

# Optimization of temperature programming in gas chromatography with respect to separation time. II. Optimization of the individual temperature programme substrategies

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

### II\*. OPTIMIZATION OF THE INDIVIDUAL TEMPERATURE PROGRAMME SUBSTRATEGIES

V. BÁRTŮ\* and S. WIČAR

*Institute of Analytical Chemistry, Czechoslovak Academy of Sciences, Leninova 82, CS-611 42 Brno (Czechoslovakia)*

and

G.-J. SCHERPENZEEL and P. A. LECLERCQ

*Department of Chemical Engineering, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven (The Netherlands)*

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#### SUMMARY

The temperature programme optimization substrategies for a mixture with non-intersecting retention time approximation functions are described. For mixtures of compounds whose elution functions intersect, the determination of strategies for possible solutions and of the corresponding substrategies for temperature programme optimization is derived. Heuristic methods for the minimization of the retention times of the most difficult to separate component pairs are presented. Further, the calculation of retention times and peak widths for optimization purposes is discussed.

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#### INTRODUCTION

In Part I<sup>1</sup>, the problem of optimizing the temperature programme for a given separation problem on a given column was converted into a minimization problem of retention times of the most difficult to separate component pairs. It was shown that these component pairs determine the total number of substrategies or the total number of partial optimization problems. The analysis was limited to mixtures that do not contain components with intersecting retention time approximation functions while simultaneously obeying the inequality

$$\max_n \{T_L[n, n]\} < \min_n \{T_H[n, n]\} \quad n \in \langle 1, 2, \dots, N - 1 \rangle \quad (1)$$

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\* For Part I, see ref. 1. Symbols used here are defined in Part I.

(i.e., mixtures of type I). These mixtures represent the majority of instances in practice.

The optimization in this instance is equivalent to the minimization of a single strategy, resulting in a single optimal temperature programme. If condition 1 is not met, at least one of the substrategies is split into two independent substrategies. In this event there is not necessarily a single optimum solution (a single optimum temperature programme).

For mixtures with intersecting approximation functions (mixtures of type II) several strategies can be derived, none of them necessarily fulfilling all the constraints. In this instance no single optimum temperature programme exists.

The optimization of each substrategy is equivalent to the minimization of the retention time of the second component of that component pair which determines the given substrategy. At the same time, several constraints<sup>1</sup> have to be fulfilled. For this purpose, the standard NAG library minimization programs<sup>2,3</sup>, based on minimization of adjacent Lagrange functions by gradient methods, were originally utilized. In the course of the optimization experiments, the disadvantages of these methods became evident (inefficient consumption of both computing time and computer memory). Therefore, a heuristic minimization algorithm has been developed.

## DISCUSSION

### *Decomposition of substrategies*

Fig. 1 illustrates the approximation functions of a type I mixture. The components  $n_z$  and  $n_z + 1$  belong to the  $k$ th substrategy, and therefore

$$T_L[n_z, n_z] > T_H[n_k, n_k] \quad (2)$$

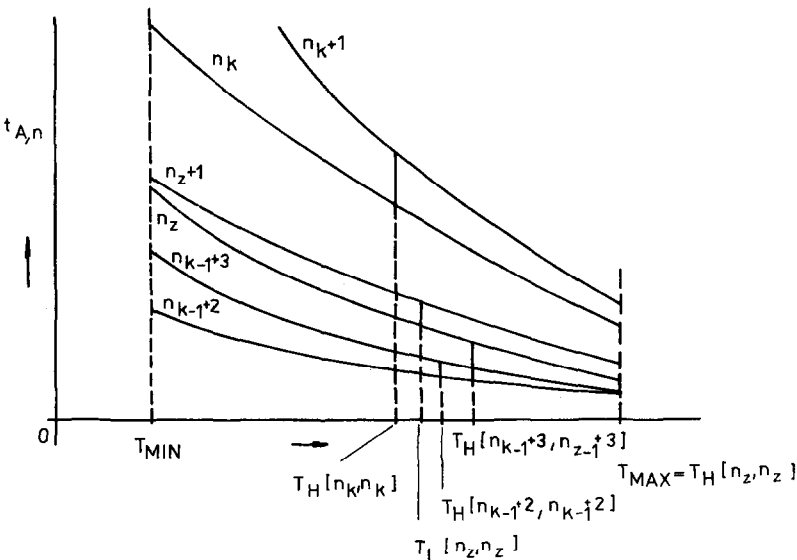


Fig. 1. Subtrajectory for the component pair  $n_z, n_z + 1$ .

