constant temperatures we obtain the dependences

$$\begin{aligned} t_{R,n} &= t_{R,n}(T) \\ s_{R,n} &= s_{R,n}(T) \end{aligned} \qquad (1)$$

From the values of $t_{R,n}$ and $s_{R,n}$ measured at m different temperatures $T_1, \ldots, T_m$ we determine approximation functions having the form

$$\begin{aligned} t_{A,n}(T) &= A_{tn}e^{B_{tn}/T} + C_{tn} \\ s_{A,n}(T) &= A_{sn}e^{B_{sn}/T} + C_{sn} \end{aligned} \qquad (2)$$

The constants A_{tn}, B_{tn}, A_{sn} and B_{sn} are calculated by the least-squares method, and C_{tn} and C_{sn} to the values so obtained are sought for iteratively so as to obtain minimum values of the sums

$$SM_t = \sum_{i=1}^{m} (t_{R,n} - t_{A,n})^2$$

$$SM_s = \sum_{i=1}^{m} (s_{R,n} - s_{A,n})^2 \qquad (3)$$

CALCULATION OF THE RETENTION TIME USING A TEMPERATURE PROGRAMME

Let us consider temperature programme shown in Fig. 1, consisting of three isothermal intervals: $\langle 0, t_1 \rangle$ at a temperature T_1, $\langle t_2, t_3 \rangle$ at a temperature $T_2 = T_3$, $\langle t_4, t_5 \rangle$ at a temperature T_4, a temperature rise interval $\langle t_1, t_2 \rangle$ at a rise rate D_r (°C/min) and a temperature fall interval $\langle t_3, t_4 \rangle$ at a fall rate D_f (°C/min). Any temperature programme for a chromatographic analysis can be obtained by a combination of the intervals of the above basic course. A temperature course as shown in

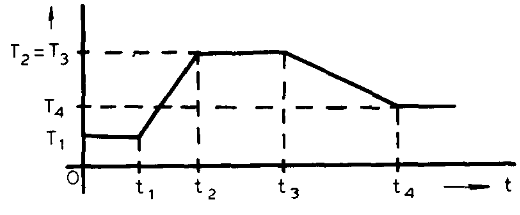

Fig. 1. A general temperature programme.

Fig. 1 can easily be set in the column oven. However, more important is the fact that both the column and its packing introduce a delay in the system; for the sake of simplicity, let us consider a delay action of the first order with a time constant H.

The time course of temperature $T(t)$ inside the column differs from that set by the temperature programme, $T_p(t)$, and is given by the equation

$$T(t) = T_N + (T_N - T_S)(1 - e^{-t/H}) + D[t - H(1 - e^{-t/H})] \tag{4}$$

where T_S is the true temperature inside the column at the end of the preceding temperature interval, T_N is the temperature set for the column oven at the beginning of the interval and D is the temperature rise and/or fall rate set at the beginning of the interval. The temperature course inside the column within the given interval depends on the magnitude and sign of $T_N - T_S$ and D.

Let us consider a column of length L. It is possible to calculate from the found approximation functions $t_{A,n}(T)$ the velocity $v_{A,n}(T)$ at which the centre of the zone of the nth component of the mixture chromatographed migrates down the column at a constant temperature T:

$$v_{A,n}(T) = L/t_{A,n}(T) \tag{5}$$

The zone centre in the column travels a distance Δl_n within the time interval $\Delta t - \Delta l_n = [L/t_{A,n}(t)]\Delta t$.

