Optimization of temperature programming in gas chromatography with respect to separation time. I. Temperature programme optimization fundamentals

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OPTIMIZATION OF TEMPERATURE PROGRAMMING IN GAS CHROMATOGRAPHY WITH RESPECT TO SEPARATION TIME

I. TEMPERATURE PROGRAMME OPTIMIZATION FUNDAMENTALS

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SUMMARY

The ranges of separability of neighbouring component pairs in a given mixture, separated isothermally on a given chromatographic column, are defined. These ranges are calculated by approximation functions fitted to the measured values of the retention times and peak widths during isothermal analyses. The sequence of the most difficult to separate component pairs is determined within the temperature separability ranges of the component pairs of the mixture. This sequence determines the strategy for calculation of the optimum temperature programme, and every step of this sequence determines the substrategy. The purpose of the strategy is to find the optimum temperature trajectory (programme) and the purpose of the substrategy is to find the optimum subtrajectory, *i.e.*, a part of the optimum trajectory. The determination of the strategy and the corresponding substrategies is presented for mixtures of components that do not change their mutual position during isothermal separations within the whole temperature range.

INTRODUCTION

Temperature programming in gas chromatography (GC) has been studied since this technique was used for the separation of mixtures with widely different boiling points of the individual components. Various workers have dealt with this problem from different viewpoints. Harris and Habgood[1] presented a relationship for the calculation of the retention time during linear temperature programming and investigated the influence of the temperature increment on the resolution of two neighbouring peaks. De Wet and Pretorius[2] studied the effects of temperature on the plate height. Giddings[3] studied the influence of temperature programming on the

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time of analysis and Giddings[4,5], Scott[6] and others studied the effect of temperature on the column efficiency and the separability of mixtures. Studying the temperature influence, these workers usually based their theories on the knowledge of the composition of the column packing and of the individual components of the mixture.

In order to optimize the temperature programme for a given separation problem, Bártů[7] and Bártů and Wičar[8] proposed a procedure in which the rate of migration and broadening of a chromatographic zone during a temperature programme, $T_P(t)$, is predicted. With respect to heat transfer, the oven–column system is regarded as a first-order static system characterized by a time constant H_c. In this model, the actual column temperature $T(t)$ differs from the measured oven temperature $T_P(t)$.

Although already published before[7,8], the set of basic equations (1–15) is summarized here for the sake of readability.

In a multi-step temperature programme, the column temperature within the kth programme step, $T_k(t)$, is

$$T_k(t) = T_{S,k} + (T_{N,k} - T_{S,k})(1 - e^{-t/H_c}) + D_k[t - H_c(1 - e^{-t/H_c})] \tag{1}$$

where D_k is the rate of increase or decrease of oven temperature in the kth step, and $T_{S,k}$ and $T_{N,k}$ are the column and oven temperatures at the beginning of the kth step, respectively. For the oven temperature in the kth step, the following equation holds:

$$T_{P,k}(t) = T_{N,k} + D_k t \tag{2}$$

Eqns. 1 and 2 are recursive; the column and the oven temperatures at the end of the kth step obviously represent the initial temperatures for the $(k + 1)$th step:

$$T_{S,k+1} = T_k(t_k); \qquad T_{N,k+1} = T_{P,k}(t_k) \tag{3}$$

where t_k is time at the end of the kth step.

At the end of the kth step, the position of the nth component zone is determined by the sum of distances passed by the zone in the column during all previous programme steps 1, 2, ..., k:

$$L_c = L_{1,n} + L_{2,n} + \ldots + L_{x,n} = \sum_{k=1}^{x} L_{k,n} \tag{4}$$

where L_c is the column length and $L_{k,n}$ is the distance travelled by the nth component zone in the kth step. By definition, $L_{x,n}$ is the distance travelled by the nth component zone within the xth step when the zone leaves the column.

In a dimensionless form, eqn. 4 reads

$$1 = l_{1,n} + l_{2,n} + \ldots + l_{x,n} = \sum_{k=1}^{x} l_{k,n} \tag{5}$$

where $l_{k,n} = L_{k,n}/L_c$. The distance $l_{k,n}$ are determined by

$$l_{k,n} = \int_0^{t_k} \{1/t_{A,n}[T_k(t)]\}\,\mathrm{d}t \tag{6}$$

where t_k is the duration of the kth step and

$$t_{A,n}(T) = A_{t,n} \exp\,(B_{t,n}/T) + C_{t,n} \tag{7}$$

is the approximate dependence of the retention time of the nth component on temperature, obtained by interpolation of a set of isothermal retention data[7].

Substitution of $l_{k,n}$ from eqn. 6 into eqn. 5 yields

$$1 = \sum_{k=1}^{x} \int_0^{t_{k,n}} \{1/t_{A,n}[T_k(t)]\}\,\mathrm{d}t = \int_0^{t_{AP,n}} \{1/t_{A,n}[T(t)]\}\,\mathrm{d}t \tag{8}$$

where $t_{AP,n}$ is the calculated value of the retention time of the nth component for a given temperature programme.

The retention time of the nth component is given by the sum of the upper integration limits in eqn. 8:

$$t_{AP,n} = t_{1,n} + t_{2,n} + \ldots + t_{x,n} = \sum_{k=1}^{x} t_{k,n} \tag{9}$$

where $t_{k,n}$ is the retention time increment of the nth component in the kth programme step.

