

Short Communication

Rapid simulation of chromatographic band profiles on personal computers

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ABSTRACT

The calculating power and speed of microcomputers has rapidly increased during the last few years, while their cost has decreased almost as fast. As a result, it has become possible for most chromatographers to calculate rapidly the individual elution band profiles of the components of mixtures by integrating the differential mass balance equation of chromatography. It has become possible to find out rapidly what would be the effect of possible modifications of the experimental parameters. For conventional columns having a few thousand plates, the computation takes between a few seconds and a few minutes, provided a performing algorithm is used.

Many different procedures are available for the calculation of the band profiles in overloaded elution chromatography. These algorithms are generally based on the numerical solution of the mass balance equation written for the equilibrium-dispersive model of chromatography [1,2].

$$\frac{\partial C}{\partial t} + F \cdot \frac{\partial q}{\partial t} + u \cdot \frac{\partial C}{\partial z} = D_{ap} \cdot \frac{\partial^2 C}{\partial z^2} \quad (1)$$

where C and q are the equilibrium concentrations in the mobile and stationary phases, respectively; F is the ratio of the volumes of mobile and stationary phases in the column; u is the

linear velocity of the mobile phase; t is the time and z is the length. The above model incorporates the different phenomena that cause band broadening into a single factor, the apparent dispersion coefficient, D_{ap} . This model describes very well the behavior of real chromatographic systems.

For the classical non-linear isotherms, the equilibrium-dispersive model has no analytical solution. The only way to solve eqn. 1 is through numerical algorithms. Several computational procedures have been developed by using a finite element [3] or a finite difference [4] method. The finite element method gives a more accurate solution, but requires much longer computational time. Among the finite difference methods, the Craig model (see ref. 5) and the Rouchon algorithms (see ref. 4) are widely used. The Craig model requires much longer computational time, but it is a good alternative for the calculation of band profiles in gradient elution, which

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cannot be performed with the Rouchon algorithm [2].

In a finite difference method, the continuous plane (z,t) is replaced by a grid of $(\Delta z, \Delta t)$ increments, and the partial differential equation (eqn. 1) is replaced by a difference equation. This causes a truncation error, function of Δz and Δt . This truncation error results in an additional dispersion term, of numerical origin [1,2,4]. When using the Rouchon algorithm, the right hand side of the mass balance equation is replaced by zero

$$\frac{\partial C}{\partial z} + \frac{\partial G(C)}{\partial t} = 0 \quad (2)$$

where $G = (C + Fq)/u$. The values of the time and length increments are chosen such a way that the numerical error caused when replacing eqn. 2 by the finite difference equation is identical to the dispersion described by the apparent dispersion coefficient in eqn. 1.

$$\Delta z = H \quad \Delta t = \frac{2H(k' + 1)}{u} = \frac{2t_R}{N} \quad (3)$$

where H is the height equivalent to a theoretical plate and k' is the retention factor.

Among the several possible combinations of difference terms [2], the Rouchon algorithm chooses a forward difference term for the first term of eqn. 2, and a backward difference term for the second term. This results in the following "forward-backward" difference equation

$$\frac{C_{n+1}^i - C_n^i}{\Delta z} + \frac{G_n^i - G_n^{i-1}}{\Delta t} = 0 \quad (4)$$

Successive numerical solutions of this finite difference equation for increasing values of the space increment, and then the time increment allow the calculation of the concentration at each point of the grid, by using the initial and boundary conditions. For the numerical solution of the equilibrium-dispersive model of chromatography, the numerical integral of the mass balance equation is calculated on the whole $0 \leq z \leq L$ length and $0 \leq t \leq t_2$ time interval, where $t_2 > t_R$.

However, the sample band occupies only a fraction of the column even at high values of the loading factor, and an important part of the computation time is wasted by carrying calcula-

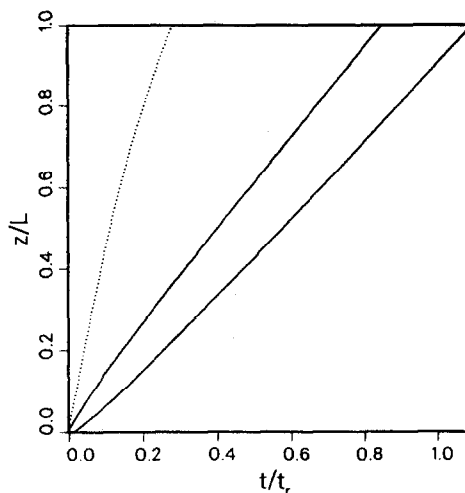


Fig. 1. The zone occupied by the band of a migrating component in the column. The upper solid line indicates the front of the band at $L_f = 1\%$; the dotted line shows the front at $L_f = 50\%$; the lower solid line shows the rear end of the band in both cases.

