MATHEMATICAL SIMULATION OF CONTINUOUS GAS CHROMATOGRAPHY V. NON-ISOTHERMAL COLUMNS

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Abstract

Concentration and flow-rate profiles have been calculated for continuous counter-current gas chromatography from a set of non-linear differential equations with non-linear boundary conditions. The accumulation of the solutes causes significant changes in the flow rate rendering total separation in some cases theoretically impossible. On increasing the column length two plateaus are developing on the profiles. Their heights are generally different and sometimes the flow rates in the lower and upper parts cannot be kept simultaneously within the separation limits. This problem can be overcome by imposing an appropriate temperature profile along the column. There are no theoretical limitations in the non-isothermal method. Total separation is always possible if there is *any* difference between the partition coefficients of the solutes.

Introduction

In the last two parts of this series [2] numerical solution methods have been reported for differential equations describing a continuous counter-current chromatographic column [1]. Now the main results are summarized and a non-isothermal method is proposed to improve the separating power of the columns.

The investigation is made in terms of the dimensionless parameters defined in Part II. The most important ones are the following:

$C1$ is the Peclet group or rather a quasi Peclet group proportional to the column length L and the flow rate of the *carrier gas* I_V^0 and inversely proportional to the diffusion coefficient D.

$C3$ is the ratio of the sample flow rate I_V^m to the carrier flow rate.

κ_i is a "normalized" capacity factor: in case of $\kappa_i > 1$ the i-th component would migrate downwards *if* the flow rate *were* equal to the carrier flow rate, i.e. if there were no accumulation of the solutes, actually if there were no solute at all in the column. The ratio $\kappa_2/\kappa_1 = k'_2/k'_1$ can be called separation factor. The less the difference in κ_1 and κ_2 the more difficult the separation.

It has been shown in Part IV that non-equilibrium can be "simulated" by the equilibrium equations. Since these are much simpler than the general ones, the equilibrium equations will be used. In this case no more parameters are needed if a linear sorption isotherm is assumed, but, of course, the composition of the sample must be given.

Accumulation of solutes

It is a general observation that the concentration of the solutes inside the column are always greater than in the departing gas or in the departing condensed phase. In other words, the steady-state concentration gradients in the column are always directed toward the central feeding zone. This is, in itself, an almost trivial result reported by a number of authors expressly or implicitly, but the rather serious consequences are never thought over and there is no systematic quantitative investigation on the topic.

In fact, this accumulation inevitably gives rise to an increase in the gas flow rate inside the column rendering the whole problem essentially non-linear and difficult to deal with.

The presented treatment takes the flow rate as a dependent variable to be calculated. The elaborated mathematical software is suitable to solve non-linear problems, so a systematic investigation is now possible.

The extent of the accumulation depends mainly on the value of κ. If κ is far from unity, the accumulation is moderate. As κ approaches unity the accumulation is becoming more and more important. Fig. 1. shows the dimensionless flow-rate profiles for different separation factors $S=\kappa_2/\kappa_1$. $C3=0.001$ is rather small, the system is always symmetrical, i.e. $\kappa_1-1=1-\kappa_2$ and the concentrations of the solutes are equal in the mixture to be separated. It is observable all the same that the profiles are turning into more and more asymmetrical as the separation factor is approaching unity.

The explanation of this increasing asymmetry is just the accumulation. κ is a "normalized" capacity factor

$$\kappa=\frac{k'}{k^*},$$

where k^* is the capacity factor of a "non-migrating" component. But k^* depends on the flow rate and thus the "true" κ depends on it, as well: the higher flow rate tends to flush upwards a component even with $\kappa>1$.

Since the accumulation is greater in case of difficult separations and, on the other hand, difficult separations are more sensitive to flow-rate changes, separation is becoming more and more difficult at a highly increased rate, when the separation factor is approaching unity.