For all the other components  $n \in \langle n_k - 1 + 2, n_k - 1 \rangle$  there holds:

$$T_L[n_z, n_z] < T_H[n, n] \quad (3)$$

Consequently, the original  $k$ th substrategy decomposes into two independent substrategies  $k_1$  and  $k_2$ . The  $k_1$ th substrategy relates to component pair  $n_z, n_z + 1$  and the  $k_2$ th substrategy to component pair  $n_k, n_k + 1$ . For the  $k - 1$ th substrategy, the last constraint (cf., Part I, eqn. 44) is

$$T_{N, 1, k_1} = T_{P, k - 1}(t_{2, k - 1}) > T_L[n_z, n_z] \quad (4)$$

In the  $k_2$ th substrategy, we seek a temperature programme  $T_{P, k_2}(t)$  involving one segment with a linear temperature decrease<sup>1</sup>. Generally, with substrategies including components of the  $n_z, n_z + 1$  type, there is not necessarily an optimal temperature programme as all the possible programmes lead to  $R_{n_z, n_z + 1} < 1$  or  $R_{n_k, n_k + 1} < 1$ . In this instance two independent separations are necessary.

If for the  $n_z, n_z + 1$  component pair in the  $k$ th substrategy the inequality

$$T_L[n_z, n_z] < T_H[n, n] \quad n = n_k - 1 + 2, \dots, n_k + 1 \quad (5)$$

is valid and, simultaneously

$$T_H[n_k - 1 + 2, n_k - 1 + 2] > T_H[n_k - 1 + 3, n_k - 1 + 3] > \dots > T_L[n_z, n_z] \quad (6)$$

(where  $n_k = n_z + 2$ ) holds, the  $k$ th substrategy decomposes into  $[n_z - (n_k - 1 + 2)]/2 + 2$  individual substrategies, provided that  $n_z - (n_k - 1 + 2)$  is even; otherwise the number of substrategies is  $[n_z - (n_k - 1 + 2) + 1]/2 + 2$ .

#### *Determination of substrategies for mixtures of type II*

The formulation of this problem is analogous to that for mixtures with non-intersecting approximation curves (mixtures of type I). For mixtures of type I there is only one strategy, i.e., a single sequence of substrategies leading to a single optimum temperature programme. In an extreme case, if some of the substrategies decompose, no single optimum temperature programme must necessarily exist. For type II mixtures, there are a number of possible strategies depending on the number of intersecting pairs. Some of these (possibly all) strategies will not lead to a satisfactory solution and other ones might, but only one of the solvable strategies leads to the shortest retention time of the last component. This strategy has the optimum trajectory.

Mixtures of type II are characterized<sup>1</sup> by non-zero elements  $T_L[n, m]$  and  $T_L[m, n]$  in the matrices  $T_L[N, N]$  and  $T_H[N, N]$ . Fig. 2 illustrates a mixture of type II containing two pairs of components with intersecting approximation functions (components 2, 3 and 5, 6). The vertical solid lines between the curves mark the upper temperature separability limit of the particular pair of components, and the dot-and-dash line marks the lower limit. In the matrices  $T_H[N, N]$  and  $T_L[N, N]$  there are, in addition to the diagonal elements, also elements with subscripts 2, 3; 3, 2; 5, 6; and 6, 5. Let the subrow belonging to the  $n$ th element be denoted as a group of

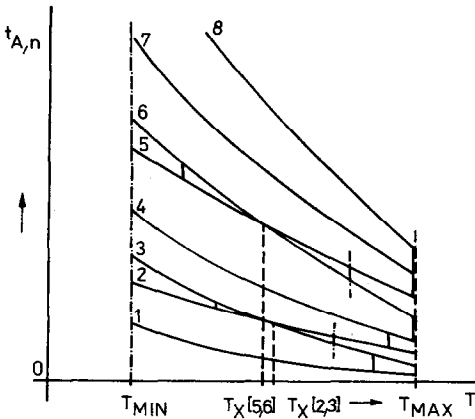


Fig. 2. Approximation functions of a mixture of type II.

