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Theoretical study of adsorptive parametric pumping and temperature swing chromatography with flow reversal

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Abstract

Different techniques of adsorptive parametric pumping have been theoretically studied with the help of a multicomponent, non-linear model. For calculations, a mixture of three components was considered. The effect of the initial concentration on the performance of parametric pumping was found to be significant. In the high initial concentration range (where the isotherm is non-linear), a combination of batch and continuous parametric pumping was investigated. It is shown that products with constant composition can be obtained. In the low initial concentration range (where the isotherm is linear), it is necessary to use a special type of adsorptive parametric pumping, called temperature swing chromatography, for separating the components. It is shown how the separation builds up from cycle to cycle, and how to influence the purity of the components with the help of the hot regeneration. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Parametric pumping; Purity; Concentration

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1. Introduction

Parametric pumping is a separation process invented by Wilhelm et al. [1] which consists of a mobile phase percolated through a fixed phase alternately in one direction and then in the other, and the changes in temperature (or in other thermodynamic variable such as pressure, pH, etc.) are applied to the phases in contact simultaneously with the changes in flow direction. It makes possible the enrichment of a given component at one end of the column and its depletion at the other end.

The principles of parametric pumping can be easily understood from Fig. 1 where the steps of the cyclic operation are illustrated with the help of a McCabe–Thiele type diagram.

The hot and cold isotherms are shown and it is clear that the uptake is larger at a cold temperature than at a hot temperature.

The operation starts with a first step to obtain the initial conditions.

Step 1. The column is equilibrated at a cold temperature with the solution to be separated and the bottom reservoir is filled with the same solution (point A on the cold isotherm). After this, a cycle consists of the following steps.

Step 2. The column is heated to the hot temperature (point B on the hot isotherm).

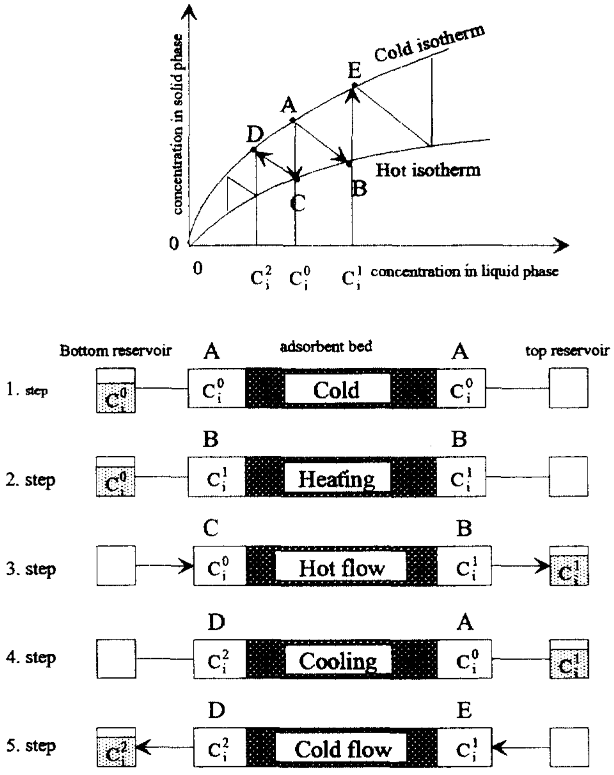

Fig. 1. Principles of parametric pumping.

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Step 3. The solution from the bottom reservoir is pumped to the top reservoir through the column at a hot temperature (points C and B on the hot isotherm).

Step 4. The column is cooled to the cold temperature (points D and A on the cold isotherm).

Step 5. The solution from the top reservoir is pumped to the bottom reservoir through the column at a cold temperature (points E and D on the cold isotherm).

Steps 2 to 5 are repeated until the desired cycle number is reached.

It can be also seen on Fig. 1 that the concentration of component *i* increases in the top reservoir and decreases in the bottom reservoir. This model gives a good qualitative understanding of how the separation develops, but it is usually insufficient to represent results quantitatively.

The analogy with distillation has been described by Grevillot and Tondeur [2,3]. At total reflux, the vapor from the top of the column is condensed and return as liquid into the column. In parametric pumping, the upward flow during the hot half-cycle is analogous to the vapor in distillation and the downward flow during the cold half-cycle is analogous to the liquid in distillation. The adsorption isotherms at the two temperatures play the role of the liquid–vapor equilibrium curve. As in total reflux distillation, in batch parametric pumping there is no feed and no withdrawals: all of the liquid collected in the top (bottom) reservoir during hot (cold) half-cycle is returned to the column during the cold (hot) half-cycle. Parametric pumping can be also operated at partial reflux in several ways (continuous, semi-continuous, intermediate feed position, etc.). The temperature change can be applied to the column itself (direct mode) or by the fluid itself (recuperative mode). Recuperative mode of operation is more adapted to large-diameter beds where the direct mode would cause radial temperature gradients.

Since 1966 many experimental and theoretical extensions have been made to the basic technique. The potentiality of the technique was demonstrated by Wilhelm and Sweed [4] when they obtained a separation factor of 10^5 in a toluene–*n*-heptane–silica gel system under total reflux conditions. Pigford et al. [5] originated an important and simple equilibrium theory and derived mathematical expressions for the performance of the batch parametric pump. By extending the equilibrium theory, Chen and Hill [6] and Chen et al. [7,8] have derived mathematical expressions for the performance of batch, continuous, and semicontinuous parametric pumps. For getting more realistic results than by using the equilibrium theory, Gupta and Sweed [9] worked out a model which takes into account the non-equilibrium effects.

