MATHEMATICAL SIMULATION OF CONTINUOUS GAS CHROMATOGRAPHY III

NUMERICAL SOLUTION OF THE EQUATIONS

GY. PARLAGH

Department of Physical Chemistry,
Technical University, H-1521 Budapest

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Summary

Mathematical foundations for the numerical solution of the equations describing a continuous chromatographic column are discussed. The method developed is applicable to other sets of ordinary non-linear differential equations with non-linear boundary conditions. A complete storage and retrieval system has been created to save intermediate and final results. Methods to obtain first approximations are given.

Introduction

In previous parts of this series [1, 2] the differential equations and boundary conditions have been given for different types of continuous chromatography. In this section the mathematical problems and methods of numerical solution are discussed.

Since neither the equations nor the boundary conditions are linear, analytical solutions are out of the question; not even a direct numerical integration (e.g. Runge—Kutta) can be applied. Some iterative method must be chosen and, in our case, the choice was limited by a rather small operative memory. A method proposed by Bakhvalov [3] has been chosen and adapted, and it proved to be so useful that it has been kept even when memory problems had been solved.

When writing algorithms, generality, versatility and adaptability were kept in view. A modular program system has been built up, with separate modules for the equations and the boundary conditions. Any modification, improvement in them entails only the correction of the appropriate module. Completely different problems can also be solved if one replaces these modules by new ones relating to the new problem.

Principle of the method [3]

Let be given a set of equations

$$\mathbf{y}' = \mathbf{F}(x, \mathbf{y}) \tag{1}$$

where $\mathbf{y}$, $\mathbf{y}'$ and $\mathbf{F}$ are vectors of m dimensions, $x \in [0, 1]$ is the independent variable, and let be given an approximation to $\mathbf{y}$, $\mathbf{Y}_n$. The next approximation $\mathbf{Y}_{n+1}$ is calculated from the *linear* set of equations

$$\mathbf{Y}'_{n+1} = \mathbf{F}(x, \mathbf{Y}_n) + \mathbb{F}'(x, \mathbf{Y}_n) \cdot (\mathbf{Y}_{n+1} - \mathbf{Y}_n) \tag{2}$$

where

$$\mathbb{F}' = \left(\frac{\partial F_i}{\partial y_i}\right)$$

(Newton's method). $\mathbf{y}$ must satisfy the boundary conditions, temporarily taken for linear ones:

$$\mathbf{B} \cdot \mathbf{y}(0) = \mathbf{b} \tag{3}$$

$$\mathbf{C} \cdot \mathbf{y}(1) = \mathbf{c} \tag{4}$$

$\mathbf{B}$ and $\mathbf{C}$ are matrices, $\mathbf{b}$ and $\mathbf{c}$ are vectors.

To compute $\mathbf{Y}_{n+1}$ from Eq. (2) one needs the values of $\mathbf{Y}_n$ for a great number of x values, and this necessitates a large space of storage. In order to save memory, $\mathbf{Y}_n$ is stored only at a limited number of x_i values, not necessarily equidistant:

$$0 = x_0 < x_1 < x_2 < \ldots < x_{l-1} < x_l = 1$$

and $\mathbf{Y}_n$ is substituted for a function $\mathbf{y}_n$, calculated — if necessary — at the intervals $[x_{k-1}, x_k)$ by numerical integration of Eq. (1) with initial conditions $\mathbf{Y}_n(x_{k-1})$. $(k = 1, 2, \ldots, l-1, l)$. So $\mathbf{y}_n$ is defined on the whole interval $[0, 1]$. It may have discontinuities at the points x_k:

$$\mathbb{D}(x_k) = \mathbf{Y}_n(x_k) - \mathbf{y}_n(x_k - 0) \tag{5}$$

but $\mathbb{D}$ approaches zero when $\mathbf{Y}_n$ approaches the true solution $\mathbf{y}$.

