



ELSEVIER

Journal of Chromatography A, 756 (1996) 73–87

JOURNAL OF
CHROMATOGRAPHY A

Modified Rouchon and Rouchon-like algorithms for solving different models of multicomponent preparative chromatography

Krzysztof Kaczmarski*, Dorota Antos

Department of Chemical Engineering, Rzeszów University of Technology, 35-959 Rzeszów ul. W. Pola 2, Poland

Received 3 April 1996; revised 12 June 1996; accepted 19 June 1996

Abstract

Modified Rouchon and Rouchon-like algorithms were used to solve multicomponent equilibrium-dispersive chromatographic models as well as a more general lumped pore diffusion model. The modified algorithms enable remarkable reduction of computation time and avoid computation errors that result from the original Rouchon approach for some cases of multicomponent chromatography. A comparison is given between the general chromatographic model, the lumped pore diffusion model and the equilibrium-dispersive model.

Keywords: Rouchon algorithm; Preparative chromatography; Equilibrium-dispersive model; Lumped pore diffusion model

1. Introduction

Several computational procedures are available for the calculation of the band profiles in preparative chromatography. Some of them have been developed by using the orthogonal collocation on finite elements (OCFE) method to solve simple [1] as well as more general [2] models of sorption dynamics in chromatographic columns. The OCFE method is regarded as one of the most accurate [1], but requires long computational times, even when it is used in a version of orthogonal collocation on moving finite elements [3].

Application of different finite difference methods for solving chromatography models was examined by Rouchon et al. [4], Czok and Guiochon [5,6], Ma and Guiochon [1] and was summarized by Guiochon

et al. [7]. One of the more interesting is the forward-backward calculation scheme (Eq. 2) proposed by Rouchon for solving the equilibrium-dispersive (ED model) chromatography column model (Eq. 1). The Rouchon algorithm gives less accurate solutions in comparison with OCFE, but this disadvantage is compensated for by considerably lower computation time [1].

$$\frac{\delta c_i}{\delta t} + F \frac{\delta \Gamma_i}{\delta t} + w \frac{\delta c_i}{\delta z} = D_a \frac{\delta^2 c_i}{\delta z^2}; \quad F = \frac{1 - \varepsilon_i}{\varepsilon_i} \rho_s \quad (1)$$

$$\frac{c_{i,z-1}^{t+1} - c_{i,z-1}^t}{\Delta t} + F \frac{\Gamma_{i,z-1}^{t+1} - \Gamma_{i,z-1}^t}{\Delta t} + w \frac{c_{i,z}^{t+1} - c_{i,z-1}^{t+1}}{\Delta z} = 0 \quad (2)$$

for $i = 1, \dots, NC$

In the finite difference scheme (Eq. 2) the approximation of the apparent dispersion term of Eq. (1) is not given. The band profile broadening caused by dispersion was simulated indirectly due to the effect

* Corresponding author.

of numerical diffusion by appropriate choice of the time and spatial increments – see Eqs. (3,4).

$$\Delta z = \frac{2D_a}{w} \quad (3)$$

$$\Delta t = \frac{\Delta z}{w}(1 + k')a \quad (4)$$

where $a=2$ was recommended [7].

Successive numerical solutions of the finite difference (Eq. 2) for increasing values of the space and then the time increments allow the calculation of concentration at each point of the grid, by using the initial and boundary conditions.

It should be noted that the Rouchon algorithm is accurate only in linear chromatography and for a single component. In nonlinear cases the Rouchon method does not give a correct solution because the retention factor k' is a function of component concentration and therefore is changing in time and space. The next source of error appears in multi-component chromatography even for a linear isotherm. It should be noted that in implementation of the Rouchon algorithm for multicomponent chromatography, appropriate interval sizes that will produce the desired band broadening were chosen for one component of the mixture. For other peaks with different retention factors, the time increment resulting from this choice had to be accepted. Such a method of time increment establishment can give unacceptable results for the calculation for a mixture of components with remarkably different values of the retention factor k' .

In spite of the mentioned drawback, the Rouchon algorithm was successfully used for modeling nonlinear two-component chromatography systems when the ratio of retention factors k'_2/k'_1 was relatively small [1,6,7].

The aim of this work is to present accuracy and efficiency of calculation with a modified Rouchon algorithm for the ED model and a modified Rouchon-like finite difference scheme proposed in Refs. [3,8] for the lumped pore diffusion model (POR model).

The accuracy of calculation with the different schemes will be tested by comparison with the solution obtained using the orthogonal collocation on finite elements (OCFE) technique.

2. Modification of the Rouchon algorithm for equilibrium-dispersive chromatographic model

As noted above, in the original Rouchon scheme applied for modeling multicomponent nonlinear chromatography there are two sources of error:

1. Numerical diffusion does not exactly approximate the apparent dispersion because the retention factor k' in Eq. (4) is a function of component concentration and thus is changing in time and space.
2. The time increment calculated from Eq. (4) for a chosen component from the chromatographic mixture is not adequate for the other components.

The first error can be eliminated by appropriate control of numerical diffusion [5] but is very CPU time consuming – the time of computation is about 5 times longer in comparison with the exact OCFE method and about 200 times longer in comparison with the original Rouchon method [1].

It seems that it will be very difficult to find a numerical method which will be as precise as OCFE and as fast as the Rouchon method and that is why we concentrate on the elimination of the second source error in the Rouchon algorithm.

To eliminate the second source of error in implementation of the Rouchon algorithm, integration of Eq. (1) for a multicomponent mixture was performed on the individual time grid for each component. The difference for each grid time increment was calculated from an equation analogous to [4]:

$$\Delta t_i = \frac{\Delta z}{w}(1 + k'_i)a \quad (5)$$

where k'_i is a retention factor for component i and Δz is calculated from Eq. (3).

The Rouchon scheme for each component can be rewritten as:

$$\frac{c'_{i,z-1} - c'_{i,z-1}}{\Delta t_i} + F \frac{F'_{i,z-1} - F'_{i,z-1}}{\Delta t_i} + w \frac{c'_{i,z} - c'_{i,z-1}}{\Delta z} = 0 \quad (6)$$

where $i=1,\dots,NC$. It should be noted that all advantages of the original Rouchon algorithm are preserved.

In the following paragraphs, several comparisons of solutions of Eq. (1) coupled with the Langmuir isotherm

$$\Gamma_i = \frac{\Gamma_i^\infty K_i c_i}{1 + \sum_{j=1}^{NC} K_j c_j} \quad (7)$$

obtained by using the modified Rouchon algorithm and the OCFE algorithm are presented. It should be noted that for calculation of the adsorbent surface concentration Γ_i , the value of concentration c_j in the fluid phase must be known. In the modified Rouchon algorithm, the concentration with index “ i ” is computed for different nodal points of the time grid than concentrations of other components with index “ j ”. To calculate surface concentration Γ_i , the appropriate values of concentration c_j in the denominator of Eq. (7) were obtained using linear interpolation.

In linear chromatography the retention factor k'_i in Eq. (5) is equal to the term $k'_i = FK_i \Gamma_i^\infty$. In the nonlinear case the retention factor is also approximated by the same equation.

To accelerate computation by using modified Rouchon method, the idea of eliminating from the calculation all points with a concentration below a certain threshold [9] was applied. In this work nodal points with a concentration less than $c_{i,j} \cdot 10^{-6}$ were eliminated from the computation. The error in mass balance was always less than about 0.0001%.