Sabadell and Sweed [10] carried out separation by a recuperative mode, pH pump in which pH control was maintained by acid addition at one of the end reservoirs. Shaffer and Hamrin [11] combined affinity chromatography and parametric pumping to reduce enzyme concentration in an aqueous solution. Also pH pump was used by Chen et al. [12–16] for the separation of proteins like hemoglobin and albumin. Oren and Soffer [17–20] extended parametric pumping to electrochemical systems for water desalting and separating isotopes. Several reviews [21–24] also show the interest in using parametric pumping for different kind of separations.

Recently Muraviev et al. [25] have studied the temperature responsiveness of Cu^{2+} and Zn^{2+} selectivities for different resins and proposed parametric pumping as a possible separation method. In our previous works amino acid separation by thermal parametric pumping on both a cation exchange resin and on an activated carbon was studied. On cation exchange, resin experiments were carried out both in a highly acidic solution and in an acid free solution [26,27]. It was shown that it is possible to concentrate the amino acids from an acidic solution and to separate them from an acid free solution. On activated carbon temperature swing chromatography was experimentally investigated for the separation of amino acids [28].

The general strategy of the present work is to show how the separation builds up in parametric pumping thereby helping the optimization of the method. Thus first the concentration fronts motion in adsorptive parametric pumping as a function of the initial concentrations is investigated with the help of a multicomponent, non-linear equilibrium model. Then possible separation methods (temperature swing chromatography and continuous parametric pumping) are discussed in both low (linear isotherm) and high (non-linear isotherm) initial concentration ranges.

2. Theory

Let us consider a thermal direct mode batch parametric pump which is a cyclic operation device with a hot upwards half-cycle and a cold downward half-cycle. We assume instantaneous local equilibrium, plug flow, instantaneous heating and cooling, flow reversal in phase with temperature change and constant density. We consider a three-component system A, B, C. Examples will use three amino acids: arginine, histidine and lysine.

The material balance over a differential volume element of an adsorption column is:

$$v\frac{\partial C_i}{\partial z}+\frac{\partial C_i}{\partial t}+\frac{1-\varepsilon}{\varepsilon}\frac{\partial q_i}{\partial t}=0 \tag{1}$$

where C_i is the concentration of a given component in the fluid phase, q_i is the concentration in the solid phase, v is the interstitial velocity and $\varepsilon = 0.35$ is the bed void fraction.

To solve these equations, it is necessary to have a description of the uptake equilibrium on the adsorbent. The multicomponent uptake at the cold temperature can be expressed as:

$$q_i=Q_i\frac{k_iC_i}{1+\sum_{i=1}^{3}k_iC_i} \tag{2}$$

The uptake at the hot temperature is assumed to be linear:

$$q_i = K_i^h C_i \tag{3}$$

The assumptions of Langmuir type cold and linear hot isotherms and thus the parameters of the isotherms are based on the experimentally obtained cold (at 298 K) and hot (at 363 K) isotherms of arginine, histidine and lysine. The concentrations before and after the temperature change are related by:

$$C_i^c + \frac{1-\varepsilon}{\varepsilon}\frac{Q_i k_i C_i^c}{1+\sum\limits_{k=1}^{3} k_i C_i^c} = C_i^h + \frac{1-\varepsilon}{\varepsilon} K_i^h C_i^h \tag{4}$$

where C_i^c and C_i^h are the liquid phase concentrations at cold and hot temperatures, respectively.

The model was solved with the STOP–GO algorithm. The column was devided into J increments ($L = J\Delta z$), and into I time step ($T = I\Delta t$). At every $t = i\Delta t$ time and $z = j\Delta z$ place, both the liquid and solid phase concentrations were calculated. To carry out the numerical computation, the boundary conditions and the initial conditions are assigned. These conditions always change when a new half-cycle is started. The boundary condition is always the concentration of the solution in one of the reservoirs. The initial conditions for a half cycle are determined by the flow and temperature change of the previous half cycle. For calculating the separation of components A, B and C a column with length of 20 cm and cross-sectional area of 1 cm^2 is considered (the effect of radial temperature gradient is negligible).

The parameters of the cold and hot isotherms of arginine (A), histidine (B), and lysine (C) [28] used for the calculations are given in Table 1, where Q_i is the maximum of a Langmuir type isotherm, k_i is the parameter of a Langmuir type isotherm, and K_i^h is the slope of the hot isotherm. The isotherms were measured by the frontal method. At the cold temperature decreasing order of the uptake is A, B and C, and decreasing order of the temperature dependence of the isotherms is also A, B and C at not too high concentrations. However, the multicomponent Langmuir Eq. (2) is not termodynamically consistent if the Q_i are unequal (see Table 1) it is commonly used. LeVan and Vermeulen [29] compared the quantities adsorbed, calculated both by the ideal adsorbed solution theory and by the multicomponent Langmuir equation. They concluded the followings: if Q_1 was greater than Q_2, q_1 calculated by the ideal adsorbed solution theory is always greater and q_2 always less than the value given by Eq. (2). Thus probably Eq. (2) overestimates the uptake of component B and underestimates the uptake of component C, however, since the goal of the present work is just to show how the separation builds up in parametric pumping, the error of the multicomponent Langmuir equation is not important.