The distance that the zone centre of an nth component covers on its way down the column can be expressed by the integral relationship

$$L = \int_0^{t_{AP,n}} v_{A,n}[T(t)]\,dt = \int_0^{t_{AP,n}} \frac{L}{t_{A,n}[T(t)]}\,dt \tag{6}$$

where $t_{AP,n}$ is the calculated retention time of the component. For $T(t)$ = constant, *i.e.*, in the case of an isothermal analysis, the velocity $v_{A,n}[T(t)]$ is constant and there holds

$$L = \int_0^{t_{AP,n}} \frac{L}{t_{A,n}(T)}\,dt = \frac{L}{t_{A,n}(T)}\,t_{AP,n} \tag{7}$$

i.e., the retention time is given by

$$t_{AP,n} = t_{A,n}(T) \tag{8}$$

For the purpose of numerical calculations we transform the continuous variable t to the equidistant one:

$$t = m\Delta t; \qquad m = 0, 1, 2, 3, \ldots \tag{9}$$

Eqn. 4 can be rearranged to

$$T(m) = t_{\mathrm{N}} + (T_{\mathrm{N}} - T_{\mathrm{S}}\,(1 - \mathrm{e}^{-m\Delta t/H}) + D\,[t - H(1 - \mathrm{e}^{-m\Delta t/H})] \tag{10}$$

For the zone centre velocity of the nth component, we have

$$v_{\mathrm{A},n}[T(m)] = L/[A_{tn}\mathrm{e}^{B_{tn}/T(m)} + C_{tn}] \tag{11}$$

Further, let us consider a programme with merely a single temperature rise. The retention time of the nth component can be determined from the sum

$$L = \sum_{m=0}^{m_{nL}} \Delta l_n = \sum_{m=0}^{m_{nL}} (L/A_{tn}\mathrm{e}^{B_{tn}/T(m)} + C_{tn})\Delta t \tag{12}$$

and is given by

$$t_{\mathrm{AP},n} = m_{nL}\Delta t \tag{13}$$

where m_{nL} is the number of iterations.

DETERMINATION OF THE TIME CONSTANT, H

The time constant H is determined by iterative calculation. A number of measurements of retention times $t_{\mathrm{RP},n}$ at different temperature rises D_{r} are carried out, from which $t_{\mathrm{AP},n}$ are calculated for the same temperature rises as in the measurements proper while varying H from 0.4 to 1.4 min in 0.1-min steps. The value of H is determined from the case where the values $t_{\mathrm{RP},n}$ show the closest coincidence with the respective calculated values $t_{\mathrm{AP},n}$, *i.e.*, values of H are looked for such that the sum

$$S = \sum_{n} \sum_{D_{\mathrm{r}}} | t_{\mathrm{RP},n} - t_{\mathrm{AP},n} | \tag{14}$$

is minimal.

CALCULATION OF THE PEAK WIDTH USING A TEMPERATURE PROGRAMME

The peak width in the chromatogram recorded at the end of a column of length $L(s_{\mathrm{R},n})$ is related to the actual width of the zone of the nth component in the column $(S_{\mathrm{R},n})$ by the equation

$$S_{\mathrm{R},n} = s_{\mathrm{R},n}L/t_{\mathrm{R},n} = s_{\mathrm{R},n}v_n \tag{15}$$

In isothermal separations, the width $s_{\mathrm{AP},n}$ is given by the approximation function 2. If the plate height is assumed to be constant throughout the column and if the effects of the decompression and thermal expansion of the carrier gas on the zone broadening as well as the effect of temperature on the diffusion characteristics are neglected, the actual width of the zone of the nth component advancing down the column is approximately proportional to the square root of the length of the migration path l (ref. 8). Hence, at a distance l_1 from the beginning of the column the width of the zone is given by the equation

$$S_{\mathrm{A},n}(l_1) = S_{\mathrm{A},n} \sqrt{l_1}/\sqrt{L} \tag{16}$$

These holds for an increment of the zone width

$$\mathrm{d}S_{\mathrm{A},n}(l) = S_{\mathrm{A},n} \left(\frac{\sqrt{l}}{\sqrt{L}}\right)' \mathrm{d}l \tag{17}$$