The effect of flow-rate changes is very spectacular at higher sample flow rates, that is, at higher values of $C3$. Fig. 2 shows similar profiles as Fig. 1 but

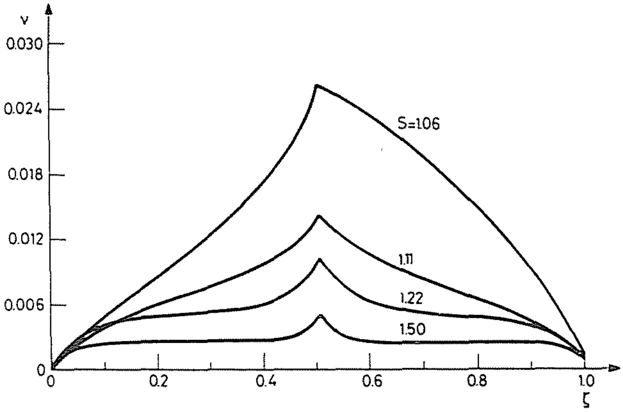

Fig. 1. Calculated flow-rate profiles in function of the separation factor S when $C3=0.001$ ($C1=150$, $C5=1200$, $y_1^m=y_2^m=0.5$)

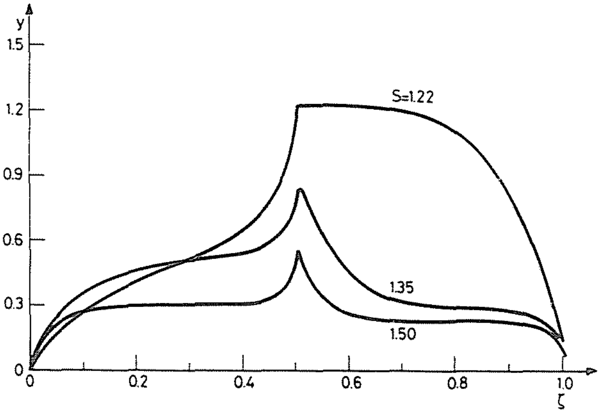

Fig. 2. Calculated flow-rate profiles in function of the separation factor S when $C3=0.01$ ($C1=150$, $C5=1200$, $y_1^m=y_2^m=0.5$)

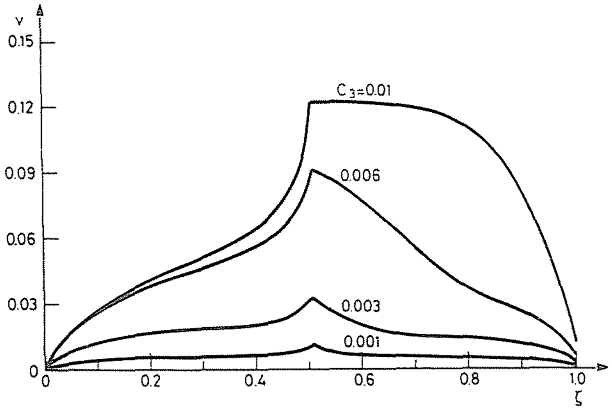

Fig. 3. Calculated flow-rate profiles in function of $C3$ with $S=1.22$ ($C1=150$, $C5=1200$, $y_1^m=y_2^m=0.5$)

with $C3=0.01$. There is practically no separation when $S<1.2$, almost the whole sample is carried upwards by the carrier gas.

Figure 3 shows directly the influence of the sample flow rate ($C3$) in case of a sample having a separation factor $\kappa_2/\kappa_1=1.2$. The separation is very good with $C3=0.001$ but it turns down spectacularly while increasing $C3$ to 0.01. This phenomenon is especially unfavourable in case of preparative counter-current gas chromatography where high throughputs would be desirable.

The effects of higher flow rates due to accumulation can partially be compensated by decreasing the flow rate of the carrier gas—or increasing κ—in order to reach an optimal total flow rate. This is, however, only a stop-gap arrangement. The flow rate is changing along the column and it is impossible to find a carrier flow rate which is optimal everywhere in the column; all the less so since the flow rate in the column depends also on the flow rate and composition of the sample.

Figures 4 to 7 are illustrating this partial compensation. The separation factor $S=1.2$ has been kept constant. The flow rate of the carrier gas is characterized by $1/\kappa_1$: this quantity is directly proportional to I_V^0.