The solution with the OCFE method was performed assuming Danckwerts boundary conditions – Eqs. (15,16) with D_a in place of $\epsilon_c D_L$. In the case of the Rouchon scheme, boundary conditions were assumed typical for HPLC:

$$c_i(t, 0) = c'_{f,i};$$

$$c'_{f,i} = \{c_{f,i} \text{ for } t \in [0, t_p]; \quad 0 \text{ for } t > t_p\} \quad (8)$$

$$\left. \frac{dc_i(t, z)}{dz} \right|_{z=L} = 0 \quad (9)$$

The OCFE method applied here is the same as that described in Refs. [1–3,7] but obtained after the discretization set of ordinal differential equations was solved using the Adams–Moulton procedure implemented in the LSODA solver [10] using a relative and absolute error equal to 10^{-6} . The

LSODA procedure automatically chooses the appropriate time increment to fulfil assumed error conditions. In each calculation the number of internal collocation points in subdomains (elements) was equal to 3. The number of subdomains was chosen in such way as to have no visible oscillation in band profile simulation.

In each calculation the following values of the parameters were assumed: $F=0.25$, $w=0.0015$, $D_a=3.75 \cdot 10^{-8}$, $\Gamma^\infty=4 \cdot 10^{-3}$. Column length was $L=0.15$ except for Fig. 8 where $L=0.25$. The values of equilibrium constants, inlet concentrations and pulse time are given below. The number of theoretical plates, calculated as $N=L/\Delta x=Lw/2D_a$, was 3000 except for Fig. 8 where $N=5000$.

All calculation were performed on a PC-Pentium 60 MHz computer. Programs were written in Micro Way NDP Fortran.

In the original Rouchon method the recommended a parameter was 2 – see Ref. [7] chapter X. Such a choice of a describes chromatographic bands for large overload conditions and relatively strongly adsorbed components well. For weaker adsorbed components and small amounts of sample, calculation with $a=2$ can give unacceptable results.

As an example in Figs. 1–4 a comparison of the ED model solution with the OCFE method (solid line) and the original Rouchon method (dashed and dotted lines) for different a , pulse times t_p and equilibrium constants $K=0.5$ or $K=10$ is given. A solution for weakly adsorbent substances obtained by

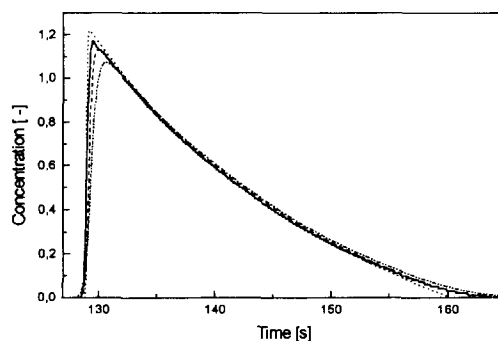


Fig. 1. Comparison of results of calculation for a one-component mixture [$K=0.5$, $c_j=1.5$, $t_p=10$ (weakly adsorbed substance and overload conditions)] obtained by using the OCFE method (solid line), and the original Rouchon method for $a=1$ (dotted line), $a=1.5$ (dashed line) and $a=2$ (dash-dotted line). NS=300.

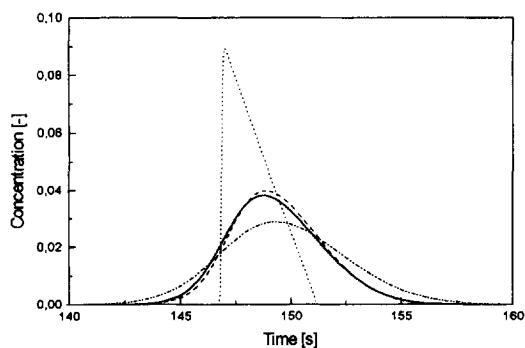


Fig. 2. Same as in Fig. 1 but $c_f=0.2$, $t_p=1$.

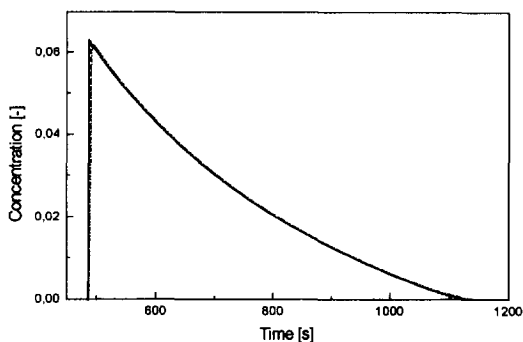


Fig. 3. Same as in Fig. 1 but $K=10$, $NS=650$.

using the finite difference method for $a=2$ gives a marked error. It should be noted that weak adsorption conditions are not a marginal problem, since Felinger and Guiochon [9] showed that in such cases the column productivity can be maximal. On the basis of analysis of the data given in Figs. 1–4 we

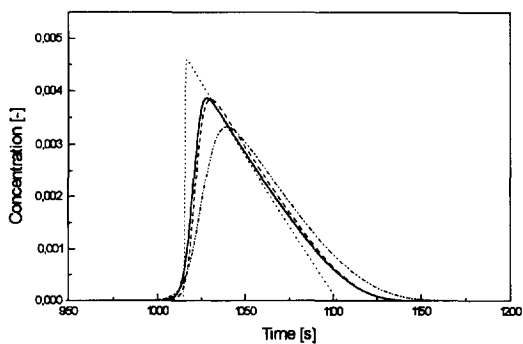


Fig. 4. Same as Fig. 1 but $c_f=0.2$, $K=10$, $t_p=1$.

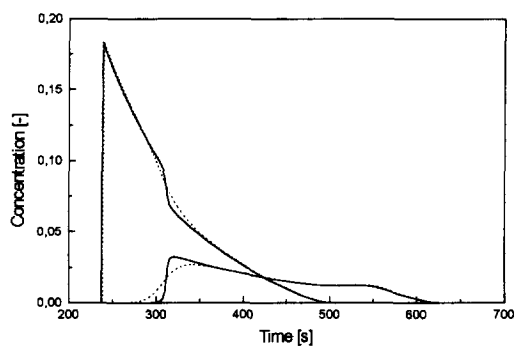


Fig. 5. Comparison of results of calculations for a two-component mixture which were obtained by using the OCFE method (solid line), and the modified Rouchon method for $a=1.5$ (dotted line). Sample composition was 1.5:0.5. $NS=350$.

decided to apply $a=1.5$ in the following calculation for modified and original versions of the Rouchon algorithm.

In Figs. 5–7 a comparison between the OCFE solutions, the original Rouchon and the modified Rouchon solutions is given for $K_1=4$, $K_2=5$, pulse time $t_p=10$ and sample compositions: 1.5:0.5, 1:1, 0.5:1.5. These problems were analyzed in Refs. [1,6,7]. In Fig. 8 the simulations for $t_p=100$, $K_1=1$, $K_2=2$, $c_{f1}=1$, $c_{f2}=1$ are presented. For small differences between equilibrium constants K_1 and K_2 , both difference methods give solutions that are indistinguishable on the applied figure scale. Times of computations, number of theoretical plates and number of subdomains in the OCFE method are presented in Table 1. With an increase of the band

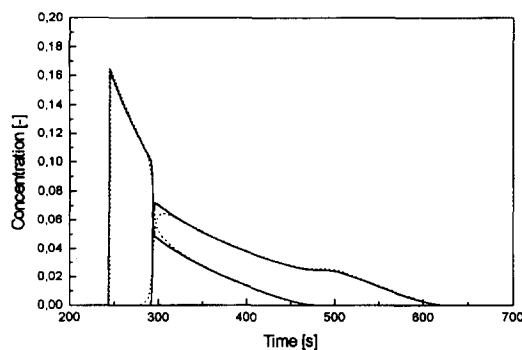


Fig. 6. Same as in Fig. 5 but the sample composition was 1.0:1.0. $NS=550$.