In the course of a temperature programme, the width of the nth component zone at the column outlet, $S_{AP,n}$, could be regarded as composed of increments generated in the individual program steps, $S_{k,n}$:

$$S_{AP,n}(t_{AP,n}) = S_{1,n} + S_{2,n} + \ldots + S_{x,n} = \sum_{k=1}^{x} S_{k,n} \tag{10}$$

The zone width increment generated within the kth programme step is given by[7,8]

$$S_{k,n} = s_{A,n}[T_k(t_{k,n})]\,\frac{\sqrt{L_c L_{k,n}(t_{k,n})}}{t_{A,n}[T_k(t_{k,n})]} - s_{A,n}[T_k(0)]\,\frac{\sqrt{L_c L_{k,n}(0)}}{t_{A,n}[T_k(0)]} \tag{11}$$

where

$$s_{A,n}(T) = A_{s,n}\,\mathrm{e}^{B_{s,n}/T} + C_{s,n} \tag{12}$$

is the approximate dependence of the width at half-height of the nth component peak on temperature, obtained by interpolation of experimental isothermal data. $L^0_{k,n}(0)$ and $L^0_{k,n}(t_{k,n})$ are the distance travelled by the nth component zone in the column at the beginning and at the end of the kth programme step, respectively.

Eqn. 11 can be expressed in its integral form:

$$S_{k,n} = \int_0^{t_{k,n}} \frac{\mathrm{d}}{\mathrm{d}t} \left\{ s_{A,n}[T_k(t)] \, \frac{\sqrt{L_c L^0_{k,n}(t)}}{t_{A,n}[T_k(t)]} \right\} \mathrm{d}t \tag{13}$$

where

$$L_{k,n}(t) = L_{1,n} + L_{2,n} + \ldots + L_{k-1,n} + \int_0^t \frac{L_c}{t_{A,n}[T_k(\tau)]} \, \mathrm{d}\tau \tag{14}$$

is the distance passed by the nth component zone in the column up to a given time t.

At the column outlet, the zone width $S_{AP,n}$ and the peak width $s_{AP,n}$ are mutually dependent according to the relationship[7,8]

$$s_{AP,n} = S_{AP,n}(t_{AP,n}) \, \frac{t_{A,n}[T_x(t_{x,n})]}{L_c} \tag{15}$$

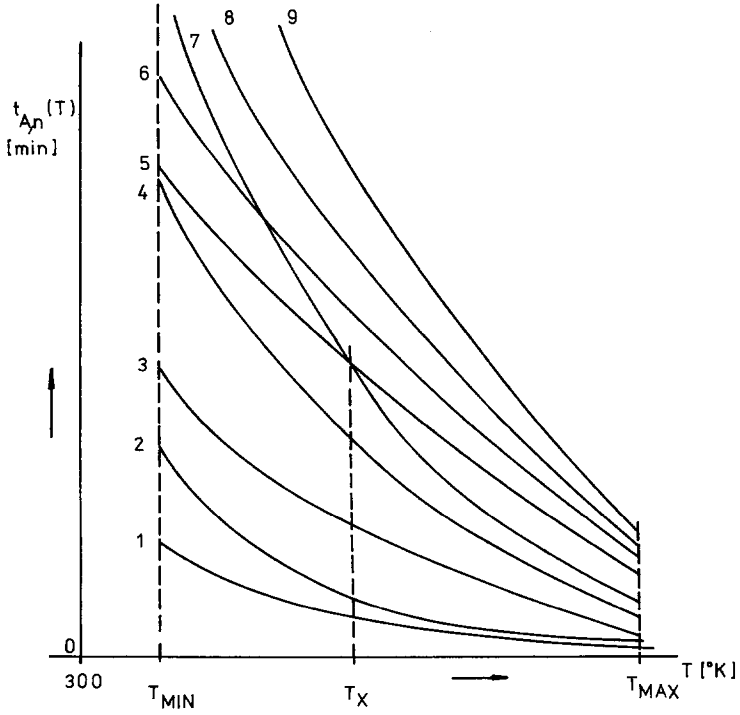

Fig. 1. An example of approximation functions of a nine-component mixture.

In the process of optimization of the temperature programme, the substantial volume of calculations is represented by the evaluation of $t_{AP,n}$ and $s_{AP,n}$ and is obviously proportional to the number of components in the mixture to be separated.

DISCUSSION

Temperature separability range

The following considerations, which lead to a significant reduction in the computation volume, are based on the analysis of the properties of the approximation functions $t_{A,n}(T)$. An example of a set of approximation functions, corresponding to a hypothetical nine-component mixture, is presented in Fig. 1. T_{MIN} and T_{MAX} are physical temperature limits determined by both the apparatus and the column. For each pair of neighbouring components m, n there are three possible arrangements of the corresponding approximation functions $t_{A,m}$ and $t_{A,n}$ (*cf.*, function numbers in Fig. 1):

A. (functions 1, 2):

$$t_{A,m}(T_{\mathrm{MIN}}) - t_{A,n}(T_{\mathrm{MIN}}) \geqslant t_{A,m}(T_{\mathrm{MAX}}) - t_{A,n}(T_{MAX})$$

B. (functions 4, 5):

$$t_{A,m}(T_{\mathrm{MIN}}) - t_{A,n}(T_{\mathrm{MIN}}) < t_{A,m}(T_{\mathrm{MAX}}) - t_{A,n}(T_{\mathrm{MAX}})$$

C. (functions 5, 7):

$$t_{A,m}(T_{\mathrm{MIN}}) > t_{A,n}(T_{\mathrm{MIN}}), \quad t_{A,m}(T_{\mathrm{MAX}}) < t_{A,n}(T_{\mathrm{MAX}})$$

In the last instance the approximation functions intersect. Consequently, there must be at least one temperature T_x in the $\langle T_{\mathrm{MIN}}, T_{\mathrm{MAX}}\rangle$ interval at which $t_{A,m}(T_x) = t_{A,n}(T_x)$ and both peaks corresponding to the m, n component pair coincide. An isothermal separation of such a pair of components at $T < T_x$ results in a retention order which is reversed at $T > T_x$ (Fig. 2).