It is suitable to introduce the function

$$\mathbf{Z}_{n+1} = \mathbf{Y}_{n+1} - \mathbf{y}_n . \tag{6}$$

Then, istead of Eq. (2)

$$\mathbf{Z}'_{n+1} = \mathbb{F}'(x, \mathbf{y}_n) \cdot \mathbf{Z}_{n+1} \tag{7}$$

is obtained which is true for every $x \in [0, 1]$ except for

$$x = x_1, x_2, \ldots, x_l .$$

At these points the function is discontinuous, the jumps being equal to those of $\mathbf{y}_n$ but with an opposite sign.

Eq. (7) can directly be integrated in the interval $[0, x_1)$ with initial values of $\mathbf{Z}(0)=0$, then, in the interval $[x_1, x_2)$ with initial values

$$\mathbf{Z}(x_1+0)=\mathbf{Z}(x_1-0)-\mathbf{D}(x_1) \tag{8}$$

and so on, up to $x=1$. Thus, in fact, the equation

$$\mathbf{Z}_0'=\mathbf{F}'(x, \mathbf{y}_n)\cdot\mathbf{Z}_0-\sum_{j=1}^{l-1}\mathbf{D}(x_j)\,\delta(x-x_j) \tag{9}$$

has to be solved, where δ is the Dirac-δ.

$\mathbf{Y}_{n+1}$ is readily obtained from $\mathbf{Z}$ by Eq. (6). It satisfies automatically the boundary conditions given by Eq. (3), if $\mathbf{y}_n$ satisfies them, but may not satisfy Eq. (4). To satisfy this latter condition, the following procedure may be applied.

One obtains a full orthogonal solution system $\boldsymbol{\eta}_1, \boldsymbol{\eta}_2, \ldots, \boldsymbol{\eta}_r$ of the homogeneous equation

$$\mathbf{B}\boldsymbol{\eta}=\mathbf{0} \tag{10}$$

where $\mathbf{B}$ is the same matrix as in Eq. (3) and r is the degeneracy of $\mathbf{B}$. Solving Eq. (7) with the initial values $\boldsymbol{\eta}_1, \boldsymbol{\eta}_2, \ldots, \boldsymbol{\eta}_r$ the solutions $\mathbf{Z}_1, \mathbf{Z}_2, \ldots, \mathbf{Z}_r$ are obtained. It is obvious that any linear combination of the type

$$\mathbf{Z}=\mathbf{Z}_0+\sum_{i=1}^{r} d_i\mathbf{Z}_i \tag{11}$$

satisfies Eq. (9), and the vector

$$\mathbf{y}(0)=\mathbf{Z}(0)+\mathbf{y}_n(0)$$

satisfies Eq. (3). The values d_i must be chosen so that Eq. (4) be satisfied as well by the vector

$$\mathbf{y}(1)=\mathbf{Z}(1)+\mathbf{y}_n(1)$$

The substitution of Eq. (11) into Eq. (6) gives an expression for $\mathbf{Y}_{n+1}$ and the substitution of $\mathbf{Y}_{n+1}(1)$ into Eq. (4) results in a set of linear equations which readily gives the values of the coefficients d_i.

If the first approximation is sufficiently good, the function $\mathbf{Z}$, as well as the coefficients d_i approach zero and $\mathbf{Y}$ approaches the true solution. Since $\mathbf{Z}$ is only a correction approaching zero, Eqs (7) and (9) need not be solved with very high accuracy, approximative solutions can be applied. Especially, the matrix $\mathbf{F}'$ can be calculated numerically, which spares much tiresome coding work.

On the other hand, there is a real danger that some of the solution vectors $\mathbf{Z}_i(x)$ tend to be quasi parallel as x grows, so that the coefficients d_i — and the final solution — cannot be obtained with acceptable accuracy. This difficulty can be overcome making use of a method proposed by Godunov [4].

The essence of this method is the following. Since *any* linear combination of the functions $\mathbf{Z}_i$ $(i=1, 2, \ldots, r)$ is a solution of Eq. (7), they can be combined at the points x_j $(j=1, 2, \ldots, l-1)$ to give r orthogonal vectors $\mathbf{Z}_i^*(x_j)$ so that

$$|\mathbf{Z}_i^*(x_j)|=1,$$

and integration can be continued in the intervals $[x_j, x_{j+1})$ with initial values $\mathbf{Z}_i^*(x_j)$. If the intervals are chosen properly, the solution system can be kept quasi orthogonal in the whole range of integration. The algorithms of transformation and re-transformation are given by Godunov [4].

