

A SYSTEMATIC APPROACH TO SMB PROCESS MODEL IDENTIFICATION FROM SMB PROCESS DATA

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Abstract: The simulated moving bed process is a continuous chromatographic separation process, which is important in various fields, from sugar to enantiomer separation. In this paper, a systematic approach to parameter identification of a kinetic SMB model is presented. In contrast to previous studies, identifiability and the influence of local minima are investigated from fictitious data obtained by simulation of different SMB processes at various operating conditions. *Copyright © 2005 IFAC*

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1. INTRODUCTION

The simulated moving bed (SMB) process is a continuous chromatographic separation process in which a counter-current movement of the liquid and solid phase is allowed by periodically switching the inlet and outlet ports. This technology is important in various fields, from sugar to enantiomer separation. However, the transfer of the SMB technology, used industrially for hydrocarbon and sugar separation, to the separation of fine chemicals is not immediate. Indeed, the conditions and requirements (product quantities and purities, characteristics of the phases, interactions, ...) are very different. The main issues are the selection of optimal operating conditions and process control, which require the development of a process model and the estimation of its parameters.

A first-principles SMB model usually includes the isotherm parameters, the column porosity, the diffusion and/or the mass transfer coefficients. Typically, all these parameters are determined from batch experiments, performed on analytical columns or on the SMB columns. Most of the methods

described in the literature suffer from a number of drawbacks. Indeed, many are based on assumptions that are usually not verified (e.g. ideal conditions) (Dose *et al.*, 1991; Guiochon *et al.*, 1994; Felinger *et al.*, 2003; Altenhöner *et al.*, 1997). Some methods require a large amount of products, like the frontal analysis. None of them gives an estimation of the error on the identified parameters. To the authors' knowledge, no systematic identifiability study has been performed.

On the other hand, only a few studies report work on model identification from SMB experiments (Zimmer *et al.*, 1999), (Toumi and Engell, 2004). In both papers, certain parameters are not identified, e.g. the diffusion coefficient in (Zimmer *et al.*, 1999) or the particle diffusion and particle porosity in (Toumi and Engell, 2004) and no confidence intervals on the estimated parameters are given.

The aim of this work is to develop an identification method to determine with good accuracy the isotherm parameters as well as the mass transfer coefficients in a SMB model from SMB experiments.

The differences with respect to previous studies are the following:

- A realistic chromatographic model, which incorporates a limited number of parameters, and competitive Langmuir isotherms (an obvious first choice) is considered.
- Identifiability and the influence of local minima are studied by performing parameter estimation from fictitious measurements obtained by simulation of a model with known parameters.
- The errors on the estimated parameters are calculated.

The text is organised as follows. The SMB process is described in section 2. In section 3, the problem statement and the identification approach are presented. Section 4 is devoted to an identifiability study and section 5 to an analysis of the basin of attraction and the existence of local minima. In section 6, the covariance matrix of the estimated parameters is calculated.

2. PROCESS DESCRIPTION

Figure 1 shows the equivalent counter-current representation of a SMB process. The system is subdivided into 4 different sections delimited by several material flow outlets and inlets. The two inlets are the input of the mixture to be separated and the input of a desorbing solvent. The system also has two withdrawal ports, one for the raffinate which mostly consists of the less adsorbable component (component 1) and another for the extract which mostly consists of the more retained component (component 2).

