

Instruction of the Code of Simulated Moving Bed Chromatography

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1 Introduction

There are two important, practical modes of carrying out industrial purifications by preparative chromatography. The most straightforward and the most frequently used of these is the cyclic batch elution chromatography. The second mode available is counter-current chromatography, in which the fluid and the solid phase flow through the column in opposite directions. In principle, there are two possibilities of this mode, the continuous true moving bed and the cyclic simulated bed method. In practical, only the latter method is widespread. Note that in this fundamental introduction, we are talking about the two components situation.

1.1 True Moving Bed Chromatography (TMB)

The configuration of TMB consists of a vertical column in which the fluid phase injected upward while the solid phase is poured into the column in the opposite direction (downward in this case). Then a feed solution is continuously injected into the stream of the fluid phase, in the middle of the column. Both components are collected in the opposite outlets.

The advantage of this continuous process over the traditional bath experiments are manifest, especially in terms of the high yields and lower consumptions. However, enormous difficulties have been encountered in the implementation of TMB, because it is nearly impossible to achieve the continuous flowing of the fragile solid phase.

1.2 Simulated Moving Bed Chromatography (SMB)

The mentioned drawbacks of TMB can be alleviated by replacing the continuous flow of the solid phase by a discontinuous one. The solid phase does not actually move, instead it “moves” periodically by switching the inlet and outlet ports, hence the name of this process. It uses a set of shorter columns, instead of a single long column in TMB, connected through complex ports. The attractive point of SMB is its efficient use of the solid beads and the yields and purity achieved are often very high. The disadvantage is the waiting time to reach the cyclic steady state (CSS).

A schematic of a SMB is shown in Fig. 1. There are two inlet ports, feed and desorbent respectively, and two withdrawal ports, raffinate and extract respectively. The feed buffer is injected into the feed port, while the desorbent in the desorbent port for regenerating the columns. The one with lower retention coefficient will be withdrawn in the raffinate port while the one with higher retention factor in the extract port. Assuming that under the proper control of the pump, we have the constant flow rate in different zones. The system can be operated either in the open loop and closed loop.

According to the position of the columns, the process can be divided into four different zones, each with a specific role in the separation process:

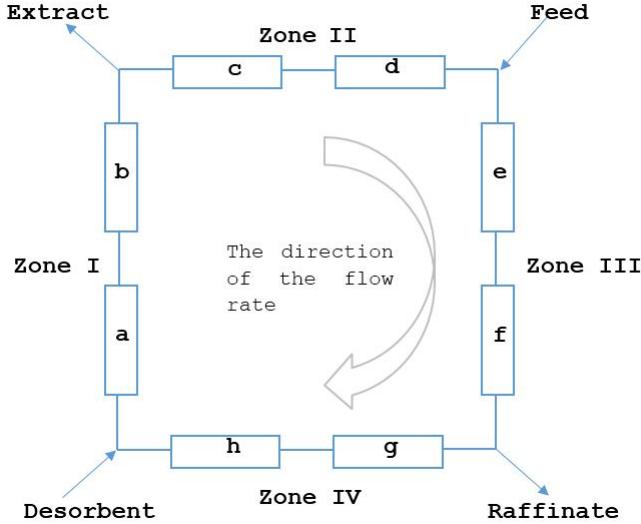


Fig. 1: Schematics of a simulated moving bed

- Zone I, between the desorbent and the extract ports where the regeneration process of the columns happens and the desorption of the more retained component takes place;
- Zone II, between the extract and the feed ports where the adsorption of the more retained component takes place;
- Zone III, between the feed and the raffinate ports where the adsorption of the less retained component takes place;
- Zone IV, between the raffinate and the desorbent ports the desorption of the less retained component takes place;

2 Modelling of Simulated Moving Bed (SMB) Separations

2.1 Column Model

After neglecting the pore and surface diffusion in the beads, the General Rate Model, which is adopted in CADET, is simplified into the Lumped Rate Model without pore diffusion:

$$\frac{\partial c_i}{\partial t} = -u \frac{\partial c_i}{\partial z} + D_{ax} \frac{\partial^2 c_i}{\partial z^2} - \frac{1}{\beta} \frac{\partial q_i}{\partial t} \quad (1)$$

For the solid phase, the mass balance equation is given by:

$$a \frac{\partial q_i}{\partial t} = k_{eff,i} (q_{eq,i} - q_i) \quad (2)$$

The initial condition of the columns are all initially empty of feed but contain only the liquid and the solid phases in equilibrium. The boundary conditions then result from the SMB design. What flows into a column depends on the composition of the fluid phase that is eluted from the previous column. In other words, what happens during a period (or a switch) is defined by the initial and the boundary conditions.