Let us define the temperature separability range for a given pair of components m, n:

$$T_H[m, n] \geqslant T \geqslant T_L[m, n] \tag{16}$$

For every T within the range given by eqn. 16 the compound pair is separated whenever the resolution is sufficient, or

$$R_{m,n} = \frac{t_{A,m}(T) - t_{A,n}(T)}{1.7\,[s_{A,m}(T) + s_{A,n}(T)]} \geqslant 1 \tag{17}$$

To determine the temperature separability range for a given mixture, first the temperatures T_x for all component pairs within the temperature limits T_{MIN}, T_{MAX} are sought, using the approximation functions $t_{A,n}(T)$. The T_x temperatures are arranged into a square matrix $T_x[N, N]$, where N is the total number of components. By convention, the matrix subscripts are determined by the isothermal retention time values at the lowest temperature T_{MIN}:

$$t_{A,1}(T_{\mathrm{MIN}}) < t_{A,2}(T_{\mathrm{MIN}}) < \ldots < t_{A,N}(T_{\mathrm{MIN}}) \tag{18}$$

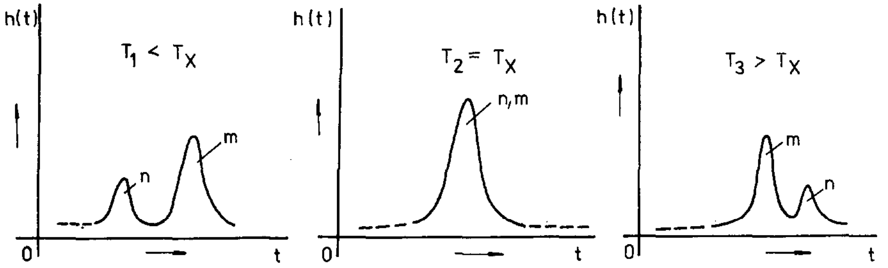

Fig. 2. Partial isothermal chromatograms with components changing their mutual positions at various temperatures.

If the mixture does not contain any component pair with intersecting approximation functions (mixtures of "type I"), then $T_x[N, N] = 0$; otherwise the non-zero elements are located above the principal diagonal:

$$T_x[i, j]\ i > j \qquad i = 1, 2, \ldots, N - 1; \qquad j = 2, 3, \ldots, N \tag{19}$$

In an isothermal separation, the resolution of a component pair i, j changes with the separation temperature. It is assumed that merely one maximum resolution value $R_M[i, j]$ exists, at a temperature $T_M[i, j]$ within the T_{MIN}–T_{MAX} range, whenever the approximation functions $t_{A,i}(T)$, $t_{A,j}(T)$ do not intersect in the same temperature range.

Two maximum resolution values are expected, if $T_x[i, j] \neq 0$ ("type II" mixtures); one, $R_M[i, j]$, at a temperature $T_M[i, j]$ in the T_{MIN}–$T_x[i, j]$ range, the other, $R_M[j, i]$, at $T_M[j, i]$ in the $T_x[i, j]$–T_{MAX} range.

The temperature dependence of the zone width is at least one order of magnitude smaller than that of the retention time. We may therefore expect that the maximum resolution value:

$$R_{m,n} = \frac{t_{A,m}(T) - t_{A,n}(T)}{1.7\ [S_{A,m}(t_{A,m}/L_c) + S_{A,n}(t_{A,n}/L_c)]} \tag{20}$$

in a given temperature range is mainly due to the maximum value of the numerator in eqn. 20. As the analytical determination of the maximum value of $R_{m,n}$ is not possible, iteration methods have to be applied. The temperature dependence of resolution is presented schematically in Fig. 3. The corresponding approximation functions intersect in (b) and (c) and do not in (a).

The maximum resolution values R_M, obtained by iteration, and the corresponding temperatures T_M are arranged into square matrices $R_M[N, N]$ and $T_M[N, N]$. In both matrices, the principal diagonals contain the resolution values and temperatures of neighbouring components, provided the corresponding approximation functions do not intersect. (The $R_M[m, n]$, $T_M[n, n]$ elements correspond to the n, $n + 1$ component pair.) In the case of intersection, two resolution values and related temperatures correspond to each component pair. For the components n, m, $T_M[n, m]$ and $R_M[n, m]$ are in the $T_X[n, m]$–T_{MAX} range and $T_M[m, n]$ and $R_M[m, n]$ are in the T_{MIN}–$T_X[n, m]$ range. The resolution of more remote components, *i.e.*, of those

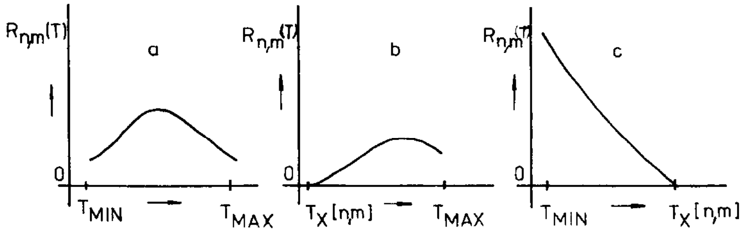

Fig. 3. Examples of the dependence of the resolution on temperature for various component pairs.

bearing the subscripts n, $n + i$ with $i \geqslant 2$, is not calculated, provided the corresponding approximation functions do not intersect.