Table 1
Parameters of the cold and hot isotherms

Component	Cold		Hot
	Q_i	k_i	K_i^h
A	111	0.184	2.59
B	19.4	0.376	1.57
C	396	0.004	0.664

3. The effect of the initial concentration on adsorptive batch parametric pumping

3.1. Results

In batch (or total reflux) parametric pumping there are neither feed nor product streams as in batch distillation. The volume of liquid and the amount of solutes remain constant throughout a run and equal to their initial values. The separation changes continuously from cycle to cycle and tends towards a constant value at cyclic steady state.

Two calculated results for the separation of components A, B and C by batch parametric pumping are shown in Figs. 2 and 3. In these figures after the cold flow in the 15th cycle the concentrations in the top reservoir are represented by axial positions 0 to 1, the liquid phase concentrations of components A, B and C in the column by axial positions 1 to 21 and the concentrations in the bottom reservoir by axial positions 21 to 22 (the volume of the displaced solution, $\Delta V = 10$ ml). In Fig. 2, the initial concentrations of the components are 1 mmol/l and 5 mmol/l in Fig. 3.

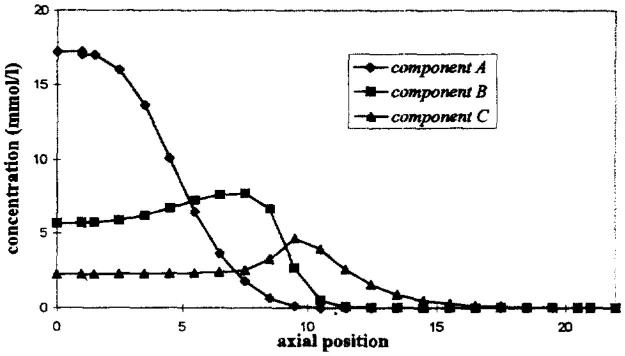

Fig. 2. Liquid phase concentration profile of adsorptive batch parametric pumping after 15 cycles (C_{init} = 1 mmol/l).

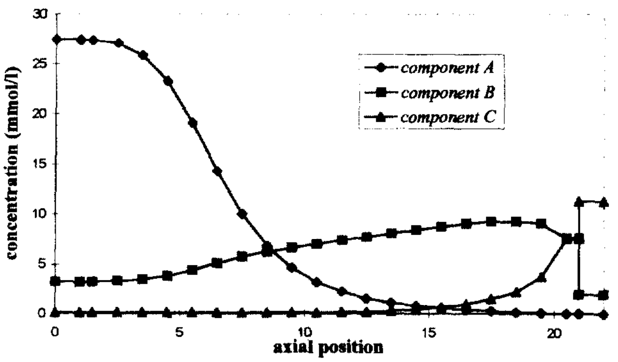

Fig. 3. Liquid phase concentration profile of adsorptive batch parametric pumping after 15 cycles (C_{init} = 5 mmol/l).

As seen in Fig. 2, the concentration of each component increases in the top reservoir and decreases in the bottom reservoir, if all the initial concentrations are low, 1 mmol/l. The situation is different if the initial concentrations are higher. In Fig. 3, when the initial concentrations are 5 mmol/l, only component A is enriched and the others are depleted in the top reservoir. At the same time the concentration of component C is increased and the others are decreased in the bottom reservoir. It can therefore be ascertained that the components can be concentrated in one reservoir if their initial concentrations are low, and if their initial concentrations are higher they can be separated and recovered from different axial positions of the column (component A can be recovered from the top reservoir, component B from the column and component C from the bottom reservoir). The effect of the initial concentrations on the parametric pumping separation is discussed below.

3.2. *Discussion*

3.2.1. *Low initial concentration range*

In case of low initial concentrations (1 mmol/l), the separation starts in the linear isotherm range, thus the capacity of the adsorbent increases significantly with the increase of the concentrations. Since the competition for the adsorbent active sites is not so intensive in this range the components behave mainly independently from each other, thus all of them move towards the reservoir which receives the hot flow, that is the top reservoir.

It can be seen in Fig. 2 that the bottom part of the column is practically free from the components A, B and C. Also Fig. 2 shows that components A, B and C arrange along the column from the top reservoir in the order A, B and C, that is the same as their temperature dependence of isotherms. This shows that even with initial linear isotherms, we can obtain not only concentration of the components but also some separation.

3.2.2. *Higher initial concentration range*

In case of higher initial concentrations the uptake of the components on the adsorbent increases, and also increases the competition for the adsorbent active sites. The best adsorbing component A occupies the top part of the column and pushes the less adsorbing components B and C towards the bottom reservoir. In the same way, competition between B and C push C into the bottom reservoir.

Consequently, the ability of an adsorptive batch parametric pump to separate a multicomponent mixture is based on the non-linear nature of the isotherms, and indeed on the interference of each species with all others in the sorption equilibrium. It is very similar to ion exchange parametric pumping systems [30–33]. If separation occurs, then the components arrange themselves in the bed in decreasing order of their affinities for the solid phase. Since the initial concentration has significant effect on the performance of adsorptive parametric pumping it is worth examining separately both the high and the low initial concentration ranges. This is done below.