The value of the peak width $s_{\mathrm{R},n}$ from which the approximation function $s_{\mathrm{A},n}(T)$ is calculated is obtained from the recorder trace and has the dimensions of time (seconds). The peak width at the end of the column can be expressed as

$$S_{\mathrm{A},n}(T) = s_{\mathrm{A},n}(T)\ v_{\mathrm{A},n}(T) \tag{18}$$

When considering a temperature programme with a single linear rise, it is possible to write for a zone width increment at a time t

$$\mathrm{d}S_{\mathrm{AP},n}(t) = \left\{s_{\mathrm{A},n}[T(t)]\ v_{\mathrm{A},n}[T(t)] \frac{\sqrt{l[T(t)]}}{\sqrt{L}}\right\}' \mathrm{d}t \tag{19}$$

and the zone width at the column outlet is given by

$$S_{\mathrm{AP},n} = \int_0^{t_{\mathrm{AP},n}} \left\{s_{\mathrm{A},n}[T(t)]\ v_{\mathrm{A},n}[T(t)] \frac{\sqrt{l[T(t)]}}{\sqrt{L}}\right\}' \mathrm{d}t \tag{20}$$

On rearranging eqn. 19 to a discrete form with the aid of eqns. 1 and 9–12, we obtain upon further rearrangement a relationship for calculating the increment of zone width of the nth component

$$S_{\mathrm{AP},n^{(m+1,m)}} = \frac{A_{sn}\mathrm{e}^{B_{sn}/T(m)} + C_{sn}}{A_{tn}\mathrm{e}^{B_{tn}/T(m)} + C_{tn}} \cdot \left[\sqrt{\sum_{m=0}^{m+1} \frac{\Delta t}{A_{tn}\mathrm{e}^{B_{tn}/T(m)} + C_{tn}}} - \sqrt{\sum_{m=0}^{m} \frac{\Delta t}{A_{tn}\mathrm{e}^{B_{tn}/T(m)} + C_{tn}}}\right] \cdot L \tag{21}$$

At the instant the zone leaves the column outlet, $m = m_{nL}$, and eqn. 13 applies for the retention time. The width of the zone of the nth component at the column outlet is given by the sum

$$S_{\mathrm{AP},n} = \sum_{m=0}^{m_{nL}} \Delta S_{\mathrm{AP},n^{(m+1,m)}} \tag{22}$$

The peak width is calculated from the width of the zone by the equation

$$s_{\mathrm{AP},n} = S_{\mathrm{AP},n}/v_{\mathrm{A},n}(m_{nL}) \tag{23}$$

where $v_{\mathrm{A},n}(m_{nL})$ is the velocity at which the zone centre leaves the column. On substituting for $V_{\mathrm{A},n}(m_{nL})$ from eqn. 11 we obtain for the peak width the equation

$$s_{\mathrm{AP},n} = S_{\mathrm{AP},n}/\{L/[A_{tn}\mathrm{e}^{B_{tn}/T\,(m_{nL})} + C_{tn}]\} \tag{24}$$

MULTIPLE TEMPERATURE PROGRAMME

In the preceding section there is the derivation of the calculation of the retention time and the peak width for most simple cases, *i.e.*, for isothermal separation and separation with a temperature programme involving a single temperature rise. The time constant H of the column with a packing causes a difference between the temperatures in the column oven and in the column. The difference between the temperature programme in the column oven $T_{\mathrm{p}}(t)$ and in that in the column $T(t)$ is illustrated in Fig. 2 (a and b, respectively). The difference between both temperatures is the larger the shorter is the individual programmed section relative to the magnitude of H and the steeper the rises and/or falls. In a multiple temperature programme, the calculation of the retention time, $t_{\mathrm{AP},n}$, and the peak width, $s_{\mathrm{AP},n}$, is carried out by means of the equations derived in preceding sections. The values of $t_{\mathrm{AP},n}$ and $S_{\mathrm{AP},n}$ can then be understood as sums of the increments on the individual time intervals:

$$t_{\mathrm{AP},n} = \sum_{k=1}^{x} \Delta t_{\mathrm{AP},nk} \tag{25}$$

$$S_{\mathrm{AP},n} = \sum_{k=1}^{x} \Delta S_{\mathrm{AP},nk} \tag{26}$$

At the beginning of the kth temperature interval, except the first one, the initial temperature T in the column differs from that set by the temperature programme in the column oven, T_{N}. The values of increments $\Delta t_{\mathrm{AP},nk}$ and $\Delta S_{\mathrm{AP},nk}$ are calculated in a similar way as shown in preceding sections. In the individual programmed intervals (t_k, t_{k+1}) the individual components migrate for the time $t_{k+1} - t_k$ or a shorter one,