In the next step, both matrixes R_M and T_M are used to determine the lower and the upper temperature separability limits according to eqns. 16 and 17. The separability limits T_L, T_H, together with the corresponding resolution values R_L, R_H, are again arranged into square matrices $T_L[N, N]$, $T_H[N, N]$, $R_L[N, N]$, and $R_H[N, N]$. The individual elements are determined by iteration. The temperatures in the principal diagonals of both T_L and T_H belong to

$$\begin{aligned} &T_L[n, n] \in \langle T_{\mathrm{MIN}}, T_M[n, n]\rangle \\ &T_H[n, n] \in \langle T_M[n, n], T_{\mathrm{MAX}}\rangle \\ &R_L[n, n] \geqslant 1, \quad R_H[n, n] \geqslant 1 \end{aligned} \tag{21}$$

provided $T_M[n, n] \neq 0$ (see Fig. 4a).

For components with intersecting approximation functions (Fig. 4b), the temperatures $T_L[N, N]$, $T_H[N, N]$ are

$$\begin{aligned} &T_L[n, m] \in \langle T_x[n, m], T_M[n, m]\rangle \\ &T_H[n, m] \in \langle T_M[n, m], T_{\mathrm{MAX}}\rangle \\ &T_L[m, n] \in \langle T_{\mathrm{MIN}}, T_M[m, n]\rangle \\ &T_H[m, n] \in \langle T_M[m, n], T_x[n, m]\rangle \\ &R_L[n, m] \geqslant 1, \quad R_H[n, m] \geqslant 1 \\ &R_L[m, n] \geqslant 1, \quad R_H[m, n] \geqslant 1 \end{aligned} \tag{22}$$

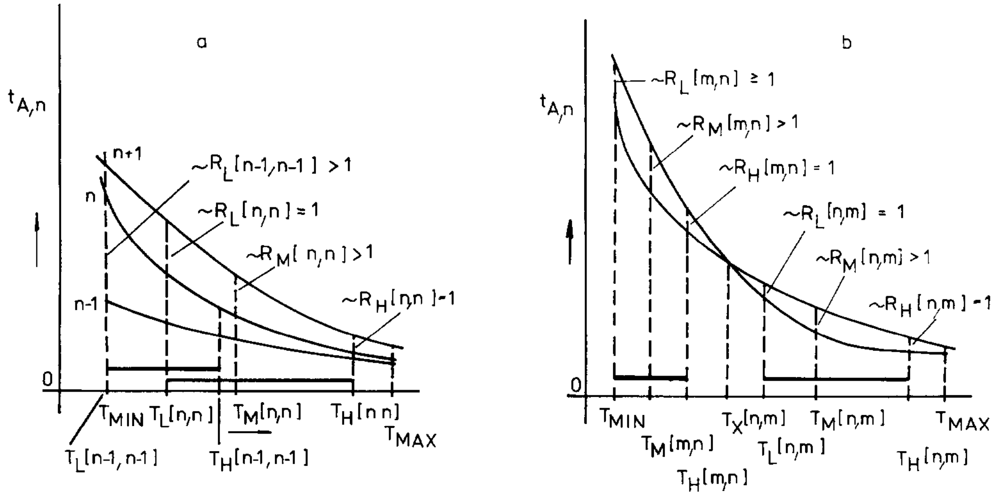

Fig. 4. Illustration of the temperature separability ranges of the components during isothermal analyses.

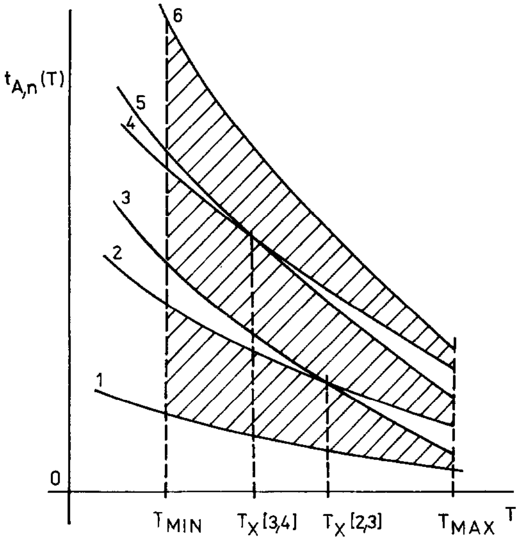

Fig. 5. Illustration of the reduced ranges for calculation of temperature separability ranges.

If any of the elements of R_H is less than one (even the maximum resolution does not satisfy), we put

$$\begin{aligned} T_H[n, m] &= T_L[n, m] = T_M[n, m] \\ R_H[n, m] &= R_L[n, m] = R_M[n, m] \end{aligned} \tag{23}$$

The matrices T_x, T_M, T_H, T_L, R_M, R_H and R_L summarize the knowledge on the mutual positions of the approximation functions in a concise form.

If the approximation functions corresponding to a component pair n, $n + 1$ do not intersect, but at least one of them is crossed by the approximation function of another more distant component (Fig. 5), the separability range of the particular pair n, $n + 1$ is to be corrected. In this instance the R_H, T_H, R_L, T_L matrices are calculated in reduced intervals, as shown by the hatched areas in Fig. 5 for $n = 1$, 3, 5.