In this case, the linear isotherm was employed for the sake of demonstration, $0 = f(c_p, q_{eq})$.

2.2 Node Balance of Columns

In order to complete the model for the SMB-process, we have to define the connection of two adjacent columns. Let the inlet concentration of the column a for the component i be denoted by $c_{a,i}^{in}$, analogously by $c_{a,i}^{out}$ the outlet concentration. Additionally inlets and outlets, like feed, raffinate, desorbent, and extract will be denoted by scripts F, R, D, and E respectively. Fig.2 illustrates the scheme of two adjacent columns j and $j + 1$. The flow rate of columns between desorbent inlet and extract outlet was defined as the cyclic flow rate.

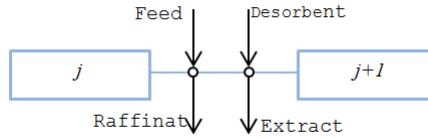


Fig. 2: The schematic of two adjacent columns

For the connecting nodes we obtain the following node equations:

$$c_{j+1,i}^{in} = \frac{c_{j,i}^{out} Q_j + \delta}{Q_{j+1}} \quad (3)$$

where the δ is varied in different inlets and outlets, and Q_j is the actual volumetric flow rate of mobile phase through column j . It is related to the liquid phase velocity (interstitial velocity) by $Q_j = \varepsilon A u_j$, where A is the column cross-section area:

$$\delta = \begin{cases} Feed & c_F Q_F \\ Desorbent & 0 \\ Raffinate & c_{j,i}^{out} Q_R \\ Extract & c_{j,i}^{out} Q_E \end{cases} \quad (4)$$

2.3 The Design of the Flow Rates and Switch Time

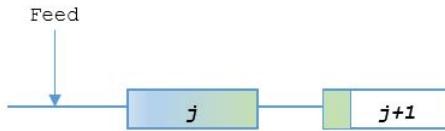
The most important parameter in the operation of either TMB and SMB is the mass flow rates Q and switch time t_s . In regard to the design of those

parameter, we refer you to the Chapter 17 of the book, Fundamentals of the preparative and non-linear chromatography.

However, the following relationships are always valid (should be valid):

$$Q_I > Q_{III} > Q_{II} > Q_{IV} \quad (5)$$

Also, the switch time should be selected in such a way that the concentration plateau of component 1 enters into column IV before the end of the period but that the concentration plateau of component 2 does not. In the following figure, the blue represents the component 1, while the green represent component 2.



3 Code Structure

There are four parts involved in my program: simulatedMovingBed, getParameter, massConservation, secColumn. The simulatedMovingBed is the main function in which the missions of switching, calculating, and plotting are implemented; The getParamter is a function where all the parameters, no matter for the chromatographic model or columns (system and operating parameters), are collected; The massConservation function is adopted after each switching to transfer the data in demand, such as outlets and last state (please see the *section of Node Blance*); The secColumn is the function which is in charge of one-column simulation (please see the manual of CADET, <http://github.com/modsim/CADET.git>).

3.1 Switch Implementation

As for the switching, it was achieved by such a shifting: each column was represented by alphabet, a, b, c, d (Here we will simplify the presentation by considering the simple case when $N = 4$). In the initial value assignment, $a = 1, b = 2, c = 3, d = 4$; then in the first round, $a = 2, b = 3, c = 4, d = 1$, and then in the following rounds, $mid = a, a = b, b = c, c = d, d = mid$.

3.2 Case Data

The data for numerical tests (Tab.1) were from the paper *Numerical method for accelerated calculation of cyclic steady state of ModiCon-SMB-process*. However the particle radius was not provided in that paper, instead I just use a artificially empirical one.