Non-linear boundary conditions

In our case the boundary conditions are neither linear nor separable. This latter means that quantities relating to both boundaries occur in the same equation.

Let us first examine the simpler case of non-equilibrium chromatography. Here at least some of the boundary conditions are linear and separated [2]:

$$\Theta_i(1)=0 \tag{12}$$

$$\frac{\mathrm{d}y_i}{\mathrm{d}\zeta}(1)=0$$

or, for two components and in the form of Eq. (4)

$$\mathbf{C}\cdot\mathbf{y}=\begin{pmatrix} 0&0&0&0&0&0&0\\ 0&0&0&0&0&0&0\\ 0&0&0&0&0&0&0\\ 0&0&0&1&0&0&0\\ 0&0&0&0&1&0&0\\ 0&0&0&0&0&1&0\\ 0&0&0&0&0&0&1 \end{pmatrix}\begin{pmatrix} v\,(1)\\ y_1\,(1)\\ y_2\,(1)\\ \Theta_1\,(1)\\ \Theta_2\,(1)\\ \mathrm{d}y_1/\mathrm{d}\zeta\,(1)\\ \mathrm{d}y_2/\mathrm{d}\zeta\,(1) \end{pmatrix}=\begin{pmatrix} 0\\0\\0\\0\\0\\0\\0 \end{pmatrix} \tag{13}$$

where the degeneracy of $\mathbf{C}$ is $r=3$. In order to remain conform to our earlier notation, the definition

$$\mathbf{y}=\begin{pmatrix} v \\ y_1 \\ y_2 \\ \Theta_1 \\ \Theta_2 \\ \mathrm{d}y_1/\mathrm{d}\zeta \\ \mathrm{d}y_2/\mathrm{d}\zeta \end{pmatrix} \tag{14}$$

will be employed, so the boundary conditions take the form

$$\begin{aligned} y_4(1)&=0 \\ y_5(1)&=0 \\ y_6(1)&=0 \\ y_7(1)&=0 \end{aligned} \tag{15}$$

Since the linear conditions occur at the upper boundary, the integration will be accomplished backwards, from 1 to 0, but this fact does not restrict the generality of the subsequent treatment.

A full orthogonal system of solutions of the homogeneous equation

$$\mathbf{C}\cdot\boldsymbol{\eta}=\mathbf{0}$$

is

$$\begin{aligned} \boldsymbol{\eta}_1&=(1\ \ 0\ \ 0\ \ 0\ \ 0\ \ 0\ \ 0)^T \\ \boldsymbol{\eta}_2&=(0\ \ 1\ \ 0\ \ 0\ \ 0\ \ 0\ \ 0)^T \\ \boldsymbol{\eta}_3&=(0\ \ 0\ \ 1\ \ 0\ \ 0\ \ 0\ \ 0)^T \end{aligned} \tag{16}$$

(superscript ^{T} means the transpose of a matrix). Solving Eq. (7) with these initial conditions one obtains the functions $\mathbf{Z}_1$, $\mathbf{Z}_2$, $\mathbf{Z}_3$, while the solution of Eq. (9) with the initial condition

$$\boldsymbol{\eta}_0=\mathbf{0}$$

gives the function $\mathbf{Z}_0$. The function

$$\mathbf{Y}_{n+1}=\mathbf{y}_n+\mathbf{Z}_0+\sum_{i=1}^{r} d_i\mathbf{Z}_i \tag{17}$$

satisfies the equation

$$\mathbb{Y}'_{n+1} = \mathbb{F}(x, \mathbf{y}_n) + \mathbb{F}'(x, \mathbf{y}_n)(\mathbb{Y}_{n+1} - \mathbf{y}_n) \tag{18}$$

on the whole interval [0, 1] and the boundary conditions given by Eq. (15) for any set of d_i.