tions in the section of the column where the concentration of the sample is negligible or zero. In Fig. 1, the area between the two solid lines indicates the territory occupied by the sample band as a function of time at a small loading (loading factor $L_f = 1\%$), for a single component elution. These two lines show the trajectories of the band front and rear. This figure demonstrates that in this case, and during the whole elution, the majority of the column is only occupied by the inert eluent and the calculations should not be performed for this section of the column. The area between the dotted line and the lower solid line represents the progressive expansion of the section occupied by the sample for a very high value of the loading factor (50%). It can be seen that the band front propagates much faster in this last case (its trajectory follows the dotted line), and that the component begins to elute just around $0.2 t_R$. On the other hand, the diffuse rear of the band travels at an almost constant velocity, independently of the loading factor (lower solid line). Because of the high efficiency of the column ($N = 5000$), the effect of back mixing is negligible. Even in this last case, still less than half of

the plane is to be considered for the integration of the mass balance equation.

The calculation of the band profile can be significantly faster if we integrate only between the boundaries shown in Fig. 1. The gain in computational time is somewhat less than indicated by the decrease in the size of the scanned territory, between the dotted and continuous lines compared to the total area of the rectangle, as the positions of the front and rear boundaries of the band should be monitored at the end of each loop to determine the boundaries of the next loop.

With the conventional implementation of the Rouchon algorithm, the computational time is proportional to the square of the number of theoretical plates, since both the time and length increments are inversely proportional to N (see eqn. 3), so the number of grid points is proportional to N^2 . When the mass balance equation is integrated only within the boundaries of the migrating band, there is a strong correlation between the loading factor and the computational time, since the higher the load, the larger the section of the column which is occupied by the band.

The computing power available in personal computers has increased tremendously in the last few years. Current models are less expensive and much faster than those available a few years ago [6]. With the new generation of 80486 and soon Pentium (Intel, CA, USA)-based personal computers, the calculation of chromatographic band profiles can be performed easily, within a reasonably short time. Calculations were performed on a 33MHz 486DX IBM clone computer, to test the time needed by programs based on the different finite difference methods. The computer programs were written in Pascal and compiled under Turbo Pascal version 6.0 (Borland, CA, USA). For the calculation of the single-component chromatogram, $k' = 4$ and a Langmuirian behavior were assumed. For the calculation of the separation of the components of a binary mixture, the following values of the retention factor $k'_1 = 4$, the separation factor $\alpha = 1.25$, and the relative concentration 3:1 were chosen, and competitive Langmuir behavior was assumed.

TABLE I

THE COMPUTATIONAL TIME NEEDED BY DIFFERENT APPROACHES FOR THE SIMULATION OF THE BAND PROFILE OF ONE COMPONENT

N	Computational time (s)				
	Original Rouchon	Modified Rouchon			
		$L_t = 1\%$	$L_t = 5\%$	$L_t = 20\%$	$L_t = 50\%$
100	0.2	0.2	0.2	0.2	0.2
200	0.8	0.5	0.6	0.6	0.6
500	4.8	2.8	3.0	3.4	3.6
1000	18.7	10.1	11.2	12.9	13.8
2000	74.4	37.7	42.9	50.1	54.1
5000	458.7	223.1	259.3	306.2	331.8
8000	1168.3	557.7	652.5	773.2	838.8

In Table I, we compare the results obtained for the calculation of the elution band profile of a single component peak with the conventional and the modified Rouchon algorithms at different loading factors. Typical calculation times are around 10–14 s at $N = 1000$, and 9–14 min at $N = 8000$, depending on the value of L_t . The modified algorithm always requires less computational time. However, the time gain depends strongly on the loading factor of the sample, and slightly on the column efficiency. The computation time increases more slowly than N^2 , since at higher efficiency the dispersion effect is smaller, and for this reason the region of the z, t space where the numerical integration should be carried out is smaller. For this reason, the modified algorithm is especially attractive at high column efficiencies. At the low loading factor $L_t = 1\%$, only 54% of the original time is needed when the column efficiency is $N = 1000$, and 48% at $N = 8000$. As we increase the loading factor to $L_t = 50\%$, the computational times also increase, to nearly three quarters of the time required by the original Rouchon algorithm.