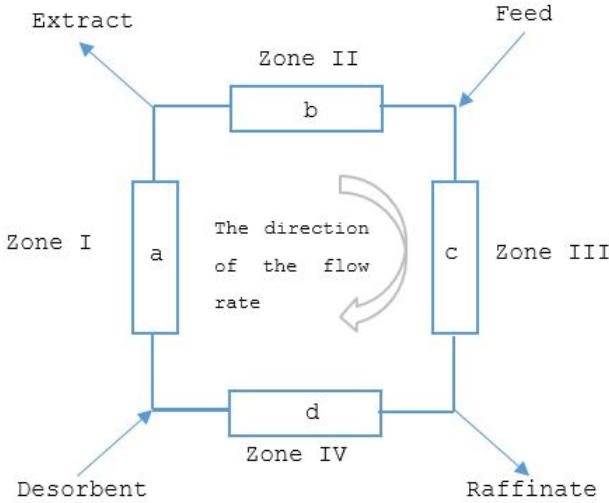


Fig. 3: Scheme of a simulated moving bed

3.3 Convergence Criterion

Until now all the system and operating parameters were well-prepared, the simulation can be launched. At the very beginning, the outlet of each columns was assumed to 0, $c_j^{out} = 0$ (here drop the subscript of components). Then the four columns in the system were simultaneously calculated, correspondingly the data in demand (like outlets from the columns and the last state of columns) were collected. Afterwards, the switch step was implemented. using the mass-Conservation function to calculate the inlet concentration of each column and transferring the last state of column i in the former switch to the initial state of column i in the next switch, we obtained the data for simulation again. The cyclic steady state (CSS) was reached once the following stopping criterion was satisfied:

$$\left\| \frac{c(z, t + nt_s) - c(z, t)}{c(z, t)} \right\| < \varepsilon \quad (6)$$

In our case, the value of 1×10^{-5} is enough for the relative error tolerance ε .

4 Demonstration of Case 1

The process needs around 80 switches to reach the so-called cyclic steady state (the relative tolerance $\varepsilon = 1 \times 10^{-4}$), using the desktop. The time periodic concentration profiles are shown in the following Fig.4. Let's have an insight into the process by sequence.

Tab. 1: Parameters of *Case 1* for the numerical tests

Number of columns	4
Dispersion coefficient	$u \times 10^{-24} \text{ m}$
Porosity	0.83
Column diameter	0.02 m
Column length	0.25 m
Switching time	$t_s = 180 \text{ s}$
Linear isotherms	$a_1 = 5.72, a_2 = 7.7$
Concentration of feed	0.55 g/l
Cyclic flow rate	$9.62 \times 10^{-7} \text{ m}^3/\text{s}$
Feed flow rate	$0.98 \times 10^{-7} \text{ m}^3/\text{s}$
Raffinate flow rate	$1.40 \times 10^{-7} \text{ m}^3/\text{s}$
Desorbent flow rate	$1.96 \times 10^{-7} \text{ m}^3/\text{s}$
Extract flow rate	$1.54 \times 10^{-7} \text{ m}^3/\text{s}$

4.1 Concentration Profiles at the End of the First Period t_s

At the beginning of the first period, all the columns are empty and the initial condition is $C_{i,j}^{out} = 0$ for all the i and j . During the whole period, the feed is injected into the system through the feed node, at a constant composition. Since the switch t_s is well-designed, so the concentration plateau of the component 1 enters into the Zone IV, while the concentration plateau of the component 2 does not.

Figure 5 illustrates the outlet profile (in our case, we do not have the immediate concentration profile, instead we use outlet profile) in the column at the time immediately before the moment when the columns are switched.

4.2 Profiles at the End of the Second Period $2t_s$

At the beginning of the second period ($t_s + \delta t$), the feed and the draw-off points are switched simultaneously to their next positions in the direction of the liquid phase flow. The evolution of the concentration profiles during this period depends on the new initial and boundary conditions for each column. Specifically, the inlet concentration (initial boundary) of Zone II during this period is the outlet chromatogram in Zone III in previous period, while the inlet concentration of Zone III during this period is the combination of the outlet chromatogram in Zone IV in previous period and *feed concentration*. As a consequence, at the end of second period, we obtain such concentration profile (Fig.6) at the outlet of each column.

4.3 Profiles at the End of the Third Period $3t_s$

Again, the column switching at the beginning of the new period changes the initial conditions in the four columns and their boundary conditions. The inlet concentration (initial boundary) of Zone I during this period is the outlet chro-