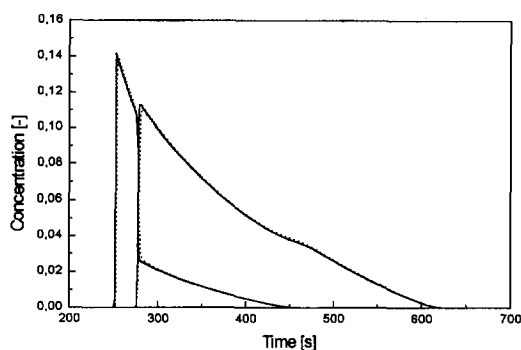


Fig. 7. Same as in Fig. 5 but the sample composition was 0.5:1.5. NS=550.

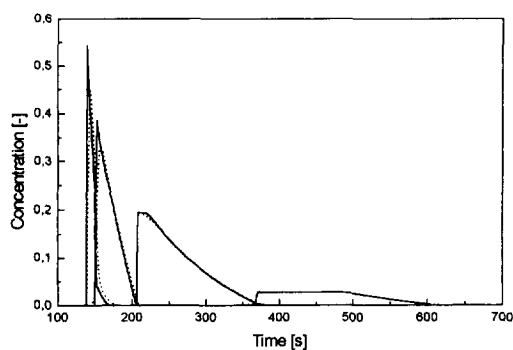


Fig. 9. Comparison of the OCFE and original Rouchon methods for a four-component mixture. NS=400.

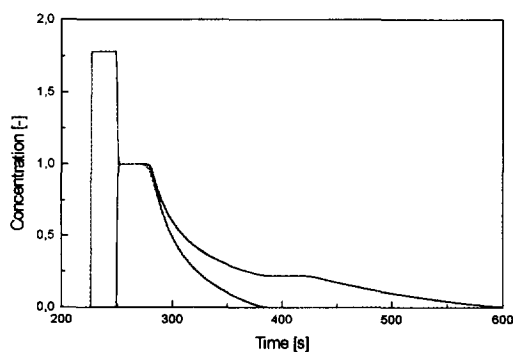


Fig. 8. Comparison of the OCFE (solid line) and modified Rouchon (dotted line) methods for very strong overload conditions. NS=800.

concentration gradient, the number of subdomains must be enlarged to avoid unrealistic oscillation of solutions. This involves a marked increase in the ratio of the computation times for the OCFE method and the finite difference method when the concentration gradient becomes steeper – see Figs. 5 and 8.

The ratio of CPU times of old to new finite difference methods is ca. 1.8 for $N=3000$ and ca. 3 for $N=16\,000$.

In the case where the concentration of one component is much larger than that of a second one and peaks overlap, the modified Rouchon method does not improve the solution compared to that of the original method.

The original Rouchon method should not be applied if differences between equilibrium constants (generally between k') are marked. In Fig. 9 the results of simulations for a four component mixture: $K_1=1$, $K_2=1.5$, $K_3=3$, $K_4=5$, $c_{f1}=0.5$, $c_{f2}=1.0$, $c_{f3}=1.5$, $c_{f4}=0.5$ and $t_p=10$ obtained by using the OCFE method and the original Rouchon method are presented. In Fig. 10 the same comparison is given for the OCFE and the modified Rouchon method. As can be seen in this case, the calculation using the original Rouchon method gives some errors especially for the first and second components. The error value depends on the required purity of components.

Table 1
Comparison of CPU times for simulation given in Figs. 5–8

Fig.	N	NS	Time (min)		
			Orthogonal collocation	Original Rouchon method	Modified Rouchon method
Fig. 5	3000	350	114.9	3.1	1.7
Fig. 6	3000	550	175.6	3.1	1.7
Fig. 7	3000	550	179.2	3.1	1.7
Fig. 8	5000	800	440.2	12.5	5.9
Similar to Figs. 5–7	16 000	–	–	120	43
Similar to Fig. 8	16 000	–	–	185.1	58.7

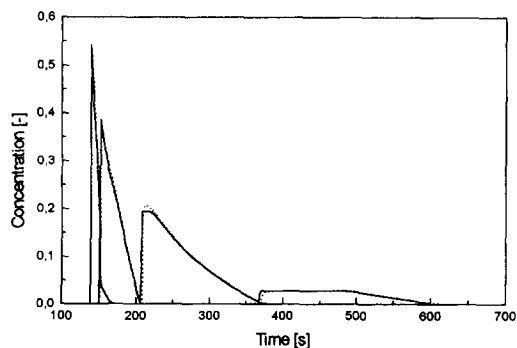


Fig. 10. Comparison of the OCFE (solid line) and modified Rouchon (dotted line) methods for a four-component mixture.

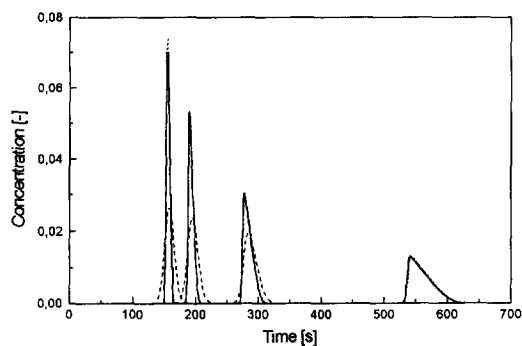


Fig. 11. Comparison of solutions obtained by the OCFE (solid line), modified (dotted line) and original (dashed line) Rouchon methods for a four-component mixture. $NS=150$.

If, for example, it is stipulated that component two is recovered with impurities of component one and three of less than 10^{-3} kmol/m³, then cut times should be about 171 s and 207 s with the OCFE or the modified Rouchon method. The original Rouchon method gives cut times equal to 181 s and 206 s. When the stipulated concentrations of component one and three are less than 10^{-6} kmol/m³, cut times should be about 179 s and 207 s for the OCFE or the modified Rouchon method and 197 s and 204 s for the original Rouchon method. Evaluating the cut points in the original Rouchon method, the first time about 30% of pure component two would be lost and the second time about 70%. Times of calculation were equal: the modified Rouchon algorithm – 3.8 min; original algorithm – 5.7 min; and the OCFE method – 2187.5 min.

Differences between band profiles and CPU times for the finite difference methods under discussion are more marked the smaller the pulse time and the greater the number of theoretical plates. In Fig. 11 the comparison of calculations for $N=2000$, $K_1=0.6$, $K_2=1$, $K_3=2$, $K_4=5$, $t_p=1$, $c_{f1}=c_{f2}=c_{f3}=c_{f4}=0.5$ for all numerical methods discussed in this work is presented. The solution obtained with the modified Rouchon method is nearly identical with that of the OCFE method while that obtained with the original Rouchon method is unacceptable.

To emphasize the gain in CPU time when calculations are not performed on nodal points at which concentrations are smaller than $c_f \cdot 10^{-6}$, the computations were carried out for a number of theoretical plates equal to 2000, 4000, 8000 and 16 000 and

CPU times were compared with the case when calculations were performed on every nodal point. From the results given in Table 2 it follows that the time of computation can be even 50 times shorter when calculations are performed only in nodal points occupied by peaks in comparison to calculations carried out for every nodal point. The time of computation with the modified Rouchon algorithm with elimination of nodal points with concentrations less than $c_f \cdot 10^{-6}$ from calculation is proportional to N^β where β was equal to 1.84 in the example given.