Strategies and substrategies for temperature program optimization

The aim of the optimization is to develop a procedure for computation of the oven temperature programme $T_p(t)$ such that for the resolution of any component pair of the separated mixture there holds

$$\begin{aligned} R_{n,m} \geqslant 1 \qquad n &= 1, 2, \ldots, N - 1 \\ m &= 2, 3, \ldots, N \end{aligned} \tag{24}$$

and, simultaneously, the retention time of the component that leaves the column last is minimal:

$$t_{AP,E} = \min \tag{25}$$

For a mixture of type I (the most common case in GC)

$$t_{A,1}(T) < t_{A,2}(T) < \ldots < t_{A,N}(T), \qquad T \in \langle T_{\mathrm{MIN}}, T_{\mathrm{MAX}} \rangle \tag{26}$$

and the resolution matrices $R_L[N, N]$, $R_H[N, N]$ together with the temperature separability matrices $T_L[N, N]$, $T_H[N, N]$ contain non-zero elements exclusively in the principal diagonal. Optimization conditions 24 and 25 can here be modified to

$$R_{n,n+1} \geqslant 1; \qquad t_{AP,N} = \min \qquad n = 1, 2, \ldots, N - 1 \tag{27}$$

The separability ranges for a nine-component mixture are presented in Fig. 6; the dashed numbers refer to T_L. The diagonal elements of the T_H matrice can be arranged to form an ascending sequence:

$$T_H[n_1, n_1] < T_H[n_2, n_2] < \ldots < T_H[n_k, n_k] \tag{28}$$

where $n_1, n_2, \ldots, n_k$ are the neighbouring pairs of components $n = 1, 2, \ldots, N - 1$, sorted with respect to the upper temperature separability limit, T_H. The first term of the sequence determines the maximum temperature at which all the components of the mixture could be separated with $R \geqslant 1$ by isothermal separation. The isothermal separation of the mixture at the temperature determined by the second term results in the separation of all components at $R \geqslant 1$, except the first pair.

Generally, the ith term of the sequence determines the temperature at which all components except the first $i - 1$ pair are separated at $R \geqslant 1$ by isothermal separation.

For the mixture in Fig. 6 the sequence

$$T_H[3, 3] < T_H[1, 1] < T_H[6, 6] < T_H[5, 5] \tag{29}$$

is obtained, or in abbreviated form

$$3, 1, 6, 5, 8, 2, 4, 7 \tag{29a}$$

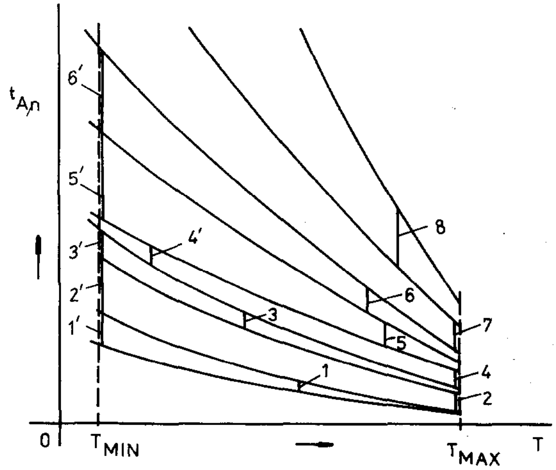

Fig. 6. Approximation functions of a nine-component mixture with marked temperature separability ranges.

Sequence 29 or 29a could serve for the design of an idealized temperature programme $T_P(t)$. Such a programme guarantees the separation of all components at $R \geqslant 1$ in a time $t_{AP,9} < t_{A,9}(T_H[3, 3])$, *i.e.*, in a time shorter than necessary for isothermal separation at $R \geqslant 1$. The idealized temperature programme starts, in accordance with sequence 29, with an isothermal step at $T_H[3, 3]$; the duration of this step is determined by the retention time of the fourth component, $t_{A,4}(T_H[3, 3])$. The temperature of the next programme step again follows from sequence 29. The second term $T_H[1, 1]$, however, is of no importance as the first pair of components will have left the column long before the elution of the fourth component is completed at the end of the first programme step. The next term, $T_H[6, 6]$, and the retention time of the seventh component, $t_{AP,7}$, therefore determine both the temperature and the duration of the second programme step. For $t_{AP,7}$ there holds

$$t_{A,7}(T_H[6, 6]) < t_{AP,7} < t_{A,7}(T_H[3, 3]) \tag{30}$$

The fourth term of sequence 29 is meaningless as both the fifth and sixth components will leave the column before the seventh component elutes. Therefore, $T_H[8, 8]$ is the temperature of the last programme step and the programme ends at $t_{AP,9}$:

$$t_{A,9}(T_H[8, 8] < t_{AP,9} < t_{A,9}(T_H[3, 3]) \tag{31}$$

The ideal temperature programme for the separation of the mixture from Fig. 6 is depicted in Fig. 7.

Generally, to design an ideal temperature programme, a new sequence is formed:

$$T_H[n_i, n_i] < T_H[n_j, n_j] < \ldots < T_H[n_1, n_1] \tag{32}$$

from eqn. 28 merely by excluding some of its terms to guarantee that

$$n_i < n_j < \ldots < n_1; \qquad n_{k+1} - n_k > 1 \tag{33}$$

The last inequality reflects the fact that, at the moment of elution of the kth component, the resolution of the k, $k + 1$ pair, $R_{k,k+1}$ is irrelevant. If $R_{k,k+1} < 1$ there is no possibility of influencing it; if $R_{k,k+1} > 1$ one has to focus on the resolution of the next component pair, $R_{k+1,k+2}$.