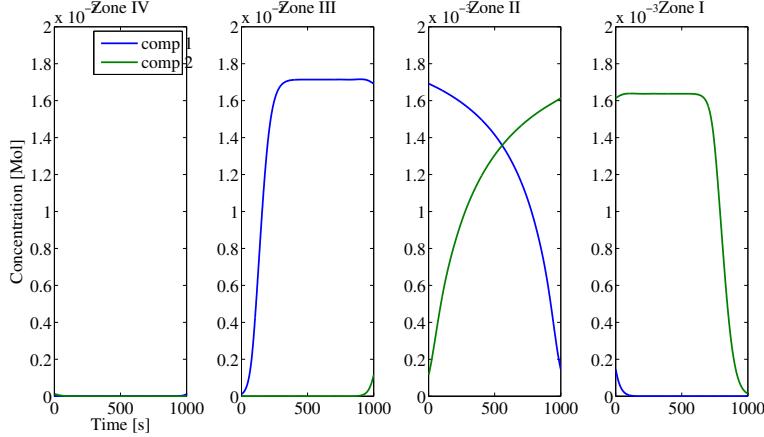


Fig. 4: The concentration profiles for the four column SMB

matogram in Zone II in previous period, while the inlet concentration of Zone II during this period is the combination of the outlet chromatogram in Zone III in previous period and *feed concentration*, while the inlet concentration (initial boundary) of Zone III during this period is the outlet chromatogram in Zone IV in previous period. The calculation of the position of the concentration follows an iteration process. The concentration profiles in the SMB train, at the end of the third period, are shown in the Fig.7.

4.4 Profiles at the End of the One Round $4t_s$

We define four switches as one round here. The iteration pattern is now clear. From one period to next, the higher and higher concentration plateaus are formed for components 1 and 2 in *Zone III*. These plateaus are transferred at the beginning of the following period into *Zone II*. These plateaus become narrower and narrower with increasing number of periods. Figure 8 is the result of one round switching.

4.5 Profiles at the End of the n th Rounds nt_s

After several rounds, the iterative point approaches the convergence region. Figure 9 and Figure 10 are the concentration profiles of 3 rounds and 5 rounds respectively.

4.6 Visualization

The following video (Fig.11) is the recording of the process of *Case 1*. This is the evolution of the column 1. Please ensure that your computer has installed the proper plug-in to display the video in the PDF file.

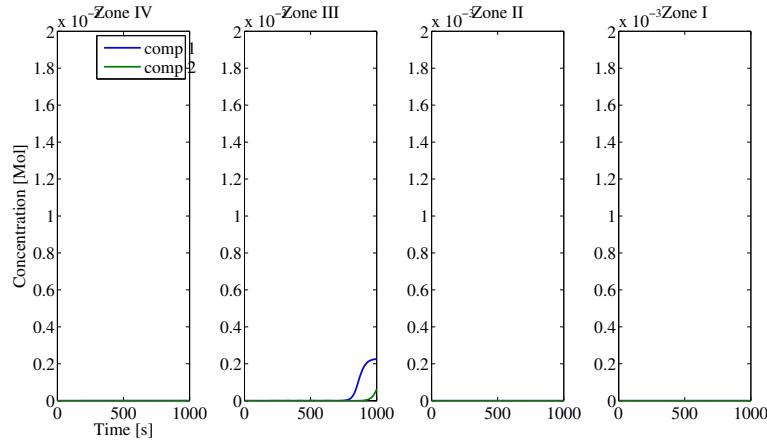


Fig. 5: Concentration profiles along the column train of a SMB unit at the end of the first period. The plotted data are the outlet concentration of each columns. From right to left is the direction of the liquid phase, and from left to right is the switching direction of the columns.

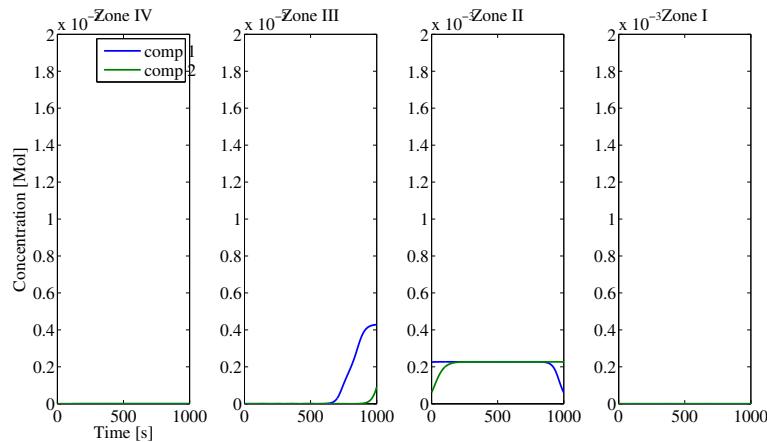


Fig. 6: Concentration profiles at the end of the second period.