elements with subscripts  $n, n; n, n + 1; \dots; n, N$  and the subcolumn as a group of elements with subscripts  $n, n; n + 1, n; \dots; N, n$ . For determining the individual strategies, the elements of the principal diagonal of the matrix  $T_H[N, N]$  are ordered according to their value. If the elements are out of the diagonal in some row (and thus in some column), first of all the lowest temperature value in the subrow (or in the subcolumn) is sought for and used as an element of the strategy, provided that

$$\max_m \{T_L[n, m]\} < \min_m \{T_H[n, m]\} \quad m = n, n + 1, \dots, N \tag{7}$$

or

$$\max_m \{T_L[m, n]\} < \min_m \{T_H[m, n]\} \quad m = n, n + 1, \dots, N \tag{8}$$

The conditions 7 and 8 signify that the components with intersecting approximation functions are separated with  $R_{n, m} > 1$  at the lowest temperature of the subrow (or the subcolumn). On the other hand, this temperature value cannot be used for determining the substrategies, because there will always be the possibility of insufficient separation ( $R_{n, m} < 1$ ) of at least for one component pair.

Hence every row in the matrix  $T_H[N, N]$  with non-zero elements out of the principal diagonal doubles every strategy step if conditions 7 and 8 are fulfilled. In the case illustrated in Fig. 2, four strategies are theoretically possible, given by the substrategies for the most difficult to separate pairs: I, 6-5; II, 3-2, 5-6; III, 2-3, 6-5, 7; and IV, 2-3, 5-6, 7 (6-5 refers to the pair of components 6 and 5, and 7 to the pair of components 7 and 8). Generally, if the approximation functions of the mixture intersect  $n$  times, then maximally  $2^n$  strategies exist.

If none of these strategies is satisfactory (*i.e.*, in every strategy then is at least one pair with resolution  $R_{n, m} < 1$ ), more analyses must be executed with partial temperature programmes.

Two situations may influence the design of individual substrategies. In the mixture being analysed, there might be component pairs or groups that are not of

interest; hence their resolution can be arbitrary. If such a pair happens to be the most difficult to separate pair, the corresponding substrategy is either changed or deleted. The other situation is exemplified by mixtures that contain components that cannot be separated at all ( $R_M[n, m] < 1$ ). Any temperature programme other than  $T_P(t) = T_M[n, m]$  leads to a further resolution loss with pairs of this type.

### Heuristic method of optimization

The retention time of a component  $t_{AP, n_1 + 1}$  is minimized in the first substrategy while looking for the optimal temperature increments  $D_{1, 1}; D_{2, 1}$ , and for the corresponding time intervals  $t_{1, 1}; t_{2, 1}$ . Moreover, the independent variable  $T_{N, 1, 1}$ , i.e., the initial temperature at the beginning of the temperature programme, is optimized.

The heuristic method for the minimization of the retention times of the most difficult to separate components is based on the following considerations, as explained for a mixture of type I. The most difficult to separate components in the  $k$ th substrategy migrate, until the components corresponding to the previous substrategy ( $n_k - 1, n_k - 1 + 1$ ) are eluted, at a mean velocity lower than the characteristic velocity (the mean velocity of the components during isothermal analysis at a temperature  $T_H$ , at which the components are separated with  $R_{n, n+1} = 1$ )<sup>2</sup>. Hence, their resolution in the column is greater than 1 until this moment. After the elution of the components  $n_k - 1, n_k - 1 + 1$ , a subtrajectory  $t_{1, k}, D_{1, k}, t_{2, k}, D_{2, k}$  is calculated, so that the pair  $n_k, n_k + 1$  is eluted in the shortest time ( $t_{1, k} + t_{2, k} = \min$ ). As the resolution value for the components  $n_k, n_k + 1$  at the beginning of the  $k$ th substrategy in the column is greater than 1, the subtrajectory at which the column temperature  $T(t) > T_H[n_k, n_k]$  can be sought in the  $k$ th substrategy. At these temperatures, in isothermal separations, the resolution would be insufficient:  $R_{n_k, n_k + 1} < 1$ . However, in the subtrajectory considered at this temperature, the