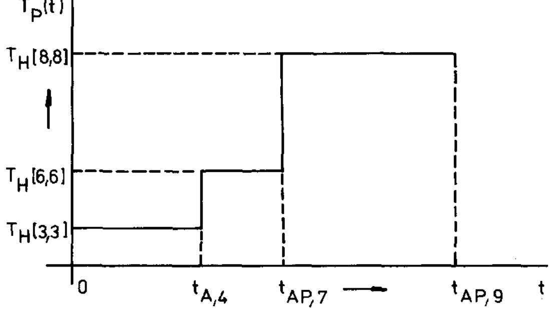

Fig. 7. Idealized temperature programme for the separation of the nine-component mixture from Fig. 6.

Sequence 29 now becomes

$$T_H[3, 3], T_H[6, 6], T_H[8, 8] \tag{34}$$

or in a concise form

$$3, 6, 8 \tag{34a}$$

The component pairs making up sequence 34 are called the most difficult to separate component pairs in the given mixture. The above-derived idealized temperature programme, $T_P^*(t)$, is of course unrealistic as it requires instant temperature changes of the column and, more important, does not satisfy optimization condition 26; it has served merely to illustrate the fundamental concept of the most difficult to separate component pair of a mixture.

With respect to the algorithm of the temperature programme optimization, sequence 32 and each of its members determine the strategy and substrategy, respectively, of the optimization process. The goal of the optimization strategy is to design the optimal temperature programme for a given separation. Consequently, the aim of each substrategy is to find the optimal subtrajectory $T_{P,k}(t)$, *i.e.*, one segment of the optimal temperature program $T_P(t)$.

To fulfil condition 26 there are merely instrumental limitations regarding the shape of the optimal segment $T_{P,k}(t)$. For the sake of simplicity, each segment $T_{P,k}(t)$ is assembled from two linear program sections, $T_{P,1,k}(t)$ and $T_{P,2,k}(t)$, one of which is isothermal and the other is represented by a linear temperature increase or decrease.

For a mixture containing N_s most difficult to separate component pairs (*i.e.*, requiring N_s substrategies), the maximum number of programme sections is 2 N_s. A completely separated N-component mixture consists of $N - 1$ component pairs. In accordance with the sequence 28:

$$T_H[n_1, n_1]\ T_H[n_2, n_2] \ldots T_H[n_{N-1}, n_{N-1}] \tag{35}$$

and the maximum number of the corresponding substrategies is determined by the component pairs 1, 3, ..., $N - 1$. The maximum number of substrategies for even and odd N is $N/2$ and $(N + 1)/2$, so the maximum number of linear programme sections is N or $N + 1$, respectively.

Fig. 8 presents two limiting acceptable subtrajectories $T_{P,1,k}(t)$ and $T_{P,2,k}(t)$ in the kth substrategy. In the following considerations, the subscript k in eqns. 1–10 is split into subscripts i, k, where $i = 1, 2$.

Solution of individual substrategies

The design of the first substrategy differs from all successive ones as $T_{N,1,1} = T_{S,1,1}$ and $T_{N,1,1}$ is an independent variable. In all other successive programme segments, the initial oven and column temperatures are different and are given by eqn. 3. Consequently, in the first substrategy we look for those values of the independent variables

$$T_{N,1,1}, D_{1,1}, D_{2,1}, t_{1,1}, t_{2,1} \tag{36}$$

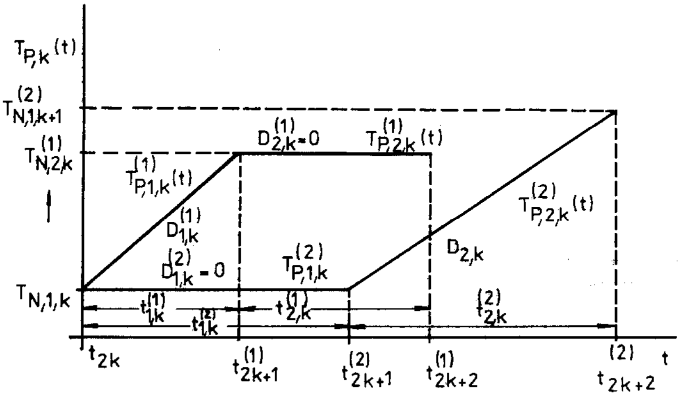

Fig. 8. Examples of subtrajectories.

that lead to the minimum of the criterion function, *i.e.*, that minimize the retention time of the second component of the first most difficult to separate component pair:

$$t_{AP,n_1+1} = t_{1,1} + t_{2,1} = \min \tag{37}$$

The criterion function 37 is defined by the sum of the upper integration limits in eqn. 8 and is subject to the following constraints:

$$\begin{aligned}
&D_{\mathrm{MIN}} < D_{i,1} < D_{\mathrm{MAX}}\\
&T_{\mathrm{MIN}} < T_{P,i,1} < T_{\mathrm{MAX}}\\
&T_L[n_1, n_1] < T_{N,1,1} < T_H[n_1, n_1]\\
&0 < t_{2,1} < t_{A,n_1+1}(T_H[n_1, n_1])\\
&R_{n_1,n_1+1} - 1 \geqslant 0\\
&t_{1,1} + t_{2,1} < t_{\mathrm{MAX}}
\end{aligned} \tag{38}$$

where t_{MAX} is an arbitrarily chosen time limit for a given separation. With regard to the next substrategy, it is desirable for the oven temperature at the end of the first substrategy, $T_{N,1,2}$, to approach the upper separability range of the next most difficult to separate component pair as closely as possible:

$$T_{N,1,2} = T_{P,2,1}(t_{2,1}) \rightarrow T_H[n_2, n_2] \tag{39}$$

In the second substrategy, the closer the subtrajectory approaches the optimum, the higher is the temperature at the end of the first substrategy. This is especially important in cases where $T_H[n, n]$ does not differ much from the maximum temperature T_{MAX}, and, consequently, the retention time cannot be decreased by further temperature increase. Condition 39 can be regarded as an extension of the constraints 38.