3. Modification of the Rouchon-like algorithm for the lumped pore diffusion model

The ED model can be used when mass transfer resistances are almost negligible. However in the separation of substances such as proteins, mass transfer resistances should be taken into account and in this case a general chromatographic model (GCh model) is recommended [11]. Calculations using the GCh model are very time-consuming and several groups of researchers have proposed simplifications of the GCh model in which, however, all mass transfer resistances were taken into account. The interesting proposition of such a simplified model called the lumped pore diffusion model (POR model) was successfully used to describe the separation of an alkylaromatic C-9 fraction or chlorotoluene isomer mixture on Y zeolites [12,13]. Unfortunately, conditions under which the GCh model

Table 2
Times of simulation for a mixture of four components for different numbers of theoretical plates

	N			
	2000	4000	8000	16 000
CPU time (s)—case (a)	42	131	444	1605
CPU time (s)—case (b)	1151	4934	21 221	87 300

Calculations were carried out using the modified Rouchon method in two cases: (a) calculation was performed only for nodal points at which concentrations were greater than $c_j \cdot 10^{-6}$; (b) calculations were performed for every nodal point.

could be substituted by the POR model are not yet given. In the following section, such conditions will be formulated and application of a modified Rouchon-like algorithm constructed for the POR model will be discussed.

3.1. Comparison of the GCh model and the POR model

If the following conditions can be assumed:

1. the multicomponent fixed-bed process is isothermal,
2. the bed is packed with porous adsorbents which are spherical and uniform in size,
3. the concentration gradient in the radial direction of the bed is negligible,
4. local equilibrium exists for each component between the pore surface and the stagnant fluid phase in macropores,
5. the dispersion and mass transfer coefficients are constant,

then the following GCh model can be formulated [2,14]:

– material balance of the i -th component in the mobile fluid phase

$$\varepsilon_e \frac{\delta c_i}{\delta t} + \frac{\delta}{\delta z}(u c_i) = \varepsilon_e D_L \frac{\delta^2 c_i}{\delta z^2} - (1 - \varepsilon_e) k_{\text{ext},i} a_p (c_i - c_{p,i}(r = R_p)) \quad (10)$$

– material balance of the i -th component in the solid phase:

$$\varepsilon_p \frac{\delta c_{p,i}}{\delta t} + (1 - \varepsilon_p) \rho_s \frac{\delta I_i}{\delta t} = D_{\text{eff}} \frac{1}{r^2} \frac{\delta}{\delta r} \left(r^2 \frac{\delta c_{p,i}}{\delta r} \right) \quad (11)$$

By summing Eq. (10) for all components, each divided by the molar density of the component, ρ_i , and assuming the additivity of volumes for the fluid mixture, the following equation for the fluid velocity can be obtained:

$$\frac{\delta u}{\delta z} = -(1 - \varepsilon_e) \sum_{i=1}^{\text{NC}} k_{\text{ext},i} a_p (c_i - c_{p,i}(r = R_p)) / \rho_i \quad (12)$$

– initial conditions for $t = 0$

$$c_i(0, z) = c_i^o \quad \text{for } 0 < z < L \quad (13)$$

$$\left. \begin{aligned} c_{p,i}(0, r, z) &= c_{p,i}^o(r, z) \\ I_i(0, r, z) &= I_i^o(r, z) \end{aligned} \right\} \text{for } 0 < z < L; 0 < r < R_p \quad (14)$$

boundary conditions for Eq. (10)

for $t > 0; z = 0$

$$u_f c'_{f,i} - u(t, 0) c_i(t, 0) = -\varepsilon_e D_L \frac{\delta c_i(t, 0)}{\delta z}; \quad c'_{f,i} = \{c_{f,i} \text{ for } t \in [0, t_p]; 0 \text{ for } t > t_p\} \quad (15)$$

for $t > 0; z = L$

$$\frac{\delta c_i(t, L)}{\delta z} = 0 \quad (16)$$

boundary conditions for Eq. (11)

for $t > 0; r = R_p$

$$D_{\text{eff}} \frac{\delta c_{p,i}(t, r)}{\delta r} = k_{\text{ext},i} (c_i - c_{p,i}(t, r)) \quad (17)$$

for $t > 0$; $r = 0$

$$\frac{\delta c_{pi}(t, r)}{\delta r} = 0 \quad (18)$$

For calculation of the mass transfer coefficient and the dispersion coefficient in the case of liquid chromatography, the following correlations are recommended [2,7,15]:

– transport coefficient in the external fluid film k_{ext} [16]

$$Sh = \frac{1.09}{\varepsilon_e} Re^{0.33} Sc^{0.33}; \quad 0.0015 \leq Re \leq 55 \quad (19)$$

– Peclet number [17]

$$\varepsilon_e \frac{d_p}{L} Pe = 0.2 + 0.011 Re^{0.48} \quad (20)$$

The material balance of the i -th component in the mobile fluid phase and solid phase in the POR model can be expressed as:

$$\varepsilon_e \frac{\delta c_i}{\delta t} + \frac{\delta}{\delta z}(uc_i) = \varepsilon_e D_L \frac{\delta^2 c_i}{\delta z^2} - (1 - \varepsilon_e) k_i a_p (c_i - \bar{c}_{pi}) \quad (21)$$

– the material balance of the i -th component in the solid phase:

$$\varepsilon_p \frac{\delta \bar{c}_{pi}}{\delta t} + (1 - \varepsilon_p) \rho_s \frac{\delta \bar{F}_i}{\delta t} = k_i a_p (c_i - \bar{c}_{pi}) \quad (22)$$

$$\frac{\delta u}{\delta z} = - (1 - \varepsilon_e) \sum_{i=1}^{NC} k_i a_p (c_i - \bar{c}_{pi}) / \rho_i \quad (23)$$

where \bar{c} and \bar{F} denote average concentration.

The overall mass transfer coefficient k is calculated from the equation:

$$k = \left(\frac{1}{k_{ext}} + \frac{1}{k_{int}} \right) \quad (24)$$

where k_{ext} and k_{int} indicate external and internal (macropore) mass transfer coefficients respectively. The external mass transfer coefficient is calculated from (Eq. 19) and the internal mass transfer coefficient from Eq. (25)

$$k_{int} = \frac{10 D_{eff}}{d_p}; \quad D_{eff} = \frac{\varepsilon_p D_m}{\Theta} \quad (25)$$

where D_m is the molecular diffusion coefficient,

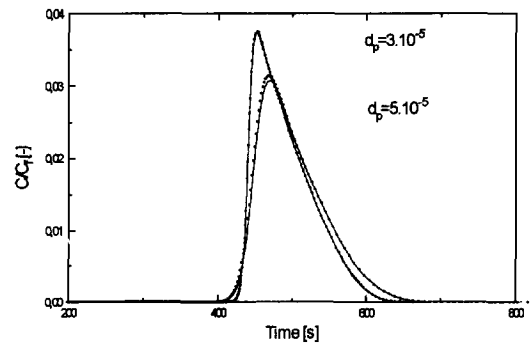


Fig. 12. Comparison of solutions obtained from calculations using the GCh model – solid line; and the POR model – dotted line. The number of the subdomain was 20 for $d_p = 5 \cdot 10^{-5}$ and 40 for $d_p = 3 \cdot 10^{-5}$.

while Θ is the tortuosity factor. The dispersion coefficient is calculated from Eq. (20), initial and boundary condition are analogous to those in the GCh model.