The remaining boundary conditions [2], using the notation defined by Eq. (14) are

$$\begin{aligned} y_1(0) &= 0 \\ y_2(1) \cdot [1 + y_1(1)] + \frac{C2}{C4} \cdot y_4(0) - C3 \cdot y_1^m &= 0 \\ y_3(1) \cdot [1 + y_1(1)] + \frac{C2}{C4} \cdot y_5(0) - C3 \cdot y_2^m &= 0 \end{aligned} \tag{19}$$

By a proper choice of the vector

$$\mathbf{d} = (d_1\ d_2\ d_3)^T$$

these latter conditions can be satisfied, too.

A self-evident method to obtain this vector is to substitute Eq. (17) into Eqs (19) and to solve the resulting equations for d_1, d_2, d_3. These equations are not linear, their solution is rather complicated even in this simple case, so that iterative methods seem to be more useful.

The "other side" values of $y_1(1)$, $y_2(1)$ and $y_3(1)$ can be considered temporarily as constants and then Eqs (19) turn into linear ones:

$$\begin{aligned} y_1(1) &= 0 \\ \alpha \cdot y_4(0) &= \beta_1 \\ \alpha \cdot y_5(0) &= \beta_2 \end{aligned} \tag{20}$$

where

$$\alpha = \frac{C2}{C4}$$

$$\begin{aligned} \beta_1 &= C3 \cdot y_1^m - y_4(1)\,[1 + y_1(1)] \\ \beta_2 &= C3 \cdot y_2^m - y_5(1)\,[1 + y_1(1)] \end{aligned} \tag{21}$$

Eqs (20) may be written in the matrix form

$$\mathbb{B} \cdot \mathbf{y} = \mathbf{b}$$

or

$$\begin{pmatrix} 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & \alpha & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & \alpha & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix} \cdot \begin{pmatrix} y_1(0) \\ y_2(0) \\ y_3(0) \\ y_4(0) \\ y_5(0) \\ y_6(0) \\ y_7(0) \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 0 \\ \beta_1 \\ \beta_2 \\ 0 \\ 0 \end{pmatrix}. \tag{22}$$

Let

$$\mathbb{Y}^0_{n+1} = \mathbf{y}_n \qquad (\text{at } x = 0, x_1, \ldots, x_{l-1})$$

be the 0-th approximation to $\mathbb{Y}_{n+1}$ and the first one, $\mathbb{Y}^1_{n+1}$ be given by Eq. (17). Eq. (22) then may be written

$$\mathbb{B} \cdot \mathbb{Y}^1_{n+1}(0) = \mathbb{b}^0$$

or, substituting Eq. (17)

$$\mathbf{B} \cdot \Sigma d_i \mathbf{Z}_i(0) = \mathbf{b}^0 - \mathbf{B} \cdot [\mathbf{Y}^0_{n+1}(0) + \mathbf{Z}_0(0)]. \tag{23}$$

If one defines the matrix

$$\mathbf{Z} = (\mathbf{Z}_1\ \mathbf{Z}_2\ \mathbf{Z}_3)$$

then Eq. (23) may be written in the compact form

$$\mathbb{B}\mathbb{Z}\mathbb{d} = \mathbb{b}^i - \mathbb{B}(\mathbb{Y}^i_{n+1} + \mathbb{Z}_0), \tag{24}$$

where $i = 0$, the matrix $\mathbb{B}\mathbb{Z}$ and the vector on the right hand side are known, so $\mathbb{d}$ can be determined.

Substituting $\mathbb{d}$ into Eq. (17) one obtains $\mathbb{Y}^1_{n+1}$ which satisfies on the boundaries the conditions given by Eqs (13) and (22), but may not satisfy Eq. (19), since

$$\mathbb{Y}^1_{n+1}(1) \neq \mathbb{Y}^0_{n+1}(1)$$

With $\mathbb{Y}^1_{n+1}(1)$ Eq. (21) gives new values for β_1 and β_2 or rather one obtains the vector $\mathbb{b}^1$. Solving Eq. (24) with $i = 1$ the next approximation can be obtained $\mathbb{Y}^2_{n+1}$. The procedure may be repeated until

$$|\mathbb{Y}^{k-1}_{n+1} - \mathbb{Y}^k_{n+1}| < \text{eps}$$

where eps is a pre-determined small positive value.