Figure 4 shows the flow-rate profiles of a sample using different carrier flow rates or rather it presents the profiles in function of κ_1. Fig. 5 and Fig. 6 are showing the concentration profiles of the light and heavy components respectively, for the same separations.

The accumulation of a component has a maximum in function of the flow rate. This maximum is for the heavy component at about $\kappa_1=0.94$ (Fig. 6), for the light one at about $\kappa_1=1.16$ (Fig. 5.). If the flow rate is above the maximum for a given component, this component accumulates mainly in the upper part. Below this flow rate the accumulation occurs predominantly in the lower part.

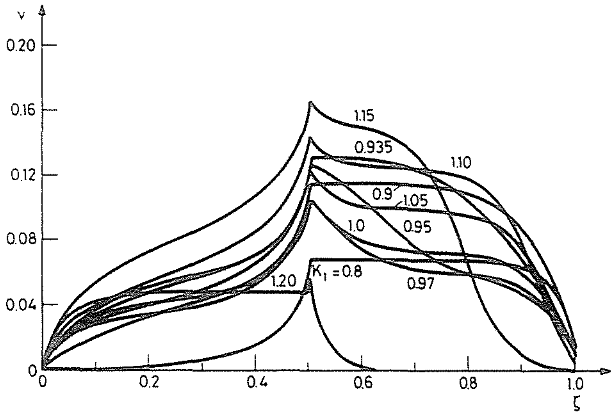

Fig. 4. Flow-rate profiles for a mixture of $S=1.20$ in function of κ_1 ($C1=150$, $C3=0.01$, $C5=1200$, $y_1^m=y_2^m=0.5$)

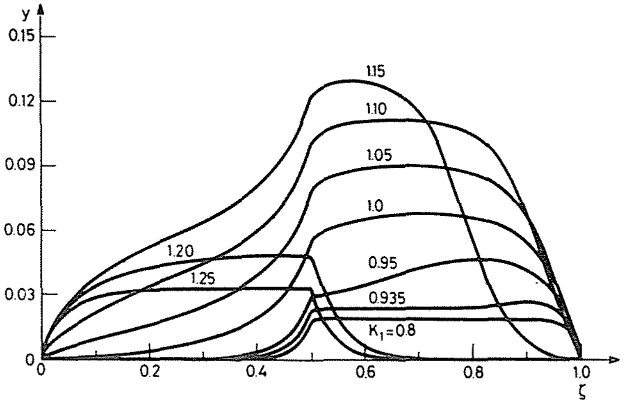

Fig. 5. Concentration profiles of the light component in function of κ_1 in the separation of a mixture of $S=1.20$ ($C1=150$, $C3=0.01$, $C5=1200$, $y_1^m=y_2^m=0.5$)

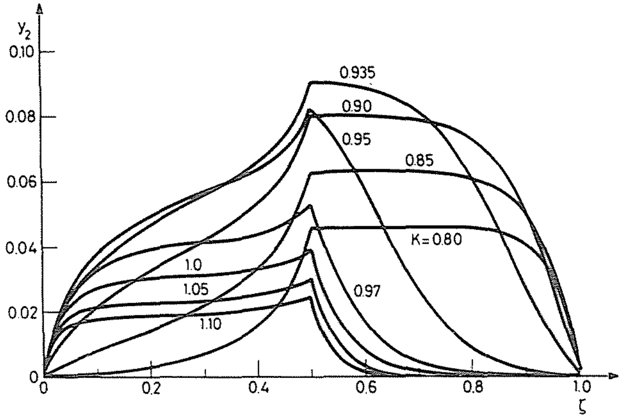

Fig. 6. Concentration profiles of the heavy component in function of κ_1 in the separation of a mixture of $S=1.20$ ($C1=150$, $C3=0.01$, $C5=1200$, $y_1^m=y_2^m=0.5$)

The accumulation of the different components influences the total flow rate in a rather complex way. There is no direct correlation between the carrier and total flow rates. The latter can change oppositely in the lower and upper parts of the column. This is still more evident from Fig. 7 where v is plotted against $1/\kappa_1$ at $\zeta=0.25$ (lower part) and $\zeta=0.75$ (upper part). There are two maxima on both curves and there is only one $1/\kappa_1$ where the flow rates are equal in both parts.