Detailed discussion of the assumptions following from the GCh model to the POR model are presented in Ref. [12].

For comparison of the GCh and POR models, both models were solved using the OCEF method. The variation of fluid velocity was ignored. The number of subdomains (elements) was equal to one for the adsorbent pellet and for the columns it is given in the figure captions. The number of internal collocation points in the subdomains was equal to 4 or 3 for the pellet and 3 for the column. The set of ordinal differential equations obtained after discretization of the POR or GCh models was solved using the LSODA procedure [10]. Relative and absolute errors were equal to 10^{-6} . All calculations were performed on a PC Pentium 60 MHz computer.

The comparison of both models is given in Fig. 12 and in Table 3 for adsorbent pellets of diameter 50 μm and 30 μm . Physico-chemical model parameters were calculated as for the hexane (eluent), benzene

Table 3
Comparison of CPU times for data given in Fig. 12

d_p (μm)	Pe	St	Bi	Time of computation (min)	
				POR model	GCh model
30	1236	4556	40.8	11.6	300
50	1236	1941	48.3	1.22	47

(sample) mixture. Other parameters were: $L=0.1$, $u_f=0.001$, $\varepsilon_c=0.33$, $\varepsilon_p=0.52$, $r_s=1960$, $\Gamma^\infty=0.002$, $K=4$, $\tau=3$, $t_p=5$, $c_f=0.6$. The dimensionless Peclet, Stanton and Biot numbers, characterizing dispersion and mass transfer resistances are given in Table 3.

As can be seen, for given data and pellet diameters less than about 30 μm both models are fully equivalent. For $d_p=50 \mu\text{m}$ the differences are still negligible. On the other hand, time of computation using the GCh model was about 30 times longer.

The Peclet number was $Pe=1236$ in these calculations. For $Pe=100$ or $Pe=10\,000$ with other parameters unchanged, differences between the solutions using the POR and the GCh models were the same as in Fig. 12. Changes in the equilibrium constant from 0.2 (very weak adsorbed substance) to 10 (strong adsorbed substance) did not influence the accuracy of computation with the POR model either. Of course, the comparison given in Fig. 12 is not general but we want to illustrate it for typical LC conditions. Much more convenient and general is the comparison of models written in the dimensionless form. After introducing the following dimensionless variables:

$$x = \frac{z}{L}; R = \frac{r}{R_p} \quad \tau = \frac{tu_f}{L\varepsilon_c}; y_i = \frac{c_i}{\rho_r}; y_{pi} = \frac{c_{pi}}{\rho_r};$$

$$Pe = \frac{u_i L}{D_L \varepsilon_c}; St_i = \frac{k_{ext} a_p L \varepsilon_c}{u_f}; Bi = \frac{k_{ext} R_p}{D_{eff}}; \xi = \frac{u}{u_f};$$

$$\varphi_i = \frac{\rho_r}{\rho_i}; q_i = \frac{\rho_s \Gamma_i}{\rho_r}; \sigma_i = \frac{\rho_s \Gamma_i^\infty}{\rho_r}$$

the GCh model can be rewritten as follows:

$$\frac{\delta y_i}{\delta \tau} + \frac{\delta}{\delta x}(\xi y_i) = \frac{1}{Pe} \frac{\delta^2 y_i}{\delta x^2} - \frac{1 - \varepsilon_c}{\varepsilon_c} St_i (y_i - y_{pi}(R=1)) \quad (26)$$

$$\varepsilon_p \frac{\delta y_{pi}}{\delta \tau} + (1 - \varepsilon_p) \frac{\delta q_i}{\delta \tau} = \frac{St_i}{3Bi_i} \frac{1}{R^2} \frac{\delta}{\delta R} \left(R^2 \frac{\delta y_{pi}}{\delta R} \right) \quad (27)$$

$$\frac{\delta \xi}{\delta x} = - \frac{1 - \varepsilon_c}{\varepsilon_c} \sum_{i=1}^{NC} St_i (y_i - y_{pi}(R=1)) \phi_i \quad (28)$$

– initial conditions for $\tau=0$

$$y_i(0, x) = y_i^o \quad \text{for } 0 < x < 1 \quad (29)$$

$$\left. \begin{aligned} y_{pi}(0, R, x) &= y_{pi}^o(R, x) \\ q_i(0, R, x) &= q_i^o(R, x) \end{aligned} \right\} \text{for } 0 < x < 1; 0 < R < 1 \quad (30)$$

boundary conditions for Eq. (26)

for $\tau > 0; x = 0$

$$y'_{fi} - \xi(\tau, 0)y_i(\tau, 0) = - \frac{1}{Pe} \frac{\delta y_i(\tau, 0)}{\delta x};$$

$$y'_{fi} = y_{fi} \text{ for } \tau \in [0, \tau_p]; y'_{fi} = 0 \text{ for } \tau > \tau_p \quad (31)$$

$$\xi(t, 0) = 1$$

for $\tau > 0; x = 1$

$$\frac{\delta y_i(\tau, x)}{\delta x} = 0 \quad (32)$$

boundary conditions for Eq. (27)

for $\tau > 0; R = 1$

$$\frac{\delta y_{pi}(\tau, R)}{\delta R} = Bi_i (y_i - y_{pi}(\tau, R)) \quad (33)$$

for $\tau > 0; R = 0$

$$\frac{\delta y_{pi}(\tau, R)}{\delta R} = 0 \quad (34)$$

With the same dimensionless variables the POR model can be rewritten as:

$$\frac{\delta y_i}{\delta \tau} + \frac{\delta}{\delta x}(\xi y_i) = \frac{1}{Pe} \frac{\delta^2 y_i}{\delta x^2} - \frac{1 - \varepsilon_c}{\varepsilon_c} \frac{St_i}{1 + Bi_i/5} (y_i - \bar{y}_{pi}) \quad (35)$$

$$\varepsilon_p \frac{\delta \bar{y}_{pi}}{\delta \tau} + (1 - \varepsilon_p) \frac{\delta \bar{q}_i}{\delta \tau} = \frac{St_i}{1 + Bi_i/5} (y_i - \bar{y}_{pi}) \quad (36)$$

$$\frac{\delta \xi}{\delta x} = - \frac{1 - \varepsilon_c}{\varepsilon_c} \sum_{i=1}^{NC} \frac{St_i}{1 + Bi_i/5} (y_i - \bar{y}_{pi}) \phi_i \quad (37)$$

analogous to initial and boundary conditions for the GCh model.

To compare the above models, calculations were executed for $Pe=1000$ and different Biot and Stanton numbers. Other parameters needed for solving dimensionless models were the same as in the example given in Fig. 12. The Peclet number was not changed because dispersion is taken into account in

the same way in both models and, as stated above, it did not influence the accuracy of computation with the POR model. An example of a comparison between these two models is given in Fig. 13.

The differences between the solutions obtained using both models are negligible with the scale used in Fig. 13. However after a scale-up as presented in the upper right corner of Fig. 13 one can see that for $Bi = 3000$ the band profiles calculated with the POR model begin distinctly earlier than with the GCh model.

The same accuracy of computation using the POR model was observed for Stanton numbers 10, 1000 and 100 000. Taking this into account we propose to use the POR model instead of the GCh one if $St/Bi > 5$.