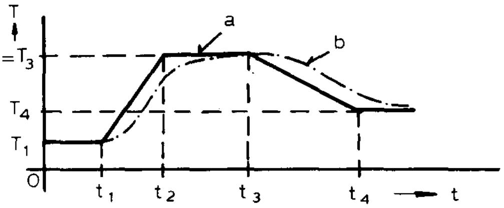

Fig. 2. Temperature programmes in the column oven and in the column.

provided that a component leaves the column outlet during an interval. Condition 12 will be adjusted to apply for a multiple temperature programme. Provided that the nth component leaves the column outlet within the interval t_{x+1}, t_x it holds

$$L = \sum_{m=0}^{m_{nL}} \Delta l_{nk} = \sum_{m=0}^{m_{n1}} \Delta l_{n1} + \sum_{m=0}^{m_{n2}} \Delta l_{n2} + \ldots + \sum_{m=0}^{m_{nx}} \Delta l_{nx} \tag{27}$$

Generally, it holds for an increment of the distance that the zone centre of the nth component of the mixture travels within the interval t_k, t_{k+1}

$$\sum_{m=0}^{m_{nk}} \Delta l_{nk} = \sum_{m=0}^{m_{nk}} \{L/[A_{tn}e^{B_{tn}/T(m)} + C_{tn}]\} \Delta t \tag{28}$$

where

$$m_{nk} = (t_{k+1} - t_k)/\Delta t \tag{29}$$

The value of $m_{nk=nx}$ is determined from eqn. 27 by iteration. For the time $t_{\mathrm{AP},n}$ from eqn. 25 it is possible to write

$$t_{\mathrm{AP},n} = \sum_{k+1}^{x} t_{\mathrm{AP},nk} = \sum_{k=1}^{x} m_{nk} \Delta t \tag{30}$$

where $m_{nk} = 0$ for $k > x$ and $m_{nL} = m_{n1} + m_{n2} + \ldots + m_{nx}$. Similarly, it holds for the width of the zone of an nth component, $S_{\mathrm{AP},n}$

$$S_{\mathrm{AP},n} = \sum_{k=1}^{x} S_{\mathrm{AP},nk} = \sum_{m=0}^{m_{n1}} \Delta S_{\mathrm{AP},n1} + \sum_{m=0}^{m_{n2}} \Delta S_{\mathrm{AP},n2} + \ldots + \sum_{m=0}^{m_{nx}} \Delta S_{\mathrm{AP},nx} \tag{31}$$

For the peak width an equation similar to eqn. 24 is obtained:

$$s_{\mathrm{AP},n} = S_{\mathrm{AP},n}/\{L/[A_{sn}e^{B_{sn}/T(m_{nx})} + C_{sn}]\} \tag{32}$$

COMPARISON OF MEASURED AND CALCULATED VALUES

The algorithm for the calculation of $t_{\mathrm{AP},n}$ and $s_{\mathrm{AP},n}$ was checked with two different three-component model mixtures: (a) mixture M: chloroform (1)–benzene (2)–toluene (3), separated on a non-polar column with 10% Apiezon L (Associated Electrical Industries, Manchester, Great Britain) on Chromosorb W (60–80 mesh) (Carlo Erba, Milan, Italy) at a carrier gas flow-rate of 23 ml/min as measured at 23°C and atmospheric pressure; (b) mixture OR: chloroform (1)–toluene (2)–*o*-xylene (3), separated on a polar column with 10% QF-1 on Chromosorb W (60–80 mesh) (both materials from Carlo Erba) at a carrier gas flow-rate of 23 ml/min as measured at 23°C and atmospheric pressure.

Both columns were made of glass and were 2 m long × 6 mm O.D., and their wall thickness was 1 mm. The calculated time constant H amounted to about 0.8 min in both instances.