The method can be improved by the following modification.

The procedure described above can be treated as an operator transforming the vector $\mathbf{Y}^i(1)$ into $\mathbf{Y}^{i+1}(1)$. If the approximation $\mathbf{Y}_n$ is sufficiently good, this operator can be approximated by a linear one

$$\mathbf{Y}^{i+1} = \mathbf{L} \cdot \mathbf{Y}^i + \mathbf{v}, \tag{25}$$

where $\mathbf{L}$ is a matrix, $\mathbf{v}$ is a vector. Such an $\mathbf{Y}$ vector must be found which by Eq. (25) transforms into itself.

In order to solve this problem, $\mathbf{L}$ and $\mathbf{v}$ have to be obtained at first. If the dimension of $\mathbf{Y}$ is r, this means the determination of $r \cdot (r+1)$ quantities. Eq. (25) represents r equations, so $r+1$ such systems of equations have to be solved:

$$\begin{aligned} \mathbf{Y}^1 &= \mathbf{L} \cdot \mathbf{Y}^0 + \mathbf{v} \\ \mathbf{Y}^2 &= \mathbf{L} \cdot \mathbf{Y}^1 + \mathbf{v} \\ &\vdots \\ \mathbf{Y}^{r+1} &= \mathbf{L} \cdot \mathbf{Y}^r + \mathbf{v} \end{aligned}$$

To reduce the number of equations and the truncation errors, this system can be transformed into

$$\begin{aligned} \mathbf{Y}^2 - \mathbf{Y}^1 &= \mathbf{L}(\mathbf{Y}^1 - \mathbf{Y}^0) \\ \mathbf{Y}^3 - \mathbf{Y}^1 &= \mathbf{L}(\mathbf{Y}^2 - \mathbf{Y}^0) \\ &\vdots \\ \mathbf{Y}^{r+1} - \mathbf{Y}^1 &= (\mathbf{L}\mathbf{Y}^r - \mathbf{Y}^0) \end{aligned} \tag{26}$$

Introducing

$$\boldsymbol{\delta}_i = \mathbf{Y}^i - \mathbf{Y}^0 \tag{27}$$

and

$$\Delta_{i-1} = \mathbf{Y}^i - \mathbf{Y}^1 \tag{28}$$

the set of Eqs (26) can be written

$$\begin{aligned} \mathbf{L} \cdot \boldsymbol{\delta}_1 &= \Delta_1 \\ \mathbf{L} \cdot \boldsymbol{\delta}_2 &= \Delta_2 \\ &\vdots \\ \mathbf{L} \cdot \boldsymbol{\delta}_r &= \Delta_r \end{aligned} \tag{29}$$

The equation determining $\mathbf{Y}$,

$$\mathbf{Y} = \mathbf{L} \cdot \mathbf{Y} + \mathbf{v}$$

can be transformed into

$$\mathbf{Y} - \mathbf{Y}^1 = \mathbf{L}(\mathbf{Y} - \mathbf{Y}^0)$$

or

$$(\mathbf{1} - \mathbf{L}) \cdot \boldsymbol{\delta} = \boldsymbol{\delta}_1 \tag{30}$$

where

$$\boldsymbol{\delta} = \mathbf{Y} - \mathbf{Y}^0$$

The set of Eqs (29) has a great number of zero elements:

$$\begin{aligned}
&\delta_{11} l_{11} + \delta_{12} l_{12} + \ldots + \delta_{1r} l_{1r} && = \Delta_{11} \\
&\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \\
&\qquad\qquad \delta_{11} l_{r1} + \delta_{12} l_{r2} + \ldots + \delta_{1r} l_{rr} = \Delta_{1r} \\
&\delta_{21} l_{11} + \delta_{22} l_{12} + \ldots + \delta_{2r} l_{1r} && = \Delta_{21} \\
&\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \\
&\qquad\qquad \delta_{21} l_{r1} + \delta_{22} l_{r2} + \ldots + \delta_{2r} l_{rr} = \Delta_{2r} \\
&\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \\
&\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \\
&\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \\
&\delta_{r1} l_{11} + \delta_{r2} l_{12} + \ldots + \delta_{rr} l_{1r} && = \Delta_{r1} \\
&\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \\
&\qquad\qquad \delta_{r1} l_{r1} + \delta_{r2} l_{r2} + \ldots + \delta_{rr} l_{rr} = \Delta_{rr}
\end{aligned} \tag{31}$$