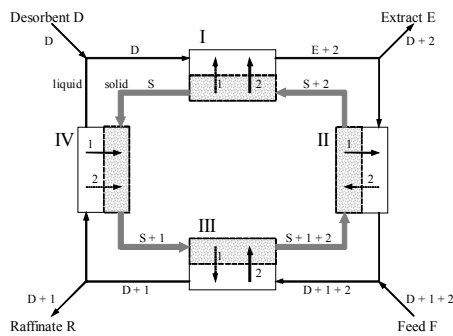


Fig. 1. Equivalent counter-current representation of a SMB process for the separation of a mixture with two species 1 and 2

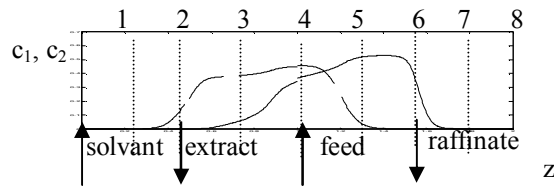


Fig. 2 : Internal concentration profile : __ component 1, --- component 2

The movement of the liquid and solid phases, as well as the adsorption-desorption phenomena taking place in each section are depicted in Fig.1. In our

simulation studies, the start-up of the plant coincides with the beginning of the injection of a continuous feed flow in the process filled with solvent.

The SMB plants considered in this study are made of 6 or 8 columns (in both cases, two columns are placed in section 2 and 3) and are used to separate two cycloketones (cyclopentanone and cyclohexanone or cyclopentanone and cycloheptanone). They are equipped with four UV detectors. Two of them measure the extract and raffinate outlet adsorbance. The two others are placed in the circulating liquid stream and give a direct measurement of the complete UV-profile after 6 or 8 switches. The sampling period of the UV detectors is less than 1% of the switching time. At steady-state, the internal concentration profiles shown in Fig. 2 are obtained at 50% of the switching period. The vertical lines indicate the 8 positions that a UV detector in the circulating stream occupies during a cycle (e.g. 8 switches) in a SMB plant with 8 columns.

3. PROBLEM STATEMENT AND IDENTIFICATION APPROACH

3.1. SMB Model

Several mathematical models describe the mass balances in chromatographic columns (Guiochon *et al.*, 1994). As a large number of simulation runs have to be performed in the course of the numerical optimization process needed for parameter estimation, the computational load for integration of the model equations must be as small as possible. Moreover, the number of unknown parameters must be limited to ensure identifiability. It turns out that the kinetic model offers these significant advantages (Grosfils and Levrie, 2004). In this model, a kinetic equation takes the band broadening into account. The model equations for column j of the SMB process are written as follows for the liquid phase:

$$\frac{\partial c_{i,j}}{\partial t} = -v_j \frac{\partial c_{i,j}}{\partial z} - \frac{1-\epsilon}{\epsilon} \frac{\partial q_{i,j}}{\partial t} \quad (1)$$

with $c_{i,j}$, the fluid concentration, $q_{i,j}$, the solid concentration, v_j , the fluid velocity, ϵ , the porosity. t denotes the time and z , the axial coordinate. $i = 1, 2$ refers to the species in the mixture to separate.

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

$$\frac{\partial q_{i,j}}{\partial t} = k_{i,j} (q_{i,j}^{eq} - q_{i,j}) \quad (2)$$

with $k_{i,j}$ the mass transfer coefficient, and $q_{i,j}^{eq}$, the adsorbed equilibrium concentration. $k_{i,j}$ is a function of the velocity in column j , which is assumed linear. Hence, a relative mass transfer coefficient, equal in all the columns of the SMB plant for each component, is defined by $k_i^{rel} = k_{i,j} / v_j$.

The adsorbed equilibrium concentration is related to the liquid-phase concentration by an adsorption equilibrium relation. Many multicomponent non-linear isotherm equations have been described. The

obvious first choice is the competitive Langmuir isotherm with the following equation:

$$q_{i,j}^{eq} = \frac{q_{si} b_i c_{i,j}}{1 + b_1 c_{1,j} + b_2 c_{2,j}} \quad (3)$$

where q_{si} and b_i are respectively the saturation capacity and the equilibrium constant of component i ($i = 1, 2$). In this study, two cases are considered. The first one assumes that the saturation capacities of the two components are identical, which is often assumed for enantiomer separation. The second case takes two different saturation capacities into account. Note that, at infinite dilution, the Langmuir isotherm reduces to a linear relation with slope $H_i = q_{si} b_i$.