3.2. Rouchon-like algorithm for the POR model

In Refs. [3,8] a Rouchon-like algorithm for the POR model is proposed.

Taking the Rouchon idea into account, the finite difference approximation of Eq. (35) is as follows:

$$y_{i,x}^{\tau+1} \xi_x^{\tau+1} = y_{i,x-1}^{\tau+1} \xi_{x-1}^{\tau-1} - \left(\frac{y_{i,x-1}^{\tau+1} - y_{i,x-1}^{\tau}}{\Delta\tau} + \frac{1 - \varepsilon_c}{\varepsilon_c} \frac{St_i}{1 + Bi_i/5} \times (y_{i,x-1}^{\tau+1} - \bar{y}_{p,i,x-1}^{\tau+1}) \right) \Delta x \quad (38)$$

Eq. (36) was approximated by the implicit scheme

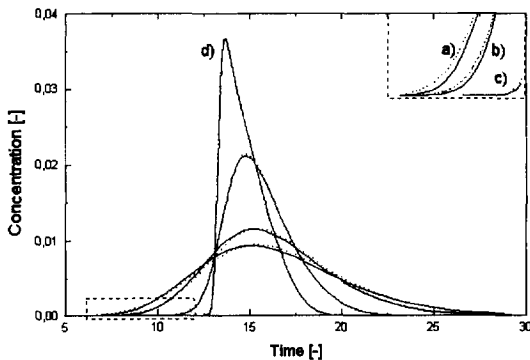


Fig. 13. Comparison of solutions obtained by the GCh model and the POR model for $Pe = 1000$ and $St = 10\,000$. The Biot number was (a) $Bi = 3000$; (b) $Bi = 2000$; (c) $Bi = 500$; (d) $Bi = 1$.

$$\bar{y}_{p,i,x}^{\tau+1} = y_{i,x}^{\tau+1} - \frac{\varepsilon_p (\bar{y}_{p,i,x}^{\tau+1} - \bar{y}_{p,i,x}^{\tau}) + (1 - \varepsilon_p) (\bar{q}_{i,x}^{\tau+1} - \bar{q}_{i,x}^{\tau})}{St_i \Delta\tau} \times \left(1 + \frac{Bi_i}{5} \right) \quad (39)$$

The Danckwerts boundary condition at the inlet of the column was replaced by $y_i(0) = y_{fi}$. The dispersion effect was simulated indirectly as in the original Rouchon scheme by appropriate choice of spatial and time increments [3,8].

$$\Delta x = \frac{2D_L \varepsilon_i}{u_f L} \quad (40)$$

$$\Delta\tau = \Delta x (1 + FKT^\infty) * a \quad (41)$$

where D_L was calculated from Eq. (20) and a was chosen as 2.9 – see Ref. [3].

Simulation of chromatographic and adsorption processes using this scheme proved to be some hundred times faster in comparison with OCFE methods [3,8].

Unfortunately the algorithm (Eqs. 38–41) has the same two disadvantages as the original Rouchon scheme discussed for the ED model. In the case of the POR model we have also concentrated on eliminating the second source of error in the algorithm (Eqs. 38–41) by integrating Eqs. (38,39) for multicomponent mixtures on the individual time grid for each component. The time increment difference for each grid was calculated from an equation analogous to Eq. (5):

$$\Delta\tau_i = \Delta x (1 + FK_i \Gamma_i^\infty) a \quad (42)$$

with the value of parameter $a = 2.9$ as recommended in Refs. [3,8].

As in the case of the modified Rouchon method the points with a concentration below $c_{i,f} \cdot 10^{-6}$ were eliminated from the computation. The error in mass balance was less than 0.0001%.

In Figs. 14–17 and in Table 4 comparison of the solutions using the OCFE method, Rouchon-like and modified Rouchon-like finite difference schemes is presented. Calculations were performed for $Pe = 1000$, $St/(1 + Bi/5) = 1000$, $\rho_i = 1$, $\varepsilon_c = 0.33$, $\varepsilon_p = 0.52$, $r_s = 1960$, $\Gamma^\infty = 2 \cdot 10^{-3}$. Other parameters are given in the captions for Figs. 14–17. The time

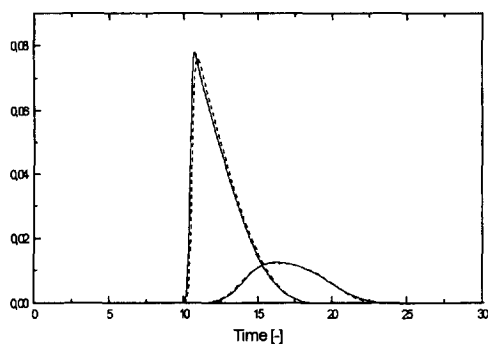


Fig. 14. Comparison of the solutions obtained by the OCFE method (solid line) and the modified Rouchon-like algorithm (dashed line). $K_1=4$, $K_2=5$, $\tau_p=0.15$, $y_{f1}=1.5$, $y_{f2}=0.5$, $NS=35$.

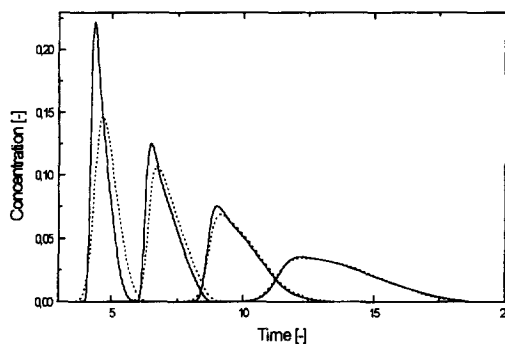


Fig. 17. Same as in Fig. 16 but the dotted line denotes the solution obtained by the unmodified Rouchon-like algorithm.

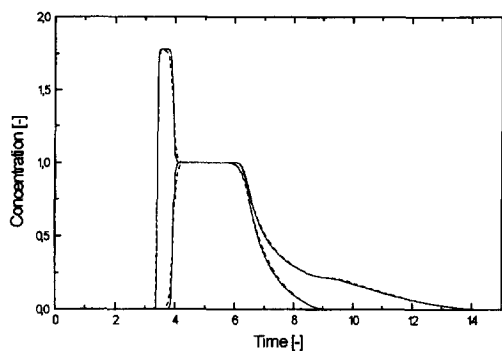


Fig. 15. Comparison of the solutions obtained by the OCFE method (solid line) and the modified Rouchon-like algorithm (dashed line). $K_1=1$, $K_2=2$, $\tau_p=4$, $y_{f1}=y_{f2}=1.0$, $NS=60$.

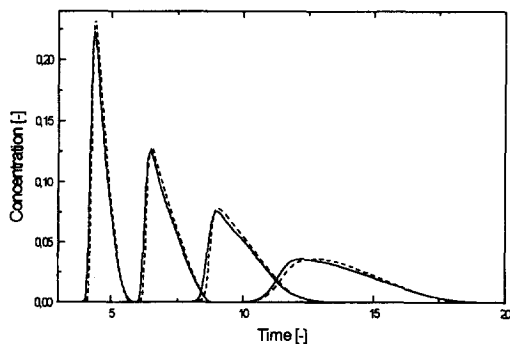


Fig. 16. Comparison of the solutions obtained by the OCFE method (solid line) and the modified Rouchon-like algorithm (dashed line). $K_1=1$, $K_2=2$, $K_3=3$, $K_4=4$, $\tau_p=0.15$, $y_{f1}=y_{f2}=y_{f3}=y_{f4}=1.0$, $NS=25$.

increment for the unmodified Rouchon-like method was calculated from Eq. (41) for the most strongly adsorbed component.