TABLE I

MEASURED AND CALCULATED VALUES OF RETENTION TIMES AND PEAK WIDTHS WITH AN ISOTHERMAL ANALYSIS, MIXTURE M

θ (°C)	$t_{R,1}$ (min)	$t_{A,1}$ (min)	$t_{R,2}$ (min)	$t_{A,2}$ (min)	$t_{R,3}$ (min)	$t_{A,3}$ (min)	$s_{R,1}$ (sec)	$s_{A,1}$ (sec)	$s_{R,2}$ (sec)	$s_{A,2}$ (sec)	$s_{R,3}$ (sec)	$s_{A,3}$ (sec)
70	5.20	5.17	8.00	7.98	19.75	19.78	24.0	24.10	32.4	32.15	69.0	68.9
110	2.39	2.43	3.24	3.30	6.00	6.14	9.75	9.38	12.0	11.71	19.88	19.76
150	1.55	1.54	1.90	1.88	2.84	2.79	5.25	5.30	6.0	6.27	8.25	8.62
190	1.20	1.19	1.38	1.36	1.77	1.74	3.75	3.89	4.5	4.46	5.63	5.35
230	1.03	1.03	1.18	1.13	1.33	1.35	3.38	3.32	3.75	3.73	4.13	4.19

TABLE II

MEASURED AND CALCULATED VALUES OF RETENTION TIMES AND PEAK WIDTHS WITH AN ISOTHERMAL ANALYSIS, MIXTURE OR

θ (°C)	$t_{R,1}$ (min)	$t_{A,1}$ (min)	$t_{R,2}$ (min)	$t_{A,2}$ (min)	$t_{R,3}$ (min)	$t_{A,3}$ (min)	$s_{R,1}$ (sec)	$s_{A,1}$ (sec)	$s_{R,2}$ (sec)	$s_{A,2}$ (sec)	$s_{R,3}$ (sec)	$s_{A,3}$ (sec)
70	2.56	2.56	6.35	6.35	14.3	14.12	9.15	9.12	18.75	18.75	38.62	38.94
110	1.51	1.53	2.45	2.50	4.03	4.13	4.88	5.10	6.98	7.37	11.85	12.02
150	1.18	1.17	1.50	1.49	1.98	1.95	3.75	3.74	4.50	4.45	5.78	5.89
190	1.03	1.02	1.16	1.15	1.34	1.33	3.38	3.18	3.75	3.51	4.35	4.09
230	0.94	0.94	1.01	1.02	1.11	1.12	2.85	2.92	3.08	3.15	3.38	3.45

TABLE III

MEASURED AND CALCULATED VALUES OF RETENTION TIMES AND PEAK WIDTHS WITH TEMPERATURE PROGRAMMES, MIXTURE M

k = 1		*k = x = 2*													
θ (°C)	$t_{k=1}$ (min)	D_r (°C/min)	$t_{RP,1}$ (min)	$t_{AP,1}$ (min)	$s_{RP,1}$ (sec)	$s_{AP,1}$ (sec)	$t_{RP,2}$ (min)	$t_{AP,2}$ (min)	$s_{RP,2}$ (sec)	$s_{AP,2}$ (sec)	$t_{RP,3}$ (min)	$t_{AP,3}$ (min)	$s_{RP,3}$ (sec)	$s_{AP,3}$ (sec)
70	0	9.5	3.88	3.90	13.12	12.70	5.00	5.06	12.00	12.6	7.47	7.50	11.85	12.2
70	0	5.6	4.29	4.26	15.0	15.5	5.76	5.78	15.38	16.2	9.16	9.32	15.75	17.1
140	0	19.5	1.64	1.58	5.1	5.07	1.98	1.9	5.48	5.57	2.74	2.6	6.15	6.19
140	0	1.8	1.73	1.66	5.7	5.83	2.16	2.08	6.68	6.92	3.29	3.18	9.38	9.51
70	2.40	19.5	4.74	4.56	13.88	13.6	5.94	5.72	11.1	11.0	7.86	7.58	8.40	8.59
70	2.40	9.5	4.89	4.8	19.5	17.7	6.51	6.38	15.4	15.6	9.55	9.46	12.75	13.4
140	1.40	19.5	1.77	1.68	6.0	5.91	2.20	2.08	7.35	6.75	3.28	3.06	8.25	7.65
140	1.40	5.6	1.77	1.68	6.45	5.95	2.21	2.10	7.50	7.01	3.42	3.2	9.38	9.23