4. Combination of batch and continuous parametric pumping in the higher initial concentration range

Adsorptive batch parametric pumping can separate the components A, B and C if the initial concentrations are high enough that the isotherms are non-linear. However, there is no beneficial results by operating additional number of cycles after limiting concentrations are reached in the reservoirs attached to each end of the column, therefore we propose the use of continuous parametric pumping.

Continuous parametric pumping offers significant advantages over the batch pump. Due to the continuous feed, it is possible to withdraw two product streams from the apparatus as long as the system operates. Furthermore, the process is capable of yielding high separation factors (however smaller than batch parametric pumping) without the necessity of solid phase regeneration.

Calculations were carried out in order to develop a method which combines the advantages of both batch and continuous parametric pumping. The simulated operation starts as batch parametric pumping, that is without feed and withdrawal. In a certain cycle, products are withdrawn from and feeds are led into the reservoirs. Then the system operates as batch parametric pumping again through a certain number of cycles. In such way, a bottom or/and a top product is produced continuously. In each calculation, the volume of displaced solution (ΔV) was 10 ml and all the initial concentrations were 5 mmol/l.

In order to be able to plan a separation like the above mentioned, first it is necessary to study the effect of the position of the feed and withdrawal (either in the bottom reservoir or at the middle of the column or in the top reservoir).

4.1. *Feed and withdrawal in the bottom reservoir*

In this process, the pump is operated batchwise during 15 cycles. Then the solution from the bottom reservoir is withdrawn and replaced by the same volume of feed solution. For this process after the 15th cold flow the liquid phase concentrations in the column and in the reservoirs are shown in Fig. 3. As can be seen from this figure only the upper part of the column is occupied by component A, the middle and the bottom part is filled with component B. In Fig. 4 the liquid phase concentrations in the column and in the reservoirs are plotted after 450 cycles (It means 30 feeds and withdrawals and 300 ml of bottom product). Since the concentration of component A in the bottom reservoir is less than its initial concentration, thus more component A is fed into than withdrawn from the system. Due to this after 450 cycles the main part of the column is occupied by component A, and only a

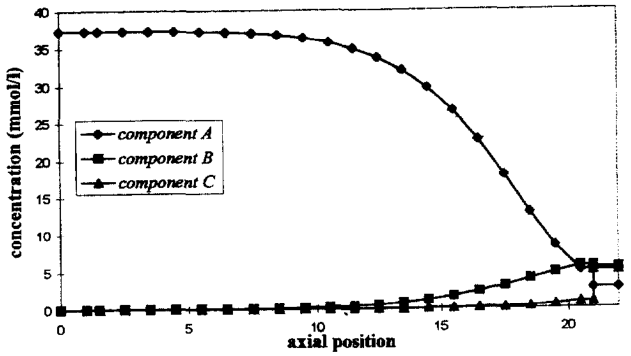

Fig. 4. Liquid phase concentration profile of adsorptive parametric pumping after 450 cycles. Feed and withdrawal in the bottom reservoir (C_{init} = 5 mmol/l).

small amount of components B and C remain in the column, as it can be seen in Fig. 4.

The purity of component A in the top reservoir and in the upper part of the column is greater than 99.9%. Of course the composition of the bottom product keeps to the initial composition after several withdrawals. Thus we never obtain a separation in the bottom product and this process is of poor interest except for understanding of the system.

4.2. *Feed and withdrawal in the top reservoir*

In this case in every 15th cycle the whole solution from the top reservoir is withdrawn and replaced by fresh feed solution.

As previously Fig. 3 represents the liquid phase concentrations in the column and in the reservoirs after 15 cycles. The concentration profiles after 450 cycles are shown on Fig. 5. Since the concentration of component A in the top reservoir is greater than its initial concentration (see Fig. 3), thus more component A is withdrawn from than fed into the system (Remember that the column was equilibrated with the solution to be separated, so until the component A content of the column is larger than that of the feed it is possible to remove more component A than it is fed). Due to this the component A content of the column decreases from withdrawal to withdrawal as well as the competition for the adsorbent active sites. Thus the less adsorbing components B and C can move towards the top reservoir, and step by step they also leave the system with the top reservoir product. One can see in Fig. 5 that after 450 cycles (30 withdrawals) the bottom part of the column is practically free from the solutes.

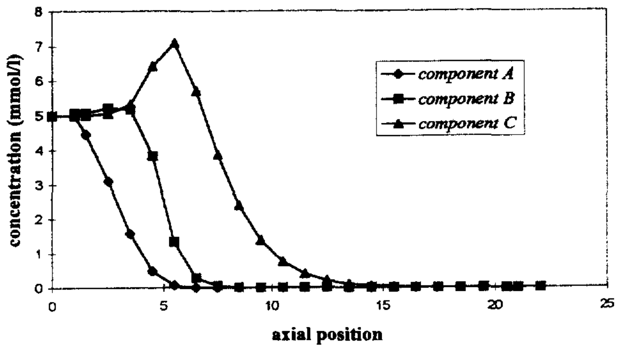

Fig. 5. Liquid phase concentration profile of adsorptive parametric pumping after 450 cycles. Feed and withdrawal in the top reservoir (C_{init} = 5 mmol/l).