To solve the minimization problem 37, t_{AP,n_1}, s_{AP,n_1} and s_{AP,n_1+1} have to be calculated (see the resolution value R_{n_1,n_1+1} in constraints 38.

For components denoted by $n < n_1$, the values of

$$t_{AP,n},\ s_{AP,n},\ R_{n,n+1},\ n = 1, 2, \ldots, n_1 - 1 \tag{40}$$

may be calculated according to eqns. 5–15. For the remaining components ($n > n_1$

+ 1), merely increments generated within the first substrategy are calculated:

$$\begin{aligned} {}^{1}l_{AP,n} &= l_{1,1,n} + l_{2,1,n} \\ {}^{1}t_{AP,n} &= t_{AP,n_1+1} \\ {}^{1}S_{AP,n} &= S_{1,1,n} + S_{2,1,n},\ n = n_1 + 2, n_1 + 3, \ldots, N \end{aligned} \tag{41}$$

where the left superscripts relate to the end of a given substrategy.

Generally, in the kth substrategy optimum values of

$$D_{1,k}, D_{2,k}, t_{1,k}, t_{2,k} \tag{42}$$

are sought for by minimizing the criterion function

$$t_{AP,n_k+1} = t_{AP,n_{k-1}+1} + t_{1,k} + t_{2,k} = \min \tag{43}$$

and are subject to the following constraints:

$$\begin{aligned} & D_{\mathrm{MIN}} < D_{i,k} < D_{\mathrm{MAX}} \\ & T_{\mathrm{MIN}} < T_{P,i,k}(t) < T_{\mathrm{MAX}} \\ & t_{1,k} + t_{2,k} < t_{\mathrm{MAX}} \\ & R_{n_k,n_k+1} - 1 \geqslant 0 \\ & T_H[n_k, n_k] < T_{N,1,k+1} = T_{P,2,k}(t_{2,k}) \leqslant T_H[n_{k+j}, n_{k+j}] \\ & j = 1, 2, \ldots, N_s - k, \qquad i = 1, 2 \end{aligned} \tag{44}$$

In the last inequality, the subscript j normally equals unity. There are some instances, however, where the resolution R_{n_k,n_k+1} substantially exceeds unity and we may therefore continue increasing the temperature up to the next T_H value (which is an equivalent of $j = 2, 3, \ldots$).

After the values of the independent variables 42 have been determined, the values

$$l = \sum_{k=1}^{x} {}^{k}l_{AP,n};\quad t_{AP,n} = \sum_{k=1}^{x} {}^{k}t_{AP,n};\quad S_{AP,n} = \sum_{k=1}^{x} {}^{k}S_{AP,n} \tag{45}$$

for $n = n_{k-1} + 2, n_{k-1} + 3, \ldots, n_{k-1}$, and resolutions

$$R_{n,n+1} \text{ for } n = n_{k-1} + 1, n_{k-1} + 2, \ldots, n_k - 1 \tag{46}$$

are calculated.

The increments for the components $n = n_k + 2, n_k + 3, \ldots, N$ in the kth substrategy are expressed by

$$\begin{aligned} {}^{k}t_{AP,n} &= t_{1,k} + t_{2,k} \\ {}^{k}S_{AP,n} &= S_{1,k,n} + S_{2,k,n} \\ {}^{k}l_{AP,n} &= l_{1,k,n} + l_{2,k,n} \end{aligned} \tag{47}$$

In the last substrategy, the last constraint 44 becomes

$$T_{P,i,k}(t) < T_{\mathrm{MAX}} \tag{48}$$

Generally, within the kth strategy the most difficult to separate components migrate in the column for a given time interval at $T > T_H[n_k, n_k]$ (where $R_{n,n+1} < 1$) and at $T < T_H[n_k, n_k]$ (where $R_{n,n+1} > 1$) for the remainder of the time.

CONCLUSIONS

This paper has introduced basic terms for the determination of the optimum temperature programme in the gas chromatographic separation of an arbitrary mixture on an arbitrary column under a constant carrier gas flow-rate. The optimization task, *i.e.*, the procedure of derivatization of substrategies and the introduction of conditions for the solution of substrategies is based on the approximation functions $t_{A,n}(T)$, $s_{A,n}(T)$ obtained during experimental isothermal analyses of the mixture.

LIST OF SYMBOLS

$A_{s,n}$	constant of the approximation function $s_{A,n}(T)$;
$A_{t,n}$	constant of the approximation function $t_{A,n}(T)$;
$B_{s,n}$	constant of the approximation function $s_{A,n}(T)$;
$B_{t,n}$	constant of the approximation function $t_{A,n}(T)$;
$C_{s,n}$	constant of the approximation function $s_{A,n}(T)$;
$C_{t,n}$	constant of the approximation function $t_{A,n}(T)$;
$D_{i,k}$	rate of the oven temperature increase or decrease in the kth substrategy and in the ith section;
D_k	rate of the oven temperature increase or decrease in the kth programme step;
D_{MAX}	maximum rate of the $D_{i,k}$ or D_k;
D_{MIN}	minimum rate of the $D_{i,k}$ or D_k;
H_c	time constant of the column in the oven;
$h(t)$	chromatogram;
L_c	column length;
$L_{k,n}$	distance travelled by the nth component zone in the kth programme step;
$L_{k,n}(t)$	distance travelled by the nth component zone until time t in the kth programme step;
$L_{k,n}(0)$	distance travelled by the nth component zone until the beginning of the kth substrategy;
$L_{x,n}$	distance travelled by the nth component zone within the xth step when the zone leaves the column;
$^{k}l_{AP,n}$	dimensionless distance travelled by the nth component zone within the kth substrategy;
$^{k}l_{AP,n}(0)$	dimensionless distance travelled by the nth component zone until the beginning of the kth substrategy;
$l_{i,k,n}$	dimensionless distance travelled by the nth component zone within the kth substrategy and ith section;