Valve switching is taken into account by considering that the concentration profiles in column j at the beginning of a switching interval are equal to the profiles obtained in the column $j + 1$ at the end of the previous period:

$$c_{i,j}(t_p = 0, z_j) = c_{i,j+1}(t_{p-1} = \Delta t, z_{j+1}) \quad (4)$$

where the index p denotes the current switching period and Δt is the switching period.

In equations (1) to (4), the parameters are the porosity, the fluid velocity in each column, the relative mass transfer coefficients of the two components and the isotherm parameters. In the next two paragraphs, a discussion on how to exploit prior knowledge on these parameters and how to deduce the set of parameters to be identified by an optimization approach is presented.

The porosity can be estimated from simple batch experiments (Altenhöner *et al.*, 1997). The fluid velocity depends on the porosity, the cross-section area of the column and the flow rate in the considered column. The first is determined as indicated above, the second is a known process characteristic and the last one is fixed by the pumps of the experimental plant. If an erroneous porosity or flow rate are used in the determination of the isotherm parameters from batch experiments, these parameters will not be correctly estimated but they will nevertheless be able to describe quite accurately the propagation of the elution fronts (Seidel-Morgenstern, 2004). In the following, it will be considered that the porosity and the flow rates are known with enough accuracy and that their influence on parameter estimation is the same as in batch.

In theory, the mass transfer coefficients have to be determined at low concentration in order to be related to the column efficiency and to avoid including the non-linearity due to the isotherm at high concentration (Guiochon *et al.*, 1994). In this study, at first, they are considered as known in order to examine whether it is possible to work with the values obtained from batch experiments at low concentration and, in a second step, they are identified together with the isotherm parameters.

In conclusion, the unknowns are, for Langmuir isotherms with identical saturation capacities, q_s , b_1 , b_2 , k_1^{rel} , k_2^{rel} , and for Langmuir isotherms with different saturation capacities, H_1 , H_2 , b_1 , b_2 , k_1^{rel} , k_2^{rel} .

3.2. Principle of Identification

Let θ be the n -dimensional vector of unknown parameters. The estimates of the parameters are calculated by minimizing a cost function, which measures the difference between experimental profile(s) and the corresponding profile(s) simulated with Eq. (1) to (4). The cost function is defined as:

$$J(\theta) = \sum_{t=1}^N (y_m(t) - y(t, \theta))^2 \quad (5)$$

with y_m , a measured UV signal to be specified below, y , the corresponding simulated UV signal and N , the number of measurements.

3.3. Optimization method and parameter constraints

The optimization method used is an algorithm for unconstrained optimization by quadratic approximation developed by Powell and called UOBYQA (Powell, 2000).

For each unknown parameter, the prior knowledge allows one to specify an interval within which the estimated value must lie: $\theta(j)_{inf} < \theta(j) < \theta(j)_{sup}$. To enforce these constraints, the following non-linear transformation is performed on each parameter:

$$\theta(j) = 0.5(\theta(j)_{sup} + \theta(j)_{inf} + (\theta(j)_{sup} - \theta(j)_{inf}) \tanh(\theta(j)^*))$$

with $\theta(j)$, the j^{th} parameter to identify, and $\theta^*(j) \in \mathfrak{R}$, the parameter which is actually determined by numerical optimization.

3.4. Initial Estimates

Let $\hat{\theta}_{init}$ denote the initial estimates of θ . This initial estimate is calculated from classical methods based on batch experiments. The RTM method gives the isotherm parameters (Guiochon *et al.*, 1994, pp. 297 - 298) and the mass transfer coefficients are determined from basic expressions of the height equivalent to a theoretical plate (Guiochon *et al.*, 1994, pp. 39 and 44). Both methods show a good compromise between accuracy and easiness (Grosfils and Levrie, 2004).