Obviously, the composition of the top reservoir product varies from withdrawal to withdrawal. First, it is mainly component A, but as its amount decreases in the column more and more component B and latter component C can leave the system by the top reservoir, thus the composition of the top product keeps to the initial composition after several withdrawals.

4.3. *Feed and withdrawal at the middle of the column*

Since at the cyclic steady state the composition of the bottom product in Section 4.1 is the same as the composition of the top product in case Section 4.2 (that is the composition of the feed), therefore it is possible to connect the two columns and to consider the feeds and withdrawals as intermediate feeds and withdrawals. Consequently, in case of feed and withdrawal by the middle of the column the upper part of the column becomes enriched in component A while the bottom part of the column becomes poor in other components, as illustrated in Fig. 6.

4.4. *Feed and withdrawal in both reservoirs*

In this case in every 15th cycle the whole bottom reservoir solution and a part of the top reservoir solution is withdrawn and replaced by fresh solution. In the previous three cases, the compositions of the products were not constant because of the non-balanced feed and product streams. By feeding and withdrawing in both reservoirs, it is possible to make these streams more balanced, and to obtain products with more uniform composition. In Fig. 7, the liquid phase concentrations in the column and in the reservoirs are illustrated after 450 cycles. The initial state of the column is obtained by percolation of a sufficient volume of feed solution to obtain uniform concentration profiles in the column. For this calculation the whole bottom reservoir solution and 20% of the top reservoir solution is replaced by fresh feed solution in

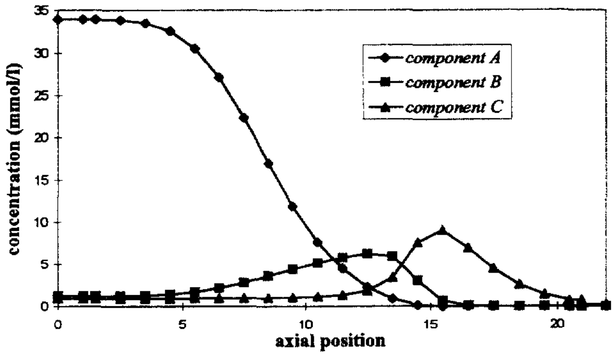

Fig. 6. Liquid phase concentration profile of adsorptive parametric pumping after 450 cycles. Feed and withdrawal at the middle of the column (C_{init} = 5 mmol/l).

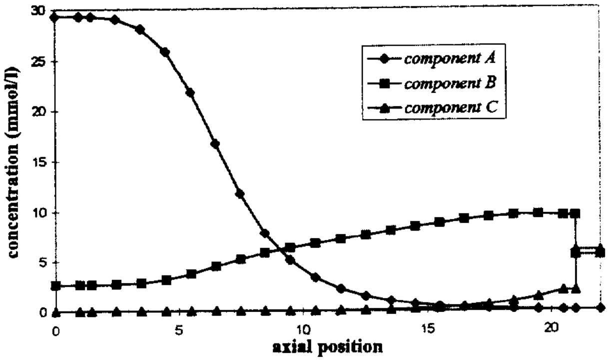

Fig. 7. Liquid phase concentration profile of adsorptive parametric pumping after 450 cycles. Feed and withdrawal in both reservoirs ($C_{init} = 5$ mmol/l).

every 15th cycle. It can be seen (compare Figs. 3 and 7) that the concentration profiles in the column are practically constant for several cycles.

Obviously the composition of both top and bottom products are practically constant (90% component A, 10% component B) in this case. These results verify that the combination of batch and continuous parametric pumping can be successfully used for different kind of separations.

5. Temperature swing chromatography with flow reversal in the low initial concentration range

In a thermal direct mode batch parametric pumping device with a hot upward half-cycle and a cold downward half-cycle all of the components will concentrate in the top reservoir and deplete in the bottom reservoir if the initial concentrations are so low that the isotherms are linear. In this way, it is not possible to separate the components but it is possible to concentrate them in one reservoir in different degrees. Therefore, in case of dilute solutions we propose the use of a special type of parametric pumping called temperature swing chromatography [26].

5.1. Temperature swing chromatography

Temperature swing chromatography (later TSC) is a kind of batch parametric pumping. In contrast with traditional direct mode batch parametric pumping in this case the column is not equilibrated with the solution to be separated before starting the experiment (first step in Fig. 1 is missing) so the column is filled with fresh adsorbent. Before starting the experiment the whole solution to be separated ($V = 1000$ ml) is poured into the top reservoir. In TSC a cycle consists of the following steps:

- cold flow (V_{cold}) from the top reservoir to the bottom reservoir
- heating
- hot flow (V_{hot}) from the bottom reservoir to the top reservoir ($V_{hot} < V_{cold}$)
- cooling

As a result of each cycle, $V_{cold} - V_{hot}$ net volume leaves the top reservoir. The cycles are repeated until the top reservoir becomes empty, then the column is regenerated at the hot temperature with 100 ml of pure solvent. In this way, two products can be obtained: one is the solution in the bottom reservoir (P1) which contains the component with less affinity to the adsorbent, and the other is the solution obtained after the hot regeneration (P2) which contains the more retained components.

TSC is capable to use the differences between the individual cold isotherms and between the degree of temperature dependence of adsorption isotherms to separate the components.