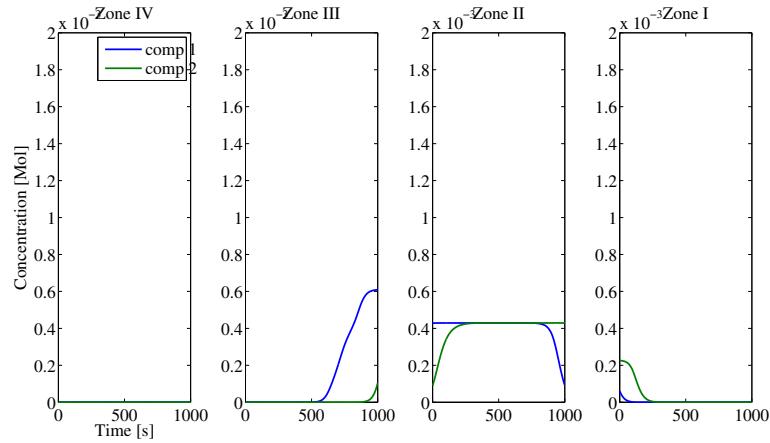


Fig. 7: Concentration profiles at the end of the third period.

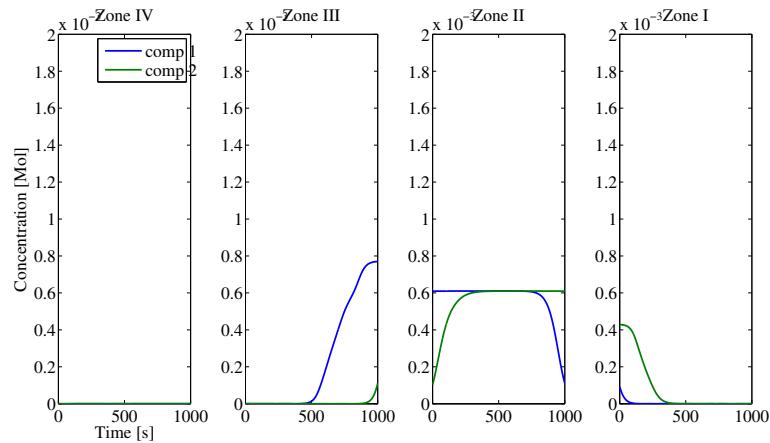


Fig. 8: Concentration profiles at the end of the fourth period (one round).

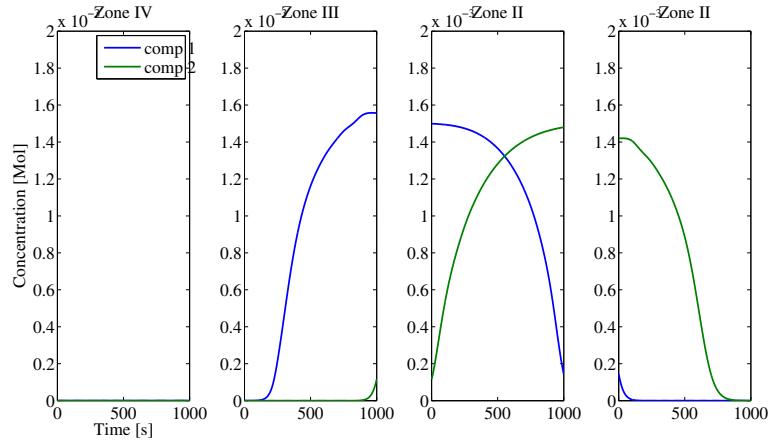


Fig. 9: Concentration profiles at the end of the 3 rounds.

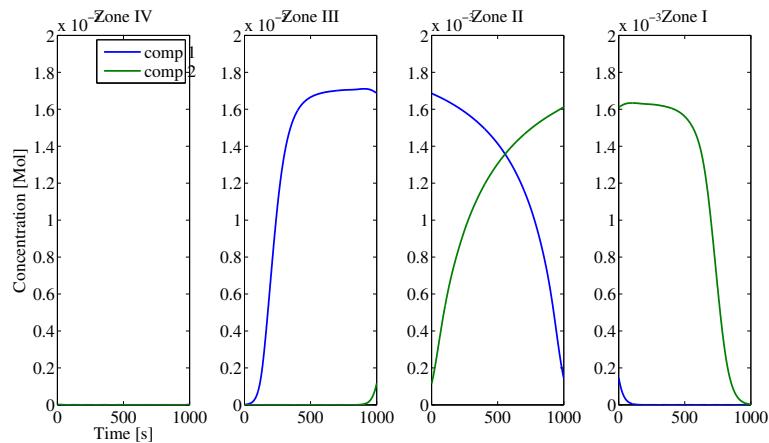


Fig. 10: Concentration profiles at the end of the 5 rounds.