An upper bound of the error on $\hat{\theta}_{init}$, $\Delta\theta_{init}$, is needed in the study of the basin of attraction presented in section 5. As a large part of the error on the initial estimate is due to the assumptions of the classical methods (e.g. no diffusion and no mass transfer resistance), the following procedure has been used to determine such a bound. The above-mentioned methods have been applied to fictitious data generated with Eqs. (1-3) for 8 realistic sets of

parameter vectors θ_i^{ex} , $i = 1, \dots, 8$ (Grosfils and Levrie, 2004). Denoting the parameter estimate obtained for θ_i^{ex} by $\hat{\theta}_{\text{init},i}^{\text{ex}}$, a bound on the estimation error for each component of θ can be computed as $\Delta\theta_{\text{init}}^{\text{ex}}(j) = \max_{i=1,\dots,8} |\theta_{\text{init},i}^{\text{ex}}(j) - \theta_i^{\text{ex}}(j)|$.

4. IDENTIFIABILITY

The main questions are:

- Which measurements (i.e. detectors and experiment duration) are the most appropriate?
- Are the isotherm parameters identifiable from SMB experiments with fixed mass transfer coefficients?
- Are the mass transfer coefficients identifiable together with the isotherm parameters from SMB experiments?

To answer these questions, two approaches are considered: sensitivity analysis and identification from fictitious measurements generated from a model with known parameters.

Note that the parameter vectors as well as the operating conditions used in the following are described in details in (Grosfils, 2004).

4.1. Sensitivity analysis

(Point *et al.*, 1996; Vande Wouwer *et al.*, 2000)

The sensitivity of measurement y with respect to parameter $\theta(j)$ is defined as: $y_{\theta(j)} = \partial y(t) / \partial \theta(j)$. If the sensitivity is high, the measurement varies significantly when changes in $\theta(j)$ are effected. To determine if the parameters $\theta(j)$, with $j = 1, \dots, n$, are identifiable simultaneously from measurement y , the following matrix is built:

$$\begin{pmatrix} \frac{1}{\Gamma} \int_0^{\Gamma} y_{\theta(1)}(t)^2 dt & \dots & \frac{1}{\Gamma} \int_0^{\Gamma} y_{\theta(1)}(t) y_{\theta(p)}(t) dt \\ \dots & \dots & \dots \\ \frac{1}{\Gamma} \int_0^{\Gamma} y_{\theta(1)}(t) y_{\theta(p)}(t) dt & \dots & \frac{1}{\Gamma} \int_0^{\Gamma} y_{\theta(p)}(t)^2 dt \end{pmatrix}$$

where $[0, \Gamma]$ is the time span of interest.

It can be proven that if the determinant of this matrix, the Gram determinant, does not vanish or if its condition number is small, the sensitivities are independent (Luenberger, 1969, p. 56) and the parameters are identifiable simultaneously from measurement y .

The detector that will be selected to record data for identification will be the one that gives the largest Gram determinant or the smallest condition number. Hence, as the detectors in the circulating loop occupy successively 6 or 8 positions in the SMB process during a cycle, the sensitivities are calculated at these

positions for several realistic values of θ and for various operating conditions. The results indicate that the sensitivities are larger at the positions where a front can be observed (cf. Fig.2: positions 2, 3, 4, 5 and 6). Moreover, the sensitivities to the mass transfer coefficients are smaller than the sensitivities to the isotherm parameters.