5.2. Fronts movement in temperature swing chromatography

The fronts movement in temperature swing chromatography had been studied using specific calculations. For these calculations, $V_{cold} = 120$ ml and $V_{hot} = 60$ ml. The initial concentration of each component is 1 mmol/l and the volume of the solution to be separated is 1000 ml. At the end the column is regenerated with 100 ml of pure solvent. Results of calculations are shown in Figs. 8–10.

In Fig. 8, the liquid phase concentrations in the column and in the reservoirs are shown after the first cold flow. One can see in this figure that according to their lower affinity components B and C have broken through the column and their concentrations in the bottom reservoir are about 0.071

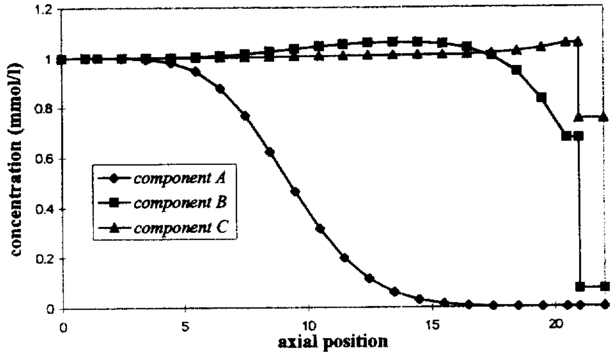

Fig. 8. Liquid phase concentration profile of temperature swing chromatography after the first cold flow ($C_{init} = 1$ mmol/l).

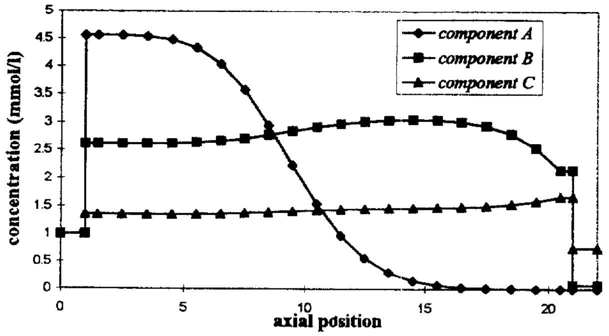

Fig. 9. Liquid phase concentration profile of temperature swing chromatography after the first heating ($C_{init} = 1$ mmol/l).

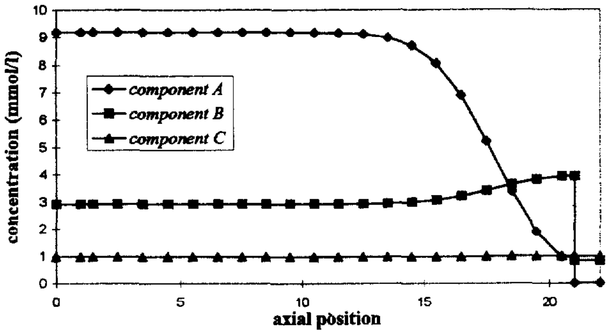

Fig. 10. Liquid phase concentration profile of temperature swing chromatography after the 16th cold flow ($C_{\mathrm{init}} = 1$ mmol/l).

mmol/l and 0.75 mmol/l, respectively. The concentration front of component A is inside the column, thus its concentration in the bottom reservoir is zero.

Next step the column is heated to the hot temperature. Fig. 9 shows the concentration profiles after heating. According to the temperature dependence of the isotherms, A concentration is the highest, B is smaller and C concentration is the smalest inside the column.

Then V_{hot} volume of the solution in the bottom reservoir is pumped back from the bottom reservoir to the top one. Owing to the hot flow the column is regenerated according to the composition of bottom reservoir solution. Thus inside the column the concentration of A is practically zero and the concentrations of B and C are equal to their concentrations in the bottom reservoir. At the same time, the concentrations increase in the top reservoir, since $V_{\mathrm{cold}} - V_{\mathrm{hot}}$ volume of the solution has definitively left the top reservoir while the amounts of the components are almost the same there. Then the column is cooled to the cold temperature.

As a result of n cycles $n(V_{\mathrm{cold}} - V_{\mathrm{hot}})$ ml solution have left the top reservoir, where the volume of the solution is $V - n(V_{\mathrm{cold}} - V_{\mathrm{hot}})$. In Fig. 10, the concentration profiles are plotted after the 16th cold flow. (This is the last cold flow, since after 15 cycles 900 ml have left the top reservoir, thus there are only 100 ml in there). It can be seen that the concentrations in the top reservoir and inside the column are significantly shifted comparing with the initial concentrations. The concentration of component A is the highest (about 9.2 mmol/l) in the top reservoir, since it does not break through the column. The concentration of component B is smaller (about 3 mmol/l) in the top reservoir, since a significant part of its amount has been transported to the bottom reservoir. According to both the smallest affinity to the adsorbent and to the smallest temperature dependence of the isotherm the concentration of component C is only about 1 mmol/l in the top reservoir. It is equal to its initial concentration which indicates that component C has been totally transported to the bottom reservoir. The concentrations of components A, B and C in the bottom reservoir (or in the P1 product) are 0.01, 0.82 and 0.98 mmol/l, respectively. Thus P1 product is mainly a mixture of components B and C.