For the calculation of individual band profiles in the case of binary separations (Table II), the time gain is somewhat larger than for the calculation of single component band profiles. When using the modified algorithm, the required computational time (20–30 s) is 40–64% of the

TABLE II

THE COMPUTATIONAL TIME NEEDED BY DIFFERENT APPROACHES FOR THE SIMULATION OF THE SEPARATION OF A BINARY MIXTURE

N	Computational time (s)					
	Craig	Original Rouchon	Modified Rouchon			
			$L_f = 1\%$	$L_f = 5\%$	$L_f = 20\%$	$L_f = 50\%$
100	24.5	0.5	0.3	0.3	0.3	0.3
200	87.7	1.9	1.0	1.1	1.3	1.3
500	486.0	11.9	5.8	6.3	7.1	7.7
1000	1815.1	46.7	21.0	23.6	27.6	30.0
2000	–	184.3	78.5	90.6	107.7	117.3
5000	–	1132.9	461.0	553.8	655.3	729.0
8000	–	2888.3	1155.7	1232.9	1662.0	1819.5

original time at $N = 1000$. This time becomes 20–30 min at $N = 8000$, with a gain of 40–63%. This may seem surprising because the empty regions are smaller in the case of a mixture than with a single component, but much computing time is saved by not calculating the profile of a component in the regions where the other one is pure, and by calculating the competitive isotherm only in the mixed region.

The calculation of individual band profiles in the case of binary separations was also carried out with the Craig algorithm (Table II). The results show that the Craig method requires computation times which are typically about 40 times longer than the conventional Rouchon algorithm. As explained previously [1], this is because the Craig algorithm requires, in each individual loop, the calculation of the composition of both phases in the plate, from its total content. The Rouchon algorithm does not require this time consuming operation.

In Fig. 2, we show a logarithmic plot of the calculation time required for the simulation of binary separations, using the Craig, the Rouchon, and the modified Rouchon algorithms. From the slope of these lines, we can determine the dependency of the execution time on the plate number. The results show that for the Rouchon algorithm, when calculating either single component or individual band profiles for binary mixtures, the time is proportional to $N^{1.98}$. For

the modified algorithm, the slopes correspond to $N^{1.90}$ at $L_f = 1\%$, $N^{1.91}$ at $L_f = 5\%$, $N^{1.95}$ at $L_f = 20\%$, and $N^{1.97}$ at $L_f = 50\%$.

The study of the influence of the experimental parameters on the separation, production rate

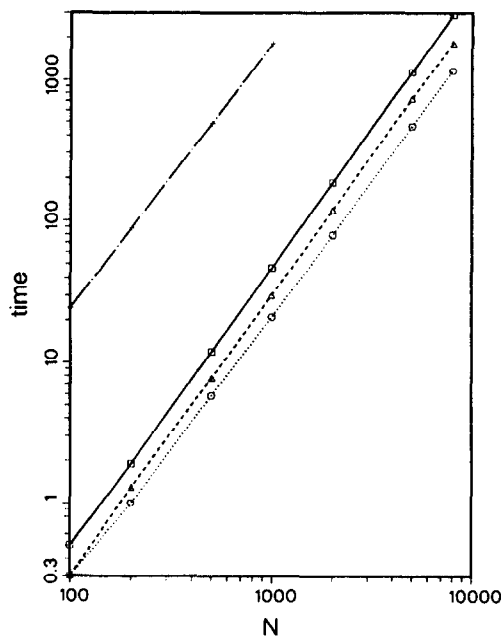


Fig. 2. The execution time (s) needed for the simulation of binary separations by the different finite difference methods. Dash-dotted line = Craig algorithm; solid line = original Rouchon method; dashed line = modified Rouchon method at $L_f = 50\%$; dotted line = modified Rouchon method at $L_f = 1\%$.

and recovery yield obtained in preparative chromatography, and to a certain extent the optimization of these parameters have become accessible to most scientists who can now begin to perform “computer experiments” in order to limit the number of actual experiments needed.

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