For small differences between equilibrium constants (saturation capacity was assumed to be constant for each component) both difference methods give the same results for concentration overload as well as mass and concentration overload conditions – Figs. 14 and 15. The accuracy of the solution even for a concentration ratio of 3:1 is very good.

In the case of substantial differences between equilibrium constants, such as in Figs. 16 and 17, the accuracy of the modified Rouchon-like algorithm can still be acceptable but not for the unmodified one. Considerable differences are especially noticeable for the first and second components.

The time of computation using finite difference methods is even several hundred times shorter in comparison with the OCFE method. CPU times for the unmodified Rouchon-like method are up to several tens percent lower in comparison with those for the modified method. This is due to the fact that, in given examples, chromatographic peaks occupied a large part of the column and the time increment for the unmodified method is calculated for the most retained component, which is greater than the time increment calculated for other components in the modified method. For more effective column and less overload conditions, the time of computation using the modified algorithm is shorter in comparison with the unmodified one. As an example CPU times for $Pe=6000$, $St/(1+Bi/5)=3000$, different pulse times and inlet sample concentrations

Table 4

Comparison between times of computation for OCFE, Rouchon-like and modified Rouchon-like methods

Fig.	CPU time (s)		
	OCFE method	Rouchon-like method	Modified Rouchon-like method
Fig. 14	3529	12.5	17.5
Fig. 15	18 524	21.2	26.2
Figs. 16 and 17	6940	31.2	38.7

 $Pe = 1000, St/(1 + Bi/5) = 1000$

are given in Table 5. Other parameters are the same as for the simulation presented in Fig. 14.

For the same overload conditions as shown in Fig. 14, the modified Rouchon-like method is 1.4 times faster than the unmodified method. For the smallest loading factor, the modified algorithm is 4.4 times faster.

4. Comparison of the ED model and the POR model

It is well known that the ED model can be successfully used for simulation of HPLC. In this section we will give criteria for the applicability of the ED model for theoretical plate numbers up to 2000.

The ED model can be easily obtained from the POR model after eliminating the term $k_i a_p (c_i - \bar{c}_{pi})$ from Eq. (21) using Eq. (22). Assuming that mass transfer resistances are negligible, which is equivalent to condition $c_i = c_{pi}$, one can obtain a form of the ED model similar to that given by Eq. (1)

$$\varepsilon_i \frac{\delta c_i}{\delta t} + (1 - \varepsilon_i) \rho_s \frac{\delta I_i}{\delta t} + u \frac{\delta c_i}{\delta z} = \varepsilon_e D_L \frac{\delta^2 c_i}{\delta z^2} \quad (43)$$

or its dimensionless equivalent:

Table 5

Comparison between times of computation for Rouchon-like and modified Rouchon-like methods

Dimensionless pulse time τ_p	Dimensionless inlet concentration	CPU time (s)	
		Rouchon-like method	Modified Rouchon-like method
0.15	$y_{i1} = 1.5, y_{i2} = 0.5$	530	380
0.015	$y_{i1} = 1.5, y_{i2} = 0.5$	470	212
0.015	$y_{i1} = 0.1, y_{i2} = 0.1$	420	95

 $Pe = 6000, St/(1 + Bi/5) = 3000.$

$$\varepsilon_i \frac{\delta y_i}{\delta \tau} + (1 - \varepsilon_i) \frac{\delta q_i}{\delta \tau} = \varepsilon_e \frac{\delta y_i}{\delta x} = \varepsilon_e \frac{1}{Pe} \frac{\delta^2 y_i}{\delta x^2} \quad (44)$$

The ED model coupled with Danckwerts boundary conditions and the POR model were solved with the OCFE method for several Peclet, Stanton and Biot numbers. Other parameters were equal $\varepsilon_e = 0.33$, $\varepsilon_p = 0.52$, $\rho_s = 1960$, $\Gamma^\infty = 0.002$, $K = 4$, $\tau_p = 0.15$, $y_j = 0.6$. Constant fluid velocity in the POR model was assumed.

In Fig. 18 an example of the results of computation for $Pe = 500$ are presented. In Table 6, CPU times for both methods are given.

For the chromatographic process carried out under typical conditions, the Reynolds number is less than 1. From Eq. (20) it follows that $Pe \cong L/d_p$. Taking into account data given in Fig. 18 it can be seen that for $St/(1 + Bi/5) > \approx 4000$ differences between ED and POR models are negligible. Accuracy of computation for Pe between 500–4000 and $St/(1 + Bi/5) = 4000$ or $Pe = 100$ and $St/(1 + Bi/5) = 2000$ is similar to that presented in Fig. 18 for $St/(1 + Bi/5) = 4000$. The criteria of applicability of the ED model can be formulated as follows: for $L/d_p > \approx 500$ the POR model can be replaced by the ED model when the condition $St/(1 + Bi/5) > \approx 4000$ is fulfilled. For lower values of the ratio, $L/d_p > \approx 100$ ($Pe = 100$), the value of the dimensionless variable $St/(1 + Bi/5)$

Table 6
Comparison of CPU times for POR and ED models

Pe	$St/(1 + Bi/5)$	Number of theoretical plates $N = Pe/2$	Time of computation (s)	
			POR model	ED model
100	2000	50	42	2
500	4000	250	67	5
1000	4000	500	434	16
4000	4000	2000	22 825	317

should be greater than about 2000. Peclet numbers lower than 100 are rather uncommon in the chromatographic process.

5. Conclusion

In the present work the modified implementation of Rouchon and Rouchon-like algorithms was tested for ED and POR models. By introducing an individual time grid for each component it was possible to simulate the chromatographic process for mixtures of components having significantly different retention factors. Elimination of nodal points with a concentration less than a certain threshold from computation resulted in an essential reduction in CPU time, especially for very efficient column and low overload conditions. Comparing a Rouchon method, modified by us, to the original one and to a Rouchon method modified by Felinger and Guoichon [9], the following conclusions can be formulated:

(1) Our algorithm is stable if condition (Eq. 5) is fulfilled. Original and Felinger modified algorithms are generally stable only when the time increment is calculated for the most retained component – for example these algorithms would be unstable when the increment time is calculated for components 1, 2 from Fig. 9 or components 1, 2, 3 from Fig. 11.

(2) Due to introduction of an individual time grid for each component, it was possible to additionally reduce the time of computation in comparison with the Felinger rapid algorithm. The maximum gain in CPU time in the Felinger modification over the original Rouchon scheme was about 2.5. Using our numerical scheme, computation times can be reduced several dozen times.

(3) Accuracy of computation is always the same for the original Rouchon method and the Felinger modified method. For small values of separation factor, our approach gives the same results as the Rouchon scheme. The improvement of accuracy of calculation over the Rouchon method using our proposed method can not be strictly evaluated. It depends on the values of the equilibrium constants of components and on the overload conditions. The improvement is larger for greater values of the separation factor and lower overload conditions – in Fig. 11 the solution for the ED model with the original Rouchon algorithm marked with dashed lines does not match entirely to the solution obtained with the modified scheme and the OCFE scheme for the first two components. The differences between these two algorithms become smaller and smaller with increasing concentration overload conditions. However it is difficult to define exactly when the accuracy of both methods is practically the same. It depends on the purity requirement for the component under consideration and on its retention factor.