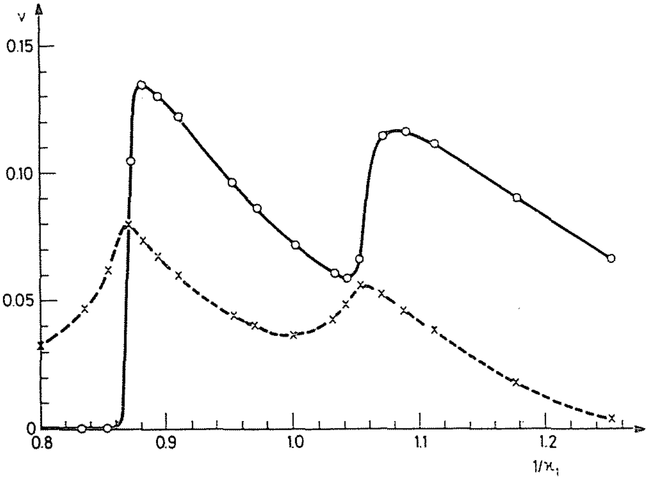

Fig. 7. Flow rates in the upper and lower parts of the column in function of the carrier flow rate represented by $1/\kappa_1$ ($S=1.20$, $C1=150$, $C3=0.01$, $C5=1200$, $y_1^m=y_2^m=0.5$)
dotted line: at $\zeta=0.25$ (lower part)
continuous line: at $\zeta=0.75$ (upper part)

Axial dispersion and column length

Dispersion in chromatography is caused by several factors. The most important ones are incorporated in the well-known van Deemter equation.

Roughly speaking, there are three main factors: molecular diffusion, unevenness of the column and the finite rate of mass transfer (non-equilibrium). In terms of HETP the effect of molecular diffusion is decreasing with increasing flow rate, the second factor is virtually constant while the third one is proportional to the flow rate:

$$H=B/u+A+C\cdot u.$$

In terms of an "effective" diffusion coefficient

$$D_{\text{eff}}=D_{\text{mol}}+\alpha\cdot u+\beta\cdot u^2$$

(u is the linear velocity proportional to the flow rate.)

In our equations the second term is neglected or, one can say, it is incorporated in the molecular diffusion coefficient. In the general equations—Eqs (10a–c) in Part II—the third term is not treated as a dispersion factor, it is taken in its physical reality as a mass transfer process. But it has been shown in Part IV that very similar profiles can be obtained using the equilibrium equations with an appropriate "effective" diffusion coefficient.

Total identity cannot be expected since there is no single D_{eff}: it is a function of the flow rate and the flow rate changes along the column. Nevertheless, the similarity is good enough to allow the use of the simpler equilibrium equations except when just the effects of the carrier flow rate are examined.

The diffusion coefficient D or D_{eff} is incorporated in the parameter $C1$ along with the column length L:

$$C1 = \frac{L \cdot I_V^0}{q \cdot D}$$

where I_V^0 is the volume flow rate of the carrier gas, q is the free cross-sectional area.

Both D and L occur only in this parameter. Any change in D can be replaced by an appropriate change in L or inversely. Multiplying L by any number has the same effect as dividing D by the same value. There is no need to examine the effects of the column length and D separately: only their ratio is important. From another point of view one can say that dispersion effects can always be eliminated—at least theoretically—by using a sufficiently long column.