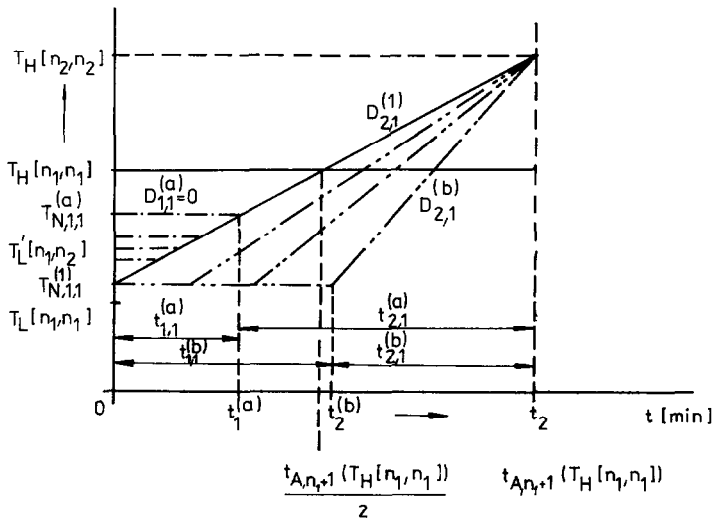


Fig. 3. Optimization of subtrajectories in the 1st substrategy.

resolution of the peak pair decreases simultaneously with the component retention time increments.

By iteration,  $t_{AP, n_k + 1}$  can be minimized. The values of  $t_{1, k}^{(i)}$ ,  $D_{1, k}^{(i)}$ ,  $t_{2, k}^{(i)}$  and  $D_{2, k}^{(i)}$  in the  $i$ th iteration step are determined according to the magnitude of  $R_{n_k, n_k + 1}^{(i)}$ , the boundary conditions being fulfilled<sup>1</sup>. For  $R_{n_k, n_k + 1}^{(i)} > 1$ , the programmed temperature can be increased in the iteration step  $i + 1$  and, consequently, the value of  $t_{AP, n_k + 1}$  can be decreased. In contrast, a temperature decrease leads to an increase in  $t_{AP, n_k + 1}$  for  $R_{n_k, n_k + 1}^{(i)} < 1$ .

Consider first the 1st substrategy where a course of the temperature programme  $T_{P, 1}(t)$ , consisting of two linear sections, is searched for so that  $R_{n, n + 1} = 1$ . Simultaneously, the temperature at the end of the first subtrajectory should be as close as possible to the temperature of  $T_H[n_2, n_2]$ . The shortest retention time of the component  $n_1 + 1$  on isothermal separation,  $t_{A, n_1 + 1}(T_H[n_1, n_1])$ , is known from the temperature separability ranges of the components. The temperature programme will be partially below the value of  $T_H[n_1, n_1]$ , and partially above this value. The retention time will be  $t_{AP, n_1 + 1} \approx t_{A, n_1 + 1}(T_H[n, n])$ . Fig. 3 illustrates the processes leading to such temperature programmes. The first estimation of the trajectory  $D_{1, 1}^{(1)}$ ,  $t_{2, 1}^{(1)}$ ,  $D_{2, 1}^{(1)}$ ,  $t_{1, 1}^{(1)}$  and  $T_{N, 1, 1}^{(1)}$  is determined as follows. The values of the temperature increments will be chosen as

$$\begin{aligned} D_{1, 1}^{(1)} &= 0 \\ D_{2, 1}^{(1)} &= 2(T_H[n_2, n_2] - T_H[n_1, n_1])/t_{A, n_1 + 1}(T_H[n_1, n_1]) \end{aligned} \quad (9)$$

and the initial temperature

$$T_{N, 1, 1}^{(1)} = T_H[n_2, n_2] - D_{2, 1}^{(1)} t_{A, n_1 + 1}(T_H[n_1, n_1]) \quad (10)$$