Similar conclusions can be formulated while com-

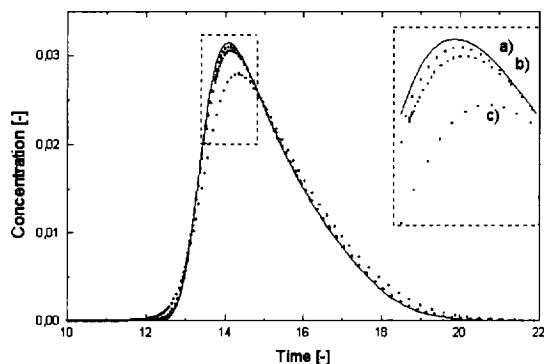


Fig. 18. Comparison between ED (solid line) and POR (dotted lines) model solutions for $Pe = 500$. (a) $St/(1 + Bi/5) = 4000$; (b) $St/(1 + Bi/5) = 2000$; (c) $St/(1 + Bi/5) = 500$.

paring the Rouchon-like method [3,8] and the modified one.

Finite difference methods based on the Rouchon proposition are not generally exact but their advantage over the robust and accurate OCFE method is that of a very small time of computation. In particular, the CPU time needed for solving the POR model with the finite difference method can be several hundred times shorter in comparison with the OCFE method. The finite difference algorithms discussed here can be very handy for fast, coarse optimizing of conditions with minimum production cost in preparative or production scale chromatography. The performance of such calculations is now possible on personal computers.

The other aim of the present work was to establish conditions for applicability of the GCh, POR and ED models which can be formulated as follows:

1. For $Pe > 100$ the POR model can be used instead of the GCh model if $St/Bi > 5$.
2. For $Pe > 100$ the ED model can be used instead of the POR model if $St/(1 + Bi/5) > 2000$.
3. For $Pe > 500$ the ED model can be used instead of POR model if $St/(1 + Bi/5) > 4000$.

6. List of symbols

a	parameter in Eqs. (4,5,41)
a_p	external surface of adsorbent pellet (m^2/m^3)
Bi	$\frac{k_{ext}R_p}{D_{eff}} = \text{Biot number}$
c	concentration in fluid phase ($kmol/m^3$)
c_p, \bar{c}_p	concentration or average concentration in macropore ($kmol/m^3$)
d_p	equivalent particle diameter (m)
D_a	apparent dispersion coefficient (m^2/s)
D_L	eddy diffusion coefficient (m^2/s)
D_m	molecular diffusion coefficient (m^2/s)
D_{eff}	effective diffusion coefficient (m^2/s) – Eq. (25)
F	$\frac{1 - \varepsilon_t}{\varepsilon_t} \rho_s$
k	overall mass transport coefficient (m/s)
k_{ext}	external mass transport coefficient (m/s)
k_{int}	internal mass transport coefficient (m/s)

K	equilibrium constant ($m^3/kmol$)
k'	retention factor
L	column length (m)
N	number of theoretical plates
NC	number of component
NS	number of subdomains (elements) in the OCFE method
Pe	$\frac{u_f L}{D_L \varepsilon_e} = \text{Peclet number}$
r	radial coordinate
R	dimensionless radial coordinate
R_p	equivalent particle radius
Re	$\frac{\rho u_f d_p}{\eta} = \text{Reynolds number}$
q, \bar{q}	dimensionless or average dimensionless adsorbed phase concentration
Sc	$\frac{\eta}{\rho D_m} = \text{Schmidt number}$
Sh	$\frac{k_{ext} d_p}{D_m} = \text{Sherwood number}$
St	$\frac{k_{ext} a_p L \varepsilon_e}{u_f} = \text{Stanton number}$
t	time (s)
t_p	time during the constant concentration c_f is fed into column (s)
u	superficial velocity (m/s)
w	interstitial velocity (m/s)
x	dimensionless axial coordinate
y	dimensionless concentration in fluid phase
y_p, \bar{y}_p	dimensionless concentration or average dimensionless concentration in macropore
z	axial coordinate (m)

6.1. Greek letters

Δt	time increment
Δx	dimensionless space increment
Δz	space increment
$\Delta \tau$	dimensionless time increment
$\Gamma, \bar{\Gamma}$	adsorbed or average adsorbed phase concentration ($kmol/kg$)
Γ^∞	adsorbent loading capacity ($kmol/kg$)
Θ	tortuosity factor
$\varepsilon_e, \varepsilon_p, \varepsilon_t$	external, internal and total void fractions
ϕ_i	$\frac{\rho_r}{\rho_t}$
η	fluid viscosity (kg/ms)

ρ	fluid molar density (kmol/m^3)
ρ_s	solid mass density (kg/m^3)
τ	dimensionless time
τ_p	dimensionless time during the constant concentration c_f is fed into column
σ_i	$\frac{\rho_s \Gamma_i^\infty}{\rho_r}$
ξ	dimensionless fluid volumetric velocity u/u_f

6.2. Subscripts

i	component index $i = 1, \dots, \text{NC}$
r	reference conditions
f	inlet value

6.3. Superscript

o	initial value
-----	---------------

References

- [1] Z. Ma and G. Guiochon, *Computers Chem. Eng.*, 13 (1991) 415.
- [2] A.J. Berninger, R.D. Whitley, X. Zhang and N.H.L. Wang, *Computers Chem. Eng.*, 15 (1991) 749.
- [3] K. Kaczmarski, *Computers Chem. Eng.*, 20 (1996) 42.
- [4] P. Rouchon, M. Schonauer, P. Valentin and G. Guiochon, *Separat. Sci.*, 22 (1987) 1793.
- [5] M. Czok and G. Guiochon, *Anal. Chem.*, 62 (1990) 189.
- [6] M. Czok and G. Guiochon, *Computers Chem. Eng.*, 14 (1990) 1435.
- [7] G. Guiochon, S. G. Shirazi and A. M. Katti, *Fundamentals of Preparative and Nonlinear Chromatography*, Academic Press, 1994, Chapters X, XI.
- [8] K. Kaczmarski and D. Antos, *Computers Chem. Eng.*, in press.
- [9] A. Felinger and G. Guiochon, *AIChEJ.* 40 (1994) 594.
- [10] A.C. Hindmarsh, Livermore solver for ordinary differential equations. Technical Report No. UCID-3001, Lawrence Livermore Laboratory, Livermore, CA (1972).
- [11] R.D. Whitley, K.E. Van Cott, J.A. Berninger and N.-H. L. Wang, *AIChEJ.* 37 (1991) 555.
- [12] M. Morbidelli, A. Servida, G. Storti and S. Carra, *Ind. Eng. Chem. Fundamen.*, 21 (1982) 123.
- [13] M. Morbidelli, G. Storti, S. Carra, G. Niederjaufner and A. Pontoglio, *Chem. Eng. Sci.*, 39 (1984) 383.
- [14] T. Gu, G.-J. Tsai and G.T. Tsao, Modeling of nonlinear multicomponent chromatography, in A. Fiechter (Editor), *Advances in Biochemical Engineering/Biotechnology*, Springer-Verlag, 1993.
- [15] G. Storti, M. Masi and M. Morbidelli, Modeling of counter-current adsorption processes, in G. Ganetsos and R.E. Barker (Editors), *Preparative and Production Scale Chromatography with Application*, Marcel Dekker, New York, 1993.
- [16] S.F. Chung and C.Y. Wen, *AIChEJ.* 14 (1968) 857–866.
- [17] E.J. Wilson and C.J. Geankoplis, *Ind. Eng. Chem. Fundam.*, 5 (1966) 9–14.