TABLE IV

MEASURED AND CALCULATED VALUES OF RETENTION TIMES AND PEAK WIDTHS WITH TEMPERATURE PROGRAMMES, MIXTURE OR

k = 1		*k = x = 2*												
θ (°C)	$t_{k=1}$ (min)	D_r (°C/min)	$t_{RP,1}$ (min)	$t_{AP,1}$ (min)	$s_{RP,1}$ (sec)	$s_{AP,1}$ (sec)	$t_{RP,1}$ (min)	$t_{AP,2}$ (min)	$s_{RP,2}$ (sec)	$s_{AP,2}$ (sec)	$t_{RP,3}$ (min)	$t_{AP,3}$ (min)	$s_{RP,3}$ (sec)	$s_{AP,3}$ (sec)
70	0	19.5	2.13	2.14	5.68	6.14	3.43	3.50	6.0	6.04	4.55	4.6	6.0	6.08
70	0	9.5	2.28	2.32	6.75	7.23	4.14	4.26	8.10	8.45	6.01	6.18	9.0	9.1
120	0	9.5	1.37	1.36	4.35	4.39	1.98	1.98	5.25	5.35	2.79	2.80	6.15	6.73
120	0	5.6	1.42	1.38	4.13	4.49	2.08	2.02	5.63	5.66	3.0	2.96	7.12	7.64
70	2.40	19.5	2.4	2.5	8.25	8.0	4.88	5.02	7.5	8.02	6.58	6.64	6.38	6.75
70	2.40	9.5	2.45	2.54	8.35	9.1	5.3	5.46	9.98	10.7	7.92	8.02	9.38	10.1
120	1.40	9.5	1.38	1.42	4.13	4.58	1.98	2.1	5.85	66.07	3.06	3.14	7.50	7.96
120	1.40	5.6	1.40	1.42	4.33	4.68	2.02	2.12	6.15	6.17	3.09	3.18	8.1	8.55

Table I gives measured and calculated values of $t_{R,n}$, $s_{R,n}$, $t_{A,n}$ and $s_{A,n}$ with mixture M under isothermal separation. Table II gives measured and calculated values of $t_{R,n}$, $s_{R,n}$, $t_{A,n}$ and $s_{A,n}$ with mixture OR under isothermal separation. Table III summarizes measured and calculated values of $t_{RP,n}$, $s_{RP,n}$, $t_{AP,n}$ and $s_{AP,n}$ with mixture M using simple temperature programmes. Table IV summarizes measured and calculated values of $t_{RP,n}$, $s_{RP,n}$, $t_{AP,n}$ and $s_{AP,n}$ with mixture OR using simple temperature programmes.

Comparison of the values of $t_{RP,n}$ and $s_{RP,n}$ with those of $t_{AP,n}$ and $s_{AP,n}$ in Tables III and IV shows very good agreement between the measured and calculated data. The difference amounts to only a few percent of the value measured. Only exceptionally does the difference approaches 10%, and this only with the comparison of the widths $s_{RP,n}$ and $s_{AP,n}$. The determination of the peak width from a recorder chart suffers *per se* from an error that can amount to as much as several percent.

CONCLUSION

There is very good agreement between the values of retention time and peak width with both simple and complex temperature programmes. In contradiction to Harris and Habgood's concept[1], the algorithm for calculation derived in this paper can be used for any multi-step temperature programme while respecting the existence of differences between the programmed temperature in the column oven and that inside the column. Such an algorithm for the calculation of retention times and peak widths is indispensable for calculating an optimum temperature programme for a given mixture on a given column, *i.e.*, for setting automatically the optimum temperature programme by means of the computer that controls the gas chromatograph.

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