5.3. Hot regeneration of the column

One can see in Fig. 10 that large amount of the component A and some component B are retained by the column, thus for recovering them it is necessary to regenerate the column. In every case, the hot regeneration was performed using 100 ml of pure solvent. The regeneration effluent can be collected in separated samples in order not to destroy the concentration profiles (here the sample volumes are 5 ml). It can be also collected in a mixed reservoir. The two possibilities will be examined.

There are different ways of carrying out the hot regeneration. The effect of the direction of regeneration flow on the composition of P2 product is studied below.

5.3.1. Feed at the bottom reservoir end, upward flow

In this way, the pure solvent is pumped from the bottom reservoir to the top one. In Fig. 11, the composition (mol%) of the samples and the concentration of component A in the samples are shown. As seen the purity of component A is always greater than 80%, however by the time the purity becomes greater than 99% its concentration has decreased to a low value (the purity becomes greater than 99% in the 14th sample in which the concentration of A component is less than 2.5 mmol/l). On the one hand, the high A component concentration in the first few samples is due to the direction of flow (since there is mainly A component near to the top reservoir end of the column). On the other hand the relatively high B and C components content of the first few samples is due to their faster regeneration. This is supported for example by the first sample. In this sample, the B and C content is 15.6% and 3.3%, respectively which is larger than that observed after mixing the samples in the reservoir (see Table 2). As a conclusion, it is possible to collect samples in which the purity of component A is high, but the concentration of the desired component is low.

5.3.2. Feed at the top reservoir end, downward flow

In this way, the pure solvent is pumped from the top reservoir to the bottom one. Since components B and C are closer to the bottom reservoir end of the column, and their regeneration is faster than that of component A, it is worth inves-

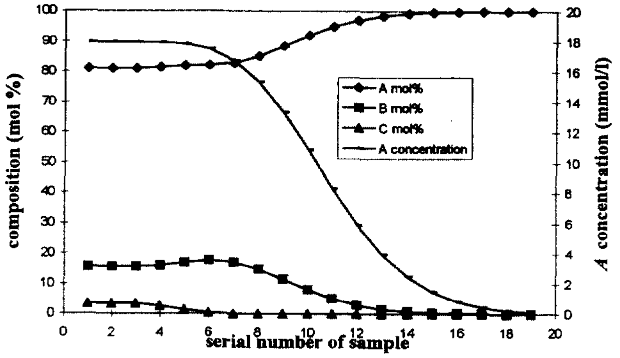

Fig. 11. Composition and A concentration of the samples in case of hot regeneration from the bottom reservoir to the top one.

Table 2
Composition of P2 product in case of different regeneration methods

Method	A component (mmol/l, mol%)	B component (mmol/l, mol%)	C component (mmol/l, mol%)
Feed at bottom end upward flow	9.83 (84.66%)	1.62 (13.96%)	0.16 (1.38%)
Feed at top end downward flow	9.82 (84.65%)	1.62 (13.96%)	0.16 (1.38%)

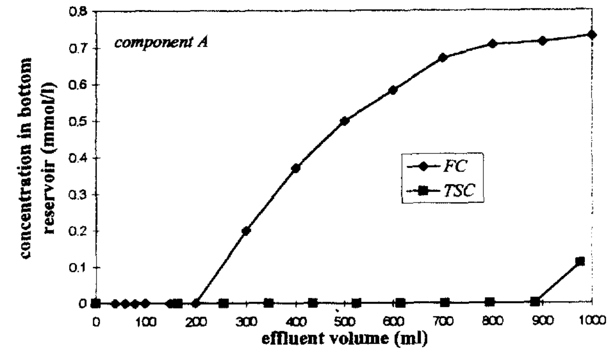

Fig. 12. Composition and A concentration of the samples in case of hot regeneration from the top reservoir to the bottom one.

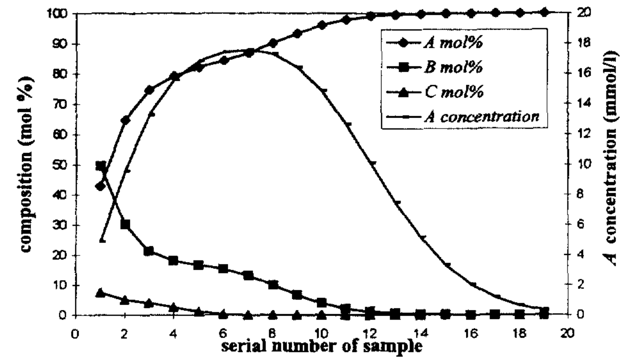

Fig. 13. Comparison of temperature swing chromatography and frontal chromatography.

tigating this case. As can be seen from Fig. 12 in the first few samples the mole fraction of component A is less than 80%; however, its concentration is also low. Since component A is further away from the bottom reservoir end, its concentration in the samples first increases from a low value to a maximum in the 7th sample, and then decreases. At the same time the concentrations and mole fractions of components B and C decrease monotonously from a relatively high value. In this way, component A with purity greater than 99% can be obtained from the 12th sample (in which the concentration of component A is 10 mmol/l).

After mixing the concentrations and mol fractions are practically the same as in the previous case (Table 2) which means that the efficiencies of the regenerations are similar.