Table 1 illustrates typical results obtained for one value of θ and specific operating conditions (similar results have been obtained for other sets of parameters and isotherms with the same saturation capacity or with different saturation capacities). This table gives the Gram determinant, D , and the condition number, c , respectively for the identification of the isotherm parameters and for the simultaneous identification of the isotherm parameters and mass transfer coefficients. In the latter case, the Gram determinant is smaller and the condition number is larger than for the identification of q_s and b_i only. This is due to the presence of smaller elements in the matrix, corresponding to the sensitivities to the mass transfer coefficients. Besides, the Gram determinant is larger or the condition number is smaller near the fronts (see Fig. 2 for the front positions). However the condition number and the Gram determinant are not always optimal at the same position. Moreover, the position of the maximum of D and of the minimum of c changes from one set of parameters and operating condition to another. Therefore, it is not possible to determine a unique optimal detector position. Hence, in the following, measurements from a detector in the circulating liquid stream will be used as it takes all the positions successively.

A study of the length of the data set to be considered for identification is also performed by computing D and c for different values of the time span Γ , again for a set of realistic values of θ and various operating conditions. No general conclusion can be drawn for the best choice of Γ , yet using the data from the start-up to steady-state offers a reasonable compromise. This approach is used in the sequel.

4.2. Identifiability study from fictitious measurements

The first step is the generation of fictitious measurements by simulation of model (1) with Eqs. (2-4), with a known parameter vector θ_f . The second step consists in estimating θ from these fictitious measurements with θ_f as initial estimate. If $\hat{\theta} = \theta_f$, the parameters are said structurally locally identifiable (Walter and Pronzato, 1997, p. 31). It means that, for almost any θ^* in the admitted parameter space, there exists a neighbourhood $V(\theta^*)$ such that,

$$\hat{\theta} \in V(\theta^*) \text{ and } y(t, \hat{\theta}) = y(t, \theta^*) \Rightarrow \hat{\theta} = \theta^*.$$

This method is applied for several realistic values of θ_f and for various operating conditions. In every case,

Table 1: Results of the sensitivity analysis for the identification of the isotherm parameters:

With $q_s = 13.6$, $b_1 = 0.3$, $b_2 = 0.695$; $C_1^{\text{feed}} = C_2^{\text{feed}} = 1.456$ vol%, $\Delta t = 150$ s, $L = 0.1191$ m, $S = 3.53e-4$ m², $Q_2 = 15.6$ ml/min, $Q_4 = 17.9$ ml/min, $Q_5 = 32.6$ ml/min, $Q_{\text{feed}} = 10.6$ ml/min, $\epsilon = 0.83$, $k_1 = 2.77$ s⁻¹, $k_2 = 1.58$ s⁻¹ at 40 ml/min, 8 columns where L is the column length, S , the cross-section area, Q_k , the fluid flow rate in zone k , Q_s , the solvent flow rate, Q_{feed} , the feed flow rate.

Identified	Time span (s)	position 1	position 2	position 3	position 4	position 5	position 6	position 7	position 8	
q_s, b_i	0 – 5000	D	1 ^e -21	1.26 ^e -9	4.7 ^e -10	5.2 ^e -10	6.3 ^e -8	5.6 ^e -8	0	0
		c	2.35 ^e 8	1.27 ^e 2	1.8 ^e 2	1.5 ^e 3	8.26 ^e 4	8.35 ^e 4	inf	Inf
k_i, q_s, b_i	0 – 5000	D	2 ^e -39	8.3 ^e -20	1.5 ^e -20	4.4 ^e -20	2.5 ^e -18	6.7 ^e -19	0	0
		c	5.9 ^e 8	7.26 ^e 3	2.4 ^e 3	4.77 ^e 3	6.2 ^e 6	8.81 ^e 7	-8.24 ^e 16	-8 ^e 15

$\hat{\theta} = \theta_f$ is obtained. Hence, in all these cases, the isotherm parameters alone as well as the isotherm parameters together with the mass transfer coefficients are structurally identifiable.