If  $T_{N, 1, 1}^{(1)} < T_L[n_1, n_1]$ , which is indicated by  $T_L[n_1, n_1]$  in Fig. 3, then  $t_1^{(1)} \neq 0$ , but holds that

$$t_1^{(1)} = \{T'_L[n_1, n_1] - (T_H[n_2, n_2] - D_{2, 1}^{(1)} t_{A, n_1 + 1}(T_H[n_1, n_1]))\}/D_{2, 1}^{(1)} \quad (11)$$

and expression 10 reduces to

$$T_{N, 1, 1}^{(1)} = T_L[n_1, n_1] \quad (12)$$

For a trajectory determined in this way  $t_{AP, n_1}^{(1)}$ ,  $t_{AP, n_1 + 1}^{(1)}$ ,  $s_{AP, n_1}^{(1)}$ ,  $s_{AP, n_1 + 1}^{(1)}$  and  $R_{n_1, n_1 + 1}^{(1)}$  are calculated. According to the magnitude of the value of  $R_{n_1, n_1 + 1}^{(1)}$  iterations are started. For  $R_{n_1, n_1 + 1}^{(1)} > 1$ , the value of  $T_{N, 1, 1} \in \langle T_{N, 1, 1}^{(1)}, T_H[n_1, n_1] \rangle$  is increased until the value of  $T_{N, 1, 1}^{(g)}$  for which  $R_{n_1, n_1 + 1}^{(g)} = 1$  is found. The subtrajectory is then determined by the values of  $T_{N, 1, 1}^{(g)}$ ,  $t_{1, 1}^{(g)}$ ,  $D_{1, 1}^{(g)} = D_{1, 1}^{(1)}$ ,  $t_{2, 1}^{(g)}$ ,  $D_{2, 1}^{(g)} = D_{2, 1}^{(1)}$ . If  $R_{n_1, n_1 + 1}^{(1)} < 1$ ,  $T_{N, 1, 1}^{(1)}$  remains constant and  $t_{1, 1}$  is changed in the course of the iterative calculations. Consequently, the magnitude of  $D_{2, 1}$  is adapted until the values of  $T_{N, 1, 1}^{(1)}$ ,  $t_{1, 1}^{(b)}$ ,  $t_{2, 1}^{(b)}$ ,  $D_{1, 1}^{(1)}$ ,  $D_{2, 1}^{(b)}$  for which  $R_{n_1, n_1 + 1} = 1$  are found. The value of  $D_{2, 1}$  is restricted by the condition  $D_{2, 1} \leq D_{MAX}$ ; if the solution leads to greater  $D_{2, 1}$

values then  $D_{2,1}^{(b)} = D_{MAX}$ . By subsequent calculations a subtrajectory is derived with a value for  $T_{N,1,2} < T_H[n_2, n_2]$ . Then it holds for the initial temperature:

$$T_{N,1,1}^{(1)} = T_H[n_1, n_1] - D_{MAX} t_{A, n_1 + 1}(T_H[1, n_1])/2 \tag{13}$$

For  $T_{N,1,1}^{(1)} < T_L[n_1, n_1]$  eqn. 11 is modified to

$$t_{1,1}^{(1)} = \{T_L[n_1, n_1] - (T_H[n_1, n_1] - D_{MAX} t_{A, n_1 + 1}(T_H[n_1, n_1]))\}/D_{MAX} \tag{14}$$

According to the magnitude of the resolution  $R_{n_1, n_1 + 1}^{(1)}$ , the subtrajectory is calculated in the same way as in the previous case.