5.4. Comparison of TSC and frontal chromatography

The comparison of TSC and frontal chromatography (later FC) is shown in Fig. 13. This figure shows the concentration of A component in the bottom reservoir as a function of the effluent volume. In the frontal chromatographic experiment, 1000 ml solution were displaced from the top to the bottom reservoir without changing the temperature and the flow direction. All the effluent was collected and mixed in the bottom reservoir. In case of TSC, also 1000 ml solution were displaced from the top to the bottom reservoir, but several temperature and flow direction changes were applied (V_{cold} = 120 ml, V_{hot} = 60 ml). One can see that, in case of FC, the concentration in the bottom reservoir increases after some delay. At the end, the reservoir contains 1000 ml of a solution at about 0.73 mmol/l and about 0.27 mmol are on the adsorbent. In case of TSC, the concentration of A component in the bottom reservoir remains zero until 900 ml and after starts to increase. Thus the appearance of A in the bottom reservoir is delayed relatively to FC. In fact, FC can be considered as a limiting case of TSC where only one half-cycle (cold) is performed.

Because of the direction change in case of TSC real flow of 180 ml corresponds to an effective flow of 60 ml, thus the time needed for TSC is three times that needed for FC (the time needed for the temperature change is negligible compared with that needed for the flow). However, in case of TSC the amount of component A taken up is more than three times greater than in case of FC. At the same time the purity of component A in the column is better in case of TSC than in case of FC. The increase of A concentration in the top reservoir (in case of TSC) leads to increased competition for the adsorbent active sites, and thus more component B and C are pushed into the bottom reservoir (in fact the role of the hot flow is to sharpen the separation).

By adjusting the operating parameters in TSC (cold and hot displaced volumes), the appearance of the components in the bottom reservoir can be chosen. In Table 3, the calculated concentrations of the components in the bottom reservoir after the last cold flow are given. If V_{cold} is small (40 ml) then the solution in the bottom reservoir contains mainly

Table 3
Composition of P1 product in case of different volumes of cold and hot flows

Volume of the flows	A component (mmol/l, mol%)	B component (mmol/l, mol%)	C component (mmol/l, mol%)
V_{cold} = 40 ml, V_{hot} = 25 ml	0 (0%)	0.179 (19.47%)	0.74 (80.5%)
V_{cold} = 80 ml, V_{hot} = 50 ml	0.007 (0.4%)	0.73 (42.51%)	0.98 (57%)
V_{cold} = 120 ml, V_{hot} = 75 ml	0.009 (0.5%)	0.83 (45.6%)	0.98 (53.87%)

C and some B components. Obviously, in this case the P2 product is a mixture of mainly A and B components. If V_{cold} is large (120 ml) then the solution in the bottom reservoir is a mixture of B and C components, and the P2 product is mainly component A. Based on the above described facts TSC can be an alternative to traditional frontal chromatography.

6. Conclusions

Different kinds of adsorptive parametric pumping separations of a three component mixture were theoretically investigated with the help of a multicomponent, non-linear model. The effect of the initial concentration of the components on the separation is found to be significant. Parametric pumping takes advantage of the interaction among the solutes and higher concentrations to bring about the separation.

Consequently, if the initial concentrations are high (and the isotherms are non-linear) then the components are separated. According to both the affinities for the solid phase and to the temperature dependence of the isotherms the enriched individual components can be obtained from either the top reservoir, the column or the bottom reservoir. In this case, a combination of batch and continuous parametric pumping was also investigated. In certain cycles, the system operates in continuous mode, thus products are withdrawn from and feeds are led into the reservoirs. It makes possible to produce purified products as long as the system works. However, in most of the cycles the system operates in batch mode, which eliminates the perturbing effect of feed and withdrawal. In this way, products with constant composition can be obtained.

If the initial concentrations are low (and the isotherms are linear) then traditional batch parametric pumping concentrates the components in one reservoir. In this case, it is necessary to apply a special type of parametric pumping, called temperature swing chromatography in order to obtain a separation. The fronts movement and the hot regeneration of the column were studied in detail. It is shown that on one hand the composition of the products strongly depends on the operating parameters (cold and hot displacement volumes), and on the other hand that the execution mode of hot regeneration is an important parameter for improving the purity of the products.

As conclusion it is necessary to emphasize that the general study presented above can be easily extended for the separation of real mixtures. These methods are very flexible, thus there are several ways and areas to carry out parametric pumping separations. Due to the analogy between temperature in parametric pumping and pressure in pressure swing adsorption probably the results of this theoretical study can be applied to pressure swing adsorption. Further theoretical and experimental investigation of the described operations will be the object of a future work.

7. Nomenclature

C_i	Concentration in the liquid-phase, (mmol/l)
C_i^c	Concentration in the liquid-phase at the cold temperature, (mmol/l)
C_i^h	Concentration in the liquid-phase at the hot temperature, (mmol/l)
K_i^h	Slope of the hot isotherm
k_i	Parameter of a Langmuir type isotherm (l/mmol)
Q_i	Maximum of a Langmuir type isotherm (mmol/l adsorbent)
q_i	Concentration in the solid phase, (mmol/l adsorbent)
t	Time, (s)
V	Volume of the solution to be separated (l)
V_{cold}	Volume of cold flow (l)
V_{hot}	Volume of hot flow (l)
v	Interstitial velocity, (cm/s)
z	Bed axial position, (cm)
ε	Bed void fraction
ΔV	Volume of displaced solution (l)

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