$l_{k,n}$	dimensionless distance travelled by the nth component zone within the kth programme step;
$l_n(t)$	dimensionless distance travelled by the th component zone from the beginning until time t;
N	total number of components in a given mixture;
N_S	total number of substrategies in the strategy;
n_k, $n_k + 1$	most difficult to separate pair in the kth substrategy;
$R_H[n, m]$	resolution of the component pair n, m at the upper limit of the temperature separability range $T_H[n, m]$;
$R_H[n, n]$	resolution of the component pair n, $n + 1$ with non-intersecting approximation function $t_{A,n}(T)$, $t_{A,n+1}(T)$;
$R_L[n, m]$	resolution of the component pair n, m at the lower limit of the temperature separability range $T_L[n, m]$;
$R_L[n, n]$	resolution of the component pair n, $n + 1$ with non-intersecting approximation functions $t_{A,n}(T)$, $t_{A,n+1}(T)$;
$R_M[n, m]$	maximum resolution of the component pair n, m at the temperature $T_M[n, m]$ within the temperature range $\langle T_{\mathrm{MIN}}, T_{\mathrm{MAX}}\rangle$;
$R_M[n, n]$	maximum resolution of the component pair n, $n + 1$ with non-intersecting approximation functions $t_{A,n}(T)$, $t_{A,n+1}(T)$;
$R_{n,m}$	resolution of the component pair n, m at a given temperature;
$S_{AP,n}$	calculated zone width of the nth component at the column outlet;
$^kS_{AP,n}$	calculated increment of the zone width of the nth component within the kth substrategy;
$^kS_{AP,n}(0)$	calculated increment of the zone width of the nth compoonent until the beginning of the kth substrategy;
$S_{i,k,n}$	calculated increment of the zone width of the nth component within the kth substrategy and the ith section;
$S_{k,n}$	calculated increment of the zone width of the nth component within the kth programme step;
$S_{x,n}$	calculated increment of the zone width of the nth component within the xth step when the zone leaves the column;
$s_{A,n}(T)$	approximation function of the width at half-height of the nth component peak on temperature;
$s_{AP,n}$	calculated peak width of the nth component at the column outlet;
T	temperature;
$T(t)$	actual temperature programme in the column;
$T_H[n, m]$	highest temperature at which the components n, m are separated with $R_{n,m} \geqslant 1$;
$T_H[n, n]$	highest temperature at which the components n, $n + 1$ with non-intersecting functions $t_{A,n}(T)$, $t_{A,n+1}(T)$ are separated with $R_{n,n+1} \geqslant 1$;
$T_{i,k}(t)$	actual temperature in the column within the kth substrategy and the ith section;
$T_k(t)$	actual temperature in the column within the kth programme step;
$T_L[n, m]$	lowest temperature at which the components n, m are separated with $R_{n,m} \geqslant 1$;
$T_L[n, n]$	lowest temperature at which the components n, $n + 1$ with non-intersecting function $t_{A,n}(T)$, $t_{A,n+1}(T)$ are separated with $R_{n,n+1} \geqslant 1$;

$T_M[n, m]$	temperature at which the components n, m are separated with the maximum resolution $R_{n,m}$;
$T_M[n, n]$	temperature at which the components n, $n + 1$ with non-intersecting function $t_{A,n}(T)$, $t_{A,n+1}(T)$ are separated with the maximum resolution $R_{n,n+1}$;
T_{MAX}	maximum allowed temperature in the oven;
T_{MIN}	minimum allowed temperature in the oven;
$T_{N,k}$	temperature in the oven at the beginning of the kth programme step;
$T_{N,i,k}$	temperature in the oven at the beginning of the ith section in the kth substrategy;
$T_P^*(t)$	idealized temperature programme;
$T_P(t)$	temperature programme in the column;
$T_{P,k}(t)$	kth step in the temperature programme $T_P(t)$;
$T_{P,i,k}(t)$	temperature programme in the column within the kth substrategy and the ith section;
$T_{S,k}$	temperature in the column at the beginning of the kth program step;
$T_{S,i,k}$	temperature in the column at the beginning of the ith section in the kth substrategy;
$T_X[n, m]$	temperature at which the functions $t_{A,n}(T)$ and $t_{A,m}(T)$ intersect;
$T_x(t_{x,n})$	temperature at which the nth component leaves the column outlet;
t	time;
$t_{A,n}(T)$	approximation function of the retention time of the nth component on temperature;
$t_{AP,n}$	calculated retention time of the nth component at the column outlet;
${}^k t_{AP,n}$	calculated retention time of the nth component within the kth substrategy;
t_k	duration of the kth programme step;
$t_{i,k}$	computed duration of the temperature programme $T_{P,i,k}(t)$;
t_{MAX}	maximum allowed time of analyses;
$t_{x,n}$	computed duration of the xth temperature programme step when the nth component leaves the column outlet.

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