*Calculation of kth substrategy*

The temperature  $T_{N,1,k}$  at the beginning of the  $k$ th substrategy is known. Fig. 4 shows the procedure for looking up the  $k$ th subtrajectory. For the enitial temperature programme in the  $k$ th subtrajectory we chose

$$\begin{aligned} D_{1,k} &= D_{MAX} \\ t_{1,k}^{(1)} &= (T_H[n_{k+1}, n_{k+1}] - T_{N,1,k})/D_{1,k} \\ D_{2,k}^{(1)} &= 0 \end{aligned} \tag{15}$$

and the value of  $t_{2,k}^{(1)}$  is implicitly given by the calculated value of  $t_{AP, n_k + 1}$  [i.e.,  $t_{2,k}^{(1)} = t_{AP, n_k + 1} - t_{2k+1}^{(1)}$ ]. If  $T_{N,1,k} > T_H[n_{k+1}, n_{k+1}]$  holds, the calculation of  $t_{1,k}^{(1)}$  involves the nearest higher temperature which fulfils the condition  $T_{N,1,k} < T_H[n_{k+j}, n_{k+j}]$ . Next, the values of  $t_{AP, n_k}$ ,  $t_{AP, n_k + 1}$ ,  $s_{AP, n_k}$ ,  $s_{AP, n_k + 1}$  and  $R_{n_k, n_k + 1}$  are calculated. If  $R_{n_k, n_k + 1}^{(1)} > \lambda$ , the other temperature programme of the same shape with the values of  $t_{1,k}^{(2)} > t_{1,k}^{(1)}$  is chosen. By

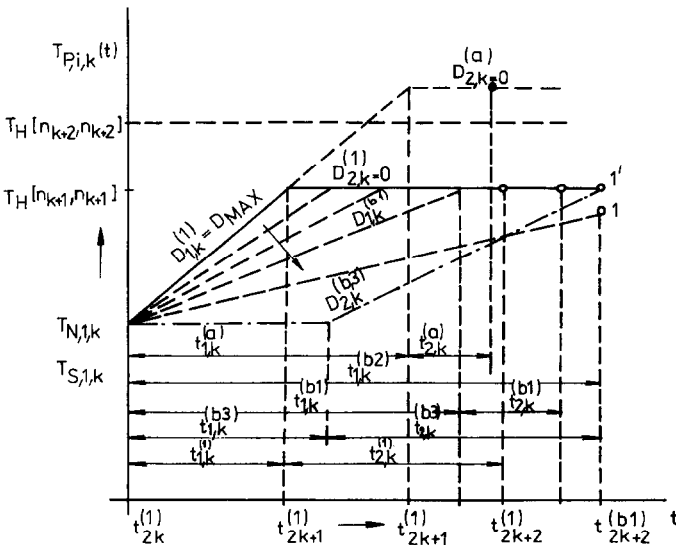


Fig. 4. Subtrajectories in the  $k$ th substrategy.



iteration, the value of  $t_{1,k}^{(a)}$  for which  $R_{n_k, n_{k+1}}^{(a)} = 1$  is calculated. If  $R_{n_k, n_{k+1}}^{(1)} < 1$ , the temperature programme in the iteration steps is set according to eqn. 15 and, at the same time, the value of  $D_{1,k}^{(i)}$  is decreased [thus increasing the value of  $t_{1,k}^{(i)}$ ]. By approximating  $R_{n_k, n_{k+1}}^{(b1)} = 1$  at the temperature  $T_{N, 2, k} = T_H[n_k, n_k]$ , the calculations are stopped. For  $T_{N, 2, k} < T_H[m_k, n_k]$  (the end point of such subtrajectory is marked by the number 1 in Fig. 4) a subtrajectory is searched for, leading to the same retention times and ending at the temperature  $T_{N, 2, k}$  (point 1 in Fig. 4). The optimum subtrajectory is defined by

$$\begin{aligned} D_{1,k}^{(1)} &= 0 \\ t_{1,k}^{(i)} + t_{2,k}^{(i)} &= t_{1,k}^{(b2)} \\ 0 < D_{2,k}^{(i)} &< D_{\text{MAX}} \end{aligned} \quad (16)$$

At the same time, the value of  $D_{2,k}^{(b3)}$  and the corresponding time intervals are determined:

$$\begin{aligned} t_{n,k}^{(b3)} &= (T_H[n_{k+1}, n_{k+1}] - T_{N, 1, k}^{(i)}) / D_{2,k}^{(b3)} \\ t_{1,k}^{(b3)} &= t_{1,k}^{(b2)} - t_{2,k}^{(b3)} \end{aligned} \quad (17)$$

and

$$R_{n_k, n_{k+1}}^{(b3)} \approx 1; \quad T_{N, 1, k+1} \approx T_H[n_{k+1}, n_{k+1}]$$

The heuristic procedure described is applied for the calculation of the optimum trajectory of type I mixtures. The same procedure is used in the case of split subtrajectories and for type II mixtures. The programme always looks for the first local minimum  $t_{AP, n_{k+1}}$ , fulfilling the given conditions for the prescribed shape of linear temperature sections.