It is evident from this way of writing that Eq. (31) is equivalent to

$$\mathbf{D} \cdot \boldsymbol{\lambda}_i = \boldsymbol{\Lambda}_i \qquad (i = 1, 2, \ldots, r) \tag{32}$$

where

$$\mathbf{D} = \begin{pmatrix} \delta_{11} & \delta_{12} & \ldots & \delta_{1r} \\ \delta_{21} & \delta_{22} & \ldots & \delta_{2r} \\ \ldots & \ldots & \ldots & \ldots \\ \delta_{r1} & \delta_{r2} & \ldots & \delta_{rr} \end{pmatrix} \tag{33}$$

and

$$\begin{aligned} \boldsymbol{\lambda}_i &= (l_{i1}\ l_{i2}\ \ldots\ l_{ir})^T \\ \boldsymbol{\Lambda}_i &= (\Delta_{1i}\ \Delta_{2i}\ \ldots\ \Delta_{ri})^T \end{aligned} \tag{34}$$

In other words, the same equation must be solved with different right-hand-side values.

It is very important to remark that the vectors $\boldsymbol{\delta}_i$ are linear combinations of the r independent vectors $\mathbf{Z}_1(1), \mathbf{Z}_2(1), \ldots, \mathbf{Z}_r(1)$: the subtraction in Eq. (27) eliminates $\mathbf{y}_n$ and $\mathbf{Z}_0$ occurring in Eq. (17). This means that the rank of matrix $\mathbf{D}$ is r (except the trivial case when some $\mathbf{Y}^i$ is the true solution and the whole procedure becomes aimless), while the original dimension of $\mathbf{Y}$ is m. In order to prevent $\mathbf{D}$ to become singular, the dimensions of $\mathbf{Y}$ — and of $\mathbf{D}$ — must be reduced by omitting elements which can be calculated. It is evident from Eq. (15) that in our case the last four elements — and only these — may be omitted.

Once having determined $\mathbf{L}$, Eq. (30) gives $\boldsymbol{\delta}$ i.e. $\mathbf{Y}(1)$, or rather a subset of $\mathbf{Y}(1)$ which may be completed by Eq. (15). If the linear approximation — Eq. (25) — is good, then $\mathbf{Y}(1)$ is the correct initial condition. If not, then $\mathbf{Y}_{n+1}^0$ can be set $\mathbf{Y}$ and the whole procedure can be repeated. This type of iteration — even when repeated many times — does not take much time since only the boundary conditions are iterated: the time-consuming numerical integrations have not to be repeated.

The complete solution $\mathbf{Y}_{n+1}$ can be obtained by numerical integration of Eq. (2) — or rather Eqs (7) and (6) — with initial conditions $\mathbf{Y}(1)$. This solution must satisfy the boundary conditions given by Eqs (15) and (19). If there is any discrepancy all the same, it is due to numerical errors. In this case the orthogonalization method of Godunov [4] may improve the results.

This method [4] is generally used by us not only in order to reduce numerical errors but also to reduce space and/or time requirement. From the retained values of $\mathbf{Z}_0, \mathbf{Z}_1, \ldots, \mathbf{Z}_r$ at the points $x_0, x_1, \ldots, x_l$ the function $\mathbf{Y}_{n+1}$ can be obtained at these points by simple linear combinations, using Eq. (17).

Initial approximation

In order to apply the method described above an appropriate initial approximation must have been found. This first approximation has been obtained essentially by three different ways:

1. linearization of the equations,
2. utilization of a known solution with similar parameters,
3. combination of two solutions.

Re 1. Linearization is the most commonly practicable method to obtain a first approximation. There are no general rules, much depends on the inventiveness of the user and on the type of the equations.