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Fig. 11: The recording video of the evolution of the column 1 in *Case 1*.

5 The Other Cases

The above *Case 1* is a 4-column case (one column in each Zone). Actually it can be extended into 8-column case once the parameter *opt.nColumn* was set to the value 8. To be simple, we just offer the final concentration profile (Fig. 12) in this case instead of listing the processes.

Another 8-column case (Tab.2) was taken from the paper, *Model-based control of a simulated moving bed chromatographic process for the separation of fructose and glucose*.

Tab. 2: Parameters of *Case 2* for the numerical tests

Number of columns	8
Dispersion coefficient	—
Porosity	0.38
Column diameter	2.6 cm
Column length	53.6 cm
Switching time	$t_s = 1552s$
Linear isotherms	$K_A = 0.54, K_B = 0.28$
Concentration of feed	0.5 g/cm ³
Cyclic flow rate	0.1395 cm ³ /s
Feed flow rate	0.020 cm ³ /s
Raffinate flow rate	0.0266 cm ³ /s
Desorbent flow rate	0.0414 cm ³ /s
Extract flow rate	0.0348 cm ³ /s

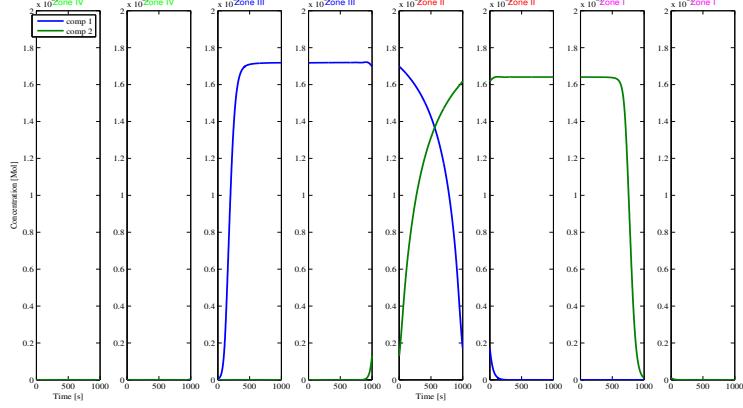


Fig. 12: The concentration profiles for the eight column SMB

The Fig. 13 is the concentration profile of the SMB fructose/glucose separation.

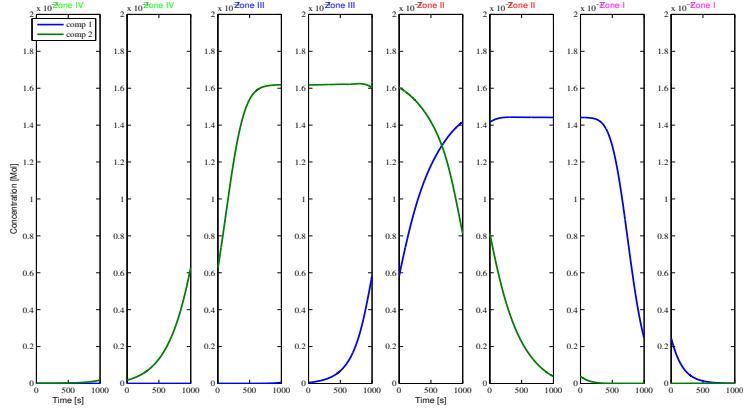


Fig. 13: The concentration profiles for the eight column SMB

The convergence to the cyclic steady state, in 8-column cases, was achieved after around 120 switching periods (300 sec), under the tolerance 1×10^{-5} . This result in approx. 140 sec on a 2.93GHz Intel Core i7 PC. In order to monitor each column, we plot the figures in terms of each column (by recording the outlet profiles of each column in one round), rather than the outlets in each switch period (such as the figures in demonstration of *Case 1*).

6 Summary

I have achieved the simply implementation of the simulated moving bed, with one column/two column in each zone. Ant the SMB process as a continuous chromatographic separation is an interesting alternative to the conventional batch chromatography. Two cases were used to demonstrate the performance of SMB, although the data are from literatures instead of real industrial plants. This code can be definitely applied to more complex cases, which are using more recent isotherms or more adopted General Rate Model. The simulation other multi-column system will develop later. The more powerful code, a novel single-column setup for reproducing the steady periodic behaviour of simulated multi-column chromatography, is presented in the branch of the *develop*. It is not only can achieve the same CSS but also less time-consuming.