#### Calculation of retention times and peak widths

While optimizing the temperature programme, the retention time increments, the zone widths and the position of components that are still in the column are calculated in individual substrategies. The distance passed by a zone in the  $k$ th substrategy is given by<sup>1</sup>

$${}^k l_{AP, n} = l_{1, k, n} + l_{2, k, n} = \int_0^{t_{1,k}} 1/t_{A, n}[T_{1, k}(t)] dt + \int_0^{t_{2,k}} 1/t_{A, n}[T_{2, k}(t)] dt \quad (18)$$

In practice, two cases can occur: either  $t_{1, k}$  and  $t_{2, k}$  are known, or one and possibly both upper limits of the integral in eqn. 18 are unknown. In the latter instance, these times are calculated from

$$1 = \sum_{i=1}^{k-1} {}^i l_{AP, n} + {}^k l_{AP, n} \quad (19)$$

The upper limits of the integrals 18 are known for the components  $n \in \langle n_k + 2, N \rangle$  in the  $k$ th substrategy. Hence,  $t_{1, k}$  and  $t_{2, k}$  are implicitly determined by the retention time of the slower component from the pair determining the  $k$ th substrategy<sup>1</sup>. The upper limit of at least one integral in eqn. 18 is unknown for the components  $n \in \langle n_k - 1 + 2, n_k + 1 \rangle$ . The peak widths are always calculated for the known values of the upper limits<sup>1</sup>.

The calculation of the function values from eqn. 18 can be divided into two groups: calculation of a definite integral of an analytically given function: and calculation of the integral to its upper limit. The calculation of a definite integral is one of the most common problems in numerical mathematics. Popular solution methods are those of Newton-Cotes, Tschebyshev and Gauss<sup>4</sup>. The implementation of these methods on computers requires discrete numbers of points of the integrated functions. The number of points can be adapted to the integration range according to the slope of the integrated function<sup>5</sup>.

The calculation of eqn. 18 and the zone width increment, eqn. 13<sup>1</sup>, can be transformed into the solution of a set of two linear differential equations. The first equation in the  $k$ th substrategy is

$$\frac{d^k l_{AP, n}}{dt} = 1/t_{A, n}[T_k(t)] \quad (20)$$

with the initial condition

$${}^k l_{AP, n}(0) = \sum_{i=1}^{k-1} {}^i l_{AP, n} \quad (21)$$

and the calculation is terminated if

$$l_{AP, n}({}^k t_{AP, n}) = 1 \quad (22)$$

The second equation is

$$\frac{d^k S_{AP, n}}{dt} = \left[ s_{A, n}[T_k(t)] \frac{L_c}{t_{A, n}[T(t)]} \sqrt{l_n(t)} \right] \quad (23)$$

with the initial condition

$${}^k S_{AP, n}(0) = \sum_{i=1}^{k-1} {}^i S_{AP, n} \quad (24)$$

In the first substrategy it is supposed that  ${}^1 l_{AP, n}(0) = l_{\text{MIN}}$ , which does not influence the solution significantly but removes the effect of singularity in eqn. 23 for  $t = 0$ . The differentials can be solved by any numerical method utilized for the solution of linear differential equation systems, e.g., by Runge-Kutta's, Adam's or Gear's methods<sup>6</sup>.

## CONCLUSION

The arrangement of substrategies in single strategies for the optimization of temperature programmes for type II mixtures has been described. An heuristic method for the minimization of the retention times of difficult to separate pairs of components, determining individual substrategies, has been presented in detail. This method is advantageous with respect to demands on computer memory and convergence speed compared with commercial programs for minimization (*cf.*, the libraries supplied with medium- or large-sized computers).

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