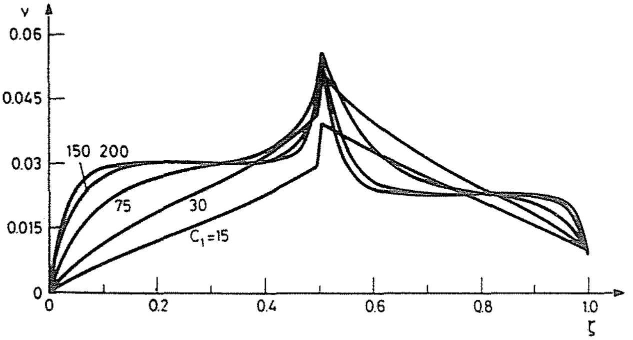

Fig. 8. Flow-rate profiles in function of $C1$ ($S=1.50$, $C3=0.01$, $C5=1200$, $y_1^m=y_2^m=0.5$)

The influence of $C1$ on the profiles is presented on Fig. 8. For low values of $C1$—short columns and/or high diffusion coefficients—the accumulation is less expressed. On increasing $C1$ the accumulation is reaching a limit. After approaching this limit the increase of $C1$ results only in broadening of the plateaus on the profiles.

This tendency to plateau formation is quite general when one increases $C1$, and the plateaus are approached asymptotically. In other words, flow rate and concentrations are practically constant in big parts of the column if axial dispersion is negligible.

Efficiency of separation

The efficiency of separation can be characterized by the purity of the "heavy" and "light" products. It is, in general, not very difficult to obtain one fairly pure product at the expense of the quality of the other, so it is important to consider both products at the same time.

It seems to be almost obvious that decrease of the dispersion effects—increase of the column length—improves separation. Fig. 9 and Table 1 are showing the impurities in the light (A) and heavy (B) components in function of $C1$. There is a definite decrease of the impurities in the bottom product but there is no improvement in the light product; there is, actually, a slight worsening.

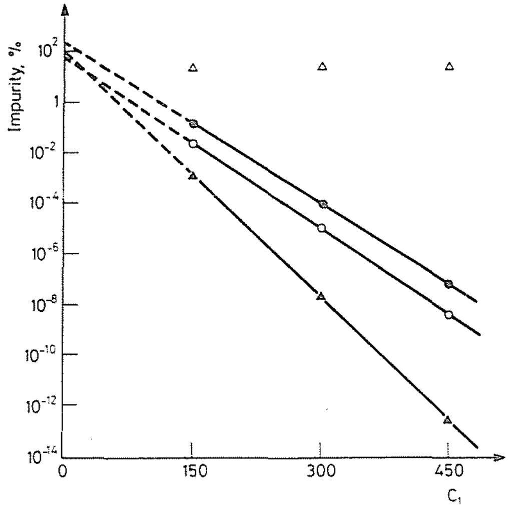

Fig. 9. Impurities in the products in function of $C1$ ($C3=0.01$, $C5=1200$, $y_1^m=y_2^m=0.5$)
△: top product ($\kappa_1=0.9$, $\kappa_2=1.1$)
▲: bottom product ($\kappa_i=0.9$, $\kappa_2=1.1$)
○: top product ($\kappa_1=0.95$, $\kappa_2=1.15$)
●: bottom product ($\kappa_1=0.95$, $\kappa_2=1.15$)

Table 1

Impurities in the top (A) and bottom (B) products in function of $C1$. ($C3=0.01$, $C5=1200$, $\kappa_1=0.9$, $\kappa_2=1.1$)

$C1$	150	300	450
B in A (%)	28.2	32.2	33.2
A in B (%)	$1.5\ 10^{-3}$	$2.5\ 10^{-8}$	$3.6\ 10^{-13}$

The cause of this seemingly surprising phenomenon is that good separation is only possible when the ratio of the gas flow rate to the flow rate of the condensed phase is within certain limits (separation range) [3]. It is true that separation is better on a longer column *if* the flow rate is within these limits. But, as it was shown earlier, flow rates in the upper and lower parts are not necessarily equal. If one sets the flow rate at optimum, let us say, in the lower part, the flow rate in the upper part may be beyond the separation limits and only the heavy component can be obtained in a fairly high purity. (If the flow rate is set optimum in the upper part, then it may occur that only the light component can be obtained in pure form.)