In our case the non-linearity is caused by the dependence of the gas velocity on sorption/desorption. If one assumes an arbitrary velocity profile $v = v(\zeta)$, the set of differential equations — and also the boundary conditions — turn into linear ones. For only one adsorbing (partitioning) component [2]:

$$\frac{\mathrm{d}^2 y}{\mathrm{d}\zeta^2} = C1\left[(1+v)\frac{\mathrm{d}y}{\mathrm{d}\zeta} + \left(C2 + \frac{\mathrm{d}v}{\mathrm{d}\zeta}\right)y - C2 \cdot y^* - C3 \cdot y^m \cdot w\right] = 0 \qquad (35)$$

$$\frac{\mathrm{d}\Theta}{\mathrm{d}\zeta} + C4(y - y^*) = 0$$

where

$$y^* = \frac{C5}{\kappa} \cdot \Theta$$

The function $v(\zeta)$ has been assumed to be zero in the lower part of the column ($\zeta < 0.5$) and $C3$ in the higher part, with continous transition in the feeding zone. With this modification Eq. (35) can be solved by standard methods for linear equations — e.g. the method proposed by Godunov [4]. Although the real velocity profile may differ very much from the assumed one, this first approximation proved to be sufficiently good for a convergent iteration.

Re 2. Once having a solution for a set of parameters, it can be used — eventually after some modifications — as a first approximation for another, not very different set of parameters. If one applies this method several times successively, the parameters can be varied practically without limitations.

Re 3. This method has been used to obtain first approximations for systems with two partitioning components. Solutions for components A and B (3 functions each) have been combined in such a way that the concentration profiles remained unchanged while the velocities — or rather the excess velocities v_A and v_B — have been added to give a new excess velocity v. Thus the new set has 5 functions.

Storage of the solutions

Since computation of a solution needs considerable time, the conservation of final and intermediate results has a great importance. And, since final results are also used as first approximations, both final and intermediate results must be stored in a readily retrievable form. It is desirable to store the actual parameters along with the solutions, and to have the possibility of reorganization and classification.

All these requirements can be fulfilled by an indexed sequential data set. A 56-digit key has been constructed comprising all the parameters. The structure of a key is the following:

0 1 2|0 0|.....

A complete solution is placed into several keyed items. The first three digits represent a serial number, common for all keys belonging to a given solution. The fourth and fifth digits are showing the type of the keyed item (e.g. "00" indicates the independent variables, "01" the values of the first function — y_1 — and so on). The remaining digits — common for the related items — comprise the parameters. So the keys for the parts of a given solution are differing only in the fourth and fifth digits.

On giving the serial number the program reconstructs the parameters and the solution functions in the points $x_0, x_1, \ldots, x_l$. Adversely, the keys — including the serial number — are automatically constructed when a new solution is added to the data set.

A special directory has been made to show the serial numbers and the parameters belonging to them. The directory indicates whether the solution is an intermediate or a final one, and is automatically updated when updating the data set.

Results

The results obtained are always reasonable that is the computed concentration functions are never negative and the orders of magnitude are realistic. Some features of the solutions for one partitioning component have been given earlier [2]. Since then, a great number of parameter sets have been tested for both one and two partitioning components. A detailed discussion of the results will be given separately, but it is worthy to be mentioned here that earlier experiences have been confirmed: there is a significant accumulation of the partitioning components inside the column, especially when κ is close to unity. With $\kappa \gg 1$ or $\kappa \ll 1$, this effect is less pronounced but still exists. The accumulation effect has been observed experimentally on moving polimer columns as well [5].

Fig. 1 and Fig. 2 present two sets of computed concentration profiles. The partition coefficients are identical: $\kappa_A = 0.8$ and $\kappa_B = 1.2$. The difference is in the flow rate of the sample to be separated.