If one wishes to obtain both components in high purity, it is indispensable to keep the flow rates in the upper and lower parts nearly equal *and* this flow rate must be nearly optimum. It is possible to choose a carrier flow rate producing equal total flows in the upper and lower parts (see Fig. 7) but there is no guarantee that this flow rate would be an optimum.

In our case (Fig. 9) the separation factor is close to that of Fig. 7. In Fig. 7 the upper and lower flow rates are nearly equal at about $1/\kappa_1 = 1.05$. If one uses $\kappa_1 = 0.95$ and $\kappa_2 = 1.15$, then separation is good for both components. These results are also plotted in Fig. 9. It is worthy of note that the curves of good separation are linear in a semi-logarithmic plot and their extrapolations are intersecting the axis of ordinates at about 100%.

This good separation is, however, rather accidental. It is partially due to the fact that the separation factor is big enough and thus a total equality of the flow rates is not necessary. But even a total equality does not help if the flow rate is far from the optimum. From Fig. 7 one could select $1/\kappa_1 = 0.86$ ($\kappa_1 = 1.16$ and $\kappa_2 = 1.4$). In this case the flow rates are strictly equal in the lower and upper parts but separation is catastrophic in the bottom product. So it can be stated that in some cases full separation cannot be achieved even on an infinitely long ideal column because of flow-rate changes due to accumulation of the solutes.

Optimal temperature profile

It is not possible to select a flow rate that is optimum everywhere in the column, but it is possible to change the *capacity factors* in such a way that the actual flow rate be an optimum. The capacity factors are very sensitive to temperature changes and it is quite possible to maintain a temperature profile assuring "optimum capacity factors" for the actual flow rates everywhere in the column. Of course, the problem is not so simple: by changing the capacity factors, a new steady state with new flow rates is produced. These new flow rates require new capacity factors and so on. Practically, a new set of equations has to be solved.

These new equations for equilibrium chromatography can be set up as follows. The flow-rate changes due to temperature differences are neglected since these differences are rather small: normally only several centigrades or even less. In fact, temperature is not involved explicitly in the subsequent treatment.

Such temperatures are imposed that the relation

$$1-\kappa_1'=\kappa_2'-1 \tag{1}$$

be maintained everywhere. κ_i' is a capacity factor normalized to the actual flow rate rather than to I_V^0. The "classical" κ_i—normalized to I_V^0—can be written as

$$\kappa_i=\kappa_i^0(1+\nu), \tag{2}$$

where κ_i^0 is the "isothermal" capacity factor normalized to I_V^0. κ_i is now a function of ζ since ν is a function of ζ. This seemingly insignificant modification compels us to reconsider the derivation of the equilibrium equations. Even if one is neglecting interactions between the solutes, Eq. (11a) in Part I must be written

$$a_i=\varphi_i(y_i, I_V)$$

or for linear isotherms and in dimensionless form

$$\Theta_i=\frac{\kappa_i^0}{C5}(1+\nu)y_i\,. \tag{3}$$

Eq. (12) in Part I becomes invalid since

$$\frac{\partial a_i}{\partial z}=\frac{\partial\varphi_i}{\partial y_i}\cdot\frac{\mathrm{d}y_i}{\mathrm{d}z}+\frac{\partial\varphi_i}{\partial I_V}\cdot\frac{\mathrm{d}I_V}{\mathrm{d}z}$$

instead of

$$\frac{\mathrm{d}a_i}{\mathrm{d}z}=\frac{\mathrm{d}\varphi_i}{\mathrm{d}y_i}\cdot\frac{\mathrm{d}y_i}{\mathrm{d}z}$$

and Eqs (13a–b) in Part I as well as Eqs (1a–b) in Part IV must be replaced.

The sorption rate S_i can be expressed from Eq. (10a) of Part I as

$$S_i=V_L\frac{a_0}{L}\cdot\frac{\mathrm{d}\Theta_i}{\mathrm{d}\zeta} \tag{4}$$

and from Eq. (3)

$$\frac{\mathrm{d}\Theta_i}{\mathrm{d}\zeta}=\frac{\kappa_i^0}{C5}\left[(1+\nu)\frac{\mathrm{d}y_i}{\mathrm{d}\zeta}+y_i\cdot\frac{\mathrm{d}\nu}{\mathrm{d}\zeta}\right] \tag{5}$$

On substituting Eqs (4) and Eq. (5) into Eq (10a) of Part I and introducing the dimensionless quantities the equation

$$\frac{d^2y_i}{d\zeta^2} - C1\left\{\left[(1+v)\frac{dy_i}{d\zeta} + y_i\cdot\frac{dv}{d\zeta}\right](1-\kappa_i^0) - C3\cdot y_i^m\cdot w\right\} = 0$$

$$(i = 1, 2, \ldots, k) \qquad (6a)$$

is obtained. Similarly from Eq. (10b) one obtains

$$\frac{dv}{d\zeta} = \frac{C3\cdot w + (1+v)\Sigma\kappa_i^0\cdot\frac{dy_i}{d\zeta}}{1-\Sigma\kappa_i^0\cdot y_i}. \qquad (6b)$$

These two—or rather $2k+1$—equations are describing the column if optimal temperature profile is maintained. The boundary conditions are the same as in the isothermal case.

The introduction of these new equations changes drastically the calculated profiles. Both products can be obtained in very high purity, if Eq. (1) is maintained and the profiles are always symmetrical if an equimolecular sample is fed. Fig. 10 shows an extreme example. The separation factor is $\kappa_2/\kappa_1 = 1.005$ and both products have only 0.16‰ impurity.

This is, of course, only a theoretical possibility. To achieve such a separation one should keep the carrier flow rate constant within 0.1‰ at least. The homogeneity requirements of the condensed phase are similar, not speaking of the enormous accumulation of the solutes. With a sample flow rate as low as 1‰ of that of the carrier ($C3 = 0.01$) the maximal flow rate is seven times higher than I_V^0 and even on the plateaus the flow rate is about $2I_V^0$.

In practice no one would try a separation with a separation factor of 1.005. These calculations are suitable, however, to show that there is no

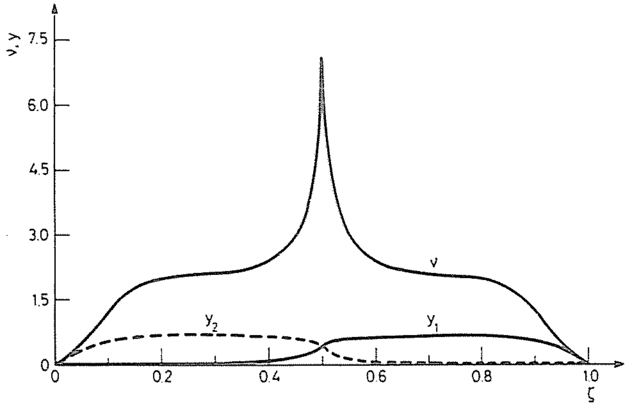

Fig. 10. Calculated concentration and flow-rate profiles for a mixture of $S = 1.005$ using optimal temperature profile ($C1 = 1500$, $C3 = 0.01$, $C5 = 1200$, $y_1^m = y_2^m = 0.5$)

theoretical limit when using a non-isothermal column. The calculations are suitable, as well, to predict the necessary conditions to be fulfilled to achieve a given separation.

Figure 11 shows a more realistic separation with a separation factor of "only" 1.06. Both products are having less than 0.015% impurity and the accumulation of the solutes at the plateaus is only about 16-fold (the total flow rate is 1.16 I_V^0). On increasing $C1$ the plateau formation (Fig. 12) is observable

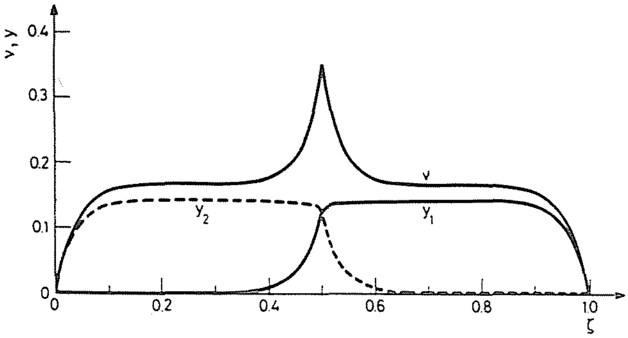

Fig. 11. Concentration and flow-rate profiles for a mixture of $S = 1.06$ using optimal temperature profile ($C1 = 750$, $C3 = 0.01$, $C5 = 1200$, $y_1^m = y_2^m = 0.5$)