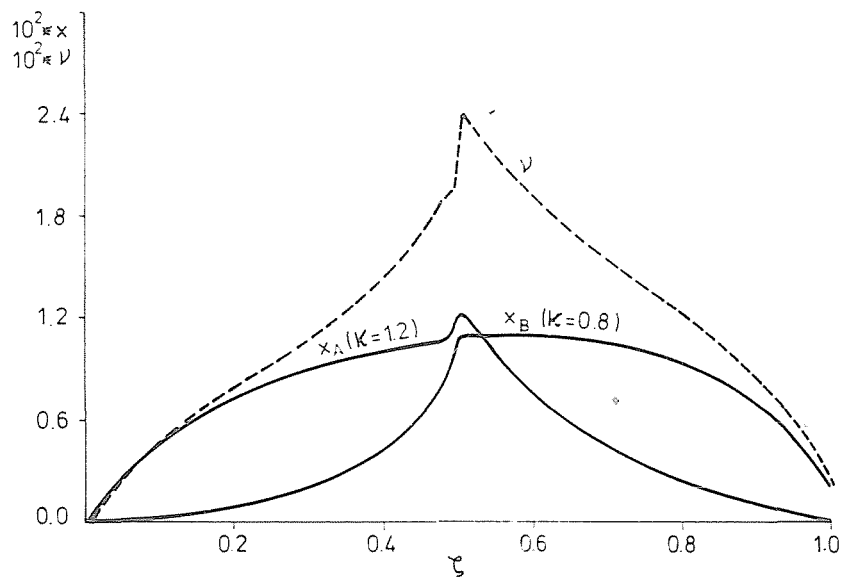

Fig. 1. Calculated concentration profiles of two partitioning components ($C3 = 0.005$).
x mole fraction in the gas phase
$\nu = \frac{v - v_0}{v_0}$ excess velocity in the gas phase
ζ relative length of the column measured from the bottom

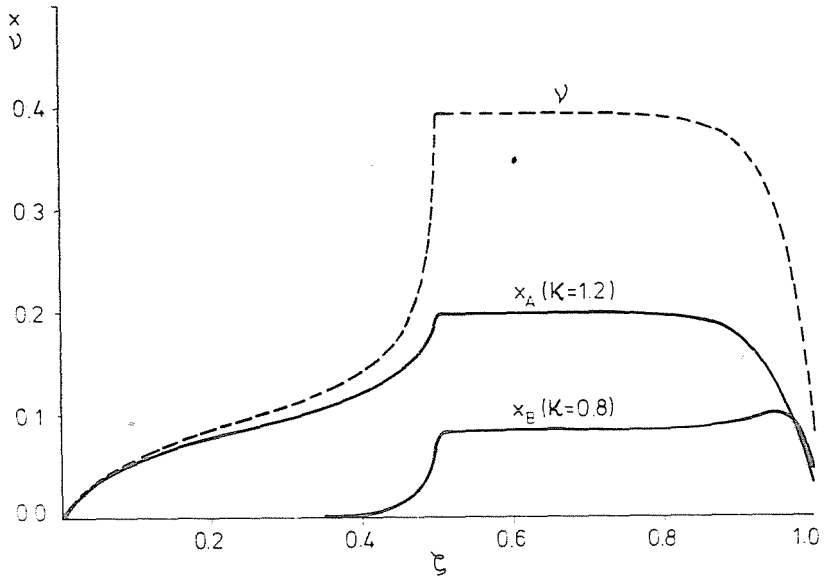

Fig. 2. Calculated concentration profiles of two partitioning components ($C3=0.1$).
x mole fraction in the gas phase
$\nu=\frac{v-v_0}{v_0}$ excess velocity in the gas phase
ζ relative length of the column measured from the bottom

Fig. 1 shows a system where the flow rate of the sample is only 0.5 per cent of the carrier flow rate ($C3=0.005$). The separation is good, component A migrates upwards, component B downwards, as can be expected from the values of κ_A and κ_B. The components are accumulated in the central part of the column — the flow rate is increased by 2.4 per cent, instead of 0.5 — but this does not affect significantly the separation.

In case of Fig. 2 the sample flow rate is 10 per cent of the carrier flow rate ($C3=0.1$). The maximum gas flow rate is increased by about 40 per cent due to the accumulation effect, and consequently both components are migrating upwards. The separation is very poor: the components cannot be separated, except a little portion of A.

It is important to emphasize that this "overloading" is not caused by saturation — the sorption isoterms have been assumed linear — but by the increased flow rate.

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Dr. Gyula PARLAGH H-1521 Budapest