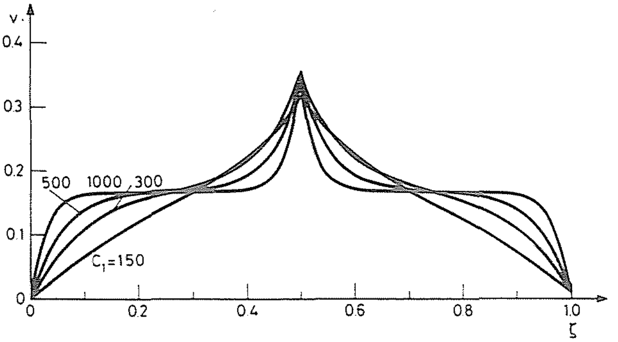

Fig. 12. Flow-rate profiles in function of $C1$ using optimal temperature profile ($S = 1.06$, $C3 = 0.01$, $C5 = 1200$, $y_1^m = y_2^m = 0.5$)

as well as the improvement of the separation (Fig. 13). The semi-logarithmic plot of the impurities vs. $C1$ gives a straight line like in the case of isothermal separations and even the intersection with the axis of ordinates is at 100% (Fig. 13).

A main advantage of the above described non-isothermal method is that the best conditions for a good separation can easily be found and such

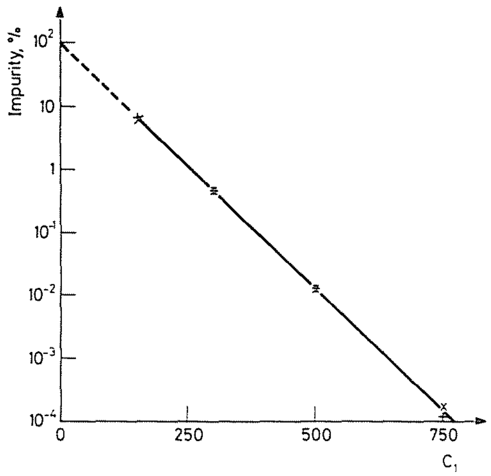

Fig. 13. Impurities in the products in function of $C1$ using optimal temperature profile ($S = 1.06$, $C3 = 0.01$, $C5 = 1200$, $y_1^m = y_2^m = 0.5$)
x: top product +: bottom product

conditions always exist. In case of an isothermal separation, the optimal carrier flow rate—even if it exists—must be found by a trial and error method. A number of concentration profiles have to be calculated that are later superfluous. The nonisothermal method gives the right solution at once.

Quasi-optimum profiles

A disadvantage of the "optimum" method is that it gives the steady-state profiles without any indication how to realize them. The profiles of Figs 10 and 11 can subsist if the steady state is established *and* the appropriate temperature profile is maintained. But the steady state may never be established if the temperature profile is maintained from the beginning of the running-up period. The temperature profile is calculated for the steady state and it may be quite unfavourable during the running-up. (This problem does not arise at the isothermal columns. There the calculated steady-state will always be established sooner or later).

It would be rather difficult to impose exactly the calculated temperature profile and, as a matter of fact, there is no need to do so either. If one applies only two different temperatures suitable for the two plateaus and a smooth transition between them in the region of the sample feeding, the temperature will still be quasi-optimum in most part of the column.

The realization of such a temperature profile is much easier than setting up a strictly optimum one. It can even be made automatically if one can measure the flow rates in the upper and lower parts of the column. This automation can solve the problem of the running-up period as well. The temperature is always adjusted to the *actual* flow rate and thus the optimum—or rather quasi-optimum—conditions can be attained in a relatively short period.

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