5. BASIN OF ATTRACTION

The basin of attraction of a minimizer is the set of all values of the initial estimates from which the optimization algorithm converges to this minimizer. As the cost function may have several minimizers, it is useful to verify if all the possible initial estimates are included into the same basin of attraction. Verification for all initial estimates cannot be achieved in practice. Yet the following procedure gives useful information from a practical point of view. The parameter identification is performed from fictitious measurements generated with Eqs. (1-4) and a known parameter vector θ_f . The initial estimates, θ_0 , are chosen at the vertices of a hypercube centered around the parameters $\hat{\theta}_{\text{init}}$. The edge length is chosen equal to at least $2\Delta\theta_{\text{init}}$ (cf. section 3.4.). Three situations are successively considered below: identification of the isotherm parameters assuming exact knowledge of the mass transfer coefficients, identification of the same parameters with incorrect mass transfer coefficients and simultaneous identification of the isotherm parameters and mass transfer coefficients. In each case, the mean, $\hat{\theta}_{\text{mean}}$, and the variance, $\text{var}(\hat{\theta})$, of the parameters $\hat{\theta}$ estimated from all the initial estimates, θ_0 , are calculated and the presence of local minima is analyzed. Indeed, when $(\hat{\theta}_{\text{mean}} - \theta_f)$ is small and $\text{var}(\hat{\theta})$ is small as well, all the initial values θ_0 can be considered to belong to the same basin of attraction. Note that similar results are obtained for isotherms with the same saturation capacity or with different saturation capacities.

5.1. Identification of the isotherm parameters

With “true” mass transfer coefficients

When the mass transfer coefficients are assumed to be known exactly, the variance of $\hat{\theta}$ is small and it can be concluded that for all the considered initial

estimates, the parameters converge to the same minimizer θ . Note that numerical oscillations may introduce local minima (due to numerical difficulties in resolving sharp spatial gradients) if the parameters of the numerical integration algorithm are not properly chosen.

With error on mass transfer coefficients

In this case, the mass transfer coefficients are not equal to the values used for the generation of the fictitious measurements. The magnitude of the error introduced is obtained from the upper bound on the initial estimate as described in section 3.4. Several local minima are observed.

5.2. Identification of the isotherm parameters and mass transfer coefficients

Several local minima are observed. However, the values of the cost function at the optimum are smaller than those achieved in the identification of the isotherm parameters with erroneous (fixed) mass transfer coefficients. The variances of the identified isotherm parameters are also smaller and the mean value of $\hat{\theta}$ are closer to θ . Moreover, for some values of θ and for some operating conditions, the number of local minima obtained for the different initializations of the optimization is also smaller.

5.3. Conclusions

In conclusion, despite the difference in the sensitivities of the measurements with respect to the isotherm parameters and with respect to the mass transfer coefficients, it is advisable to identify the mass transfer coefficients together with the isotherm parameters instead of working with fixed erroneous values of the mass transfer coefficients. As in practice the error on the initial estimates of the mass transfer coefficients is never equal to zero (cf. section 3.4), the simultaneous identification of the mass transfer coefficients and the isotherm parameters is always recommended in order to obtain more accurate parameters.

On the other hand, the parameters corresponding to local minima may lead to large errors in the SMB profiles and in the simulated purities. Even if the

profiles obtained with the operating conditions used for the identification are acceptable, large errors may appear in profiles calculated with other operating conditions. For example, the error in purity may increase by more than 10%. Hence, to find the smallest cost function as possible, a multi-start identification procedure, as the one used to study the basin of attraction, should be performed.

6. COVARIANCE MATRIX OF THE ESTIMATED PARAMETERS

Let $\hat{\theta}_N$ denote the value of the estimated parameters obtained by numerical optimization of the cost function (5). Under some assumptions (Seber and Wild, 1989), an estimate of the covariance of $\hat{\theta}_N$ is obtained from :

$$\hat{E}[\tilde{\theta}_N \tilde{\theta}_N^t] \approx \frac{J(\hat{\theta}_N)}{N-n} \left(\sum_{t=1}^N \frac{\partial y(t, \hat{\theta}_N)}{\partial \theta} \frac{\partial y(t, \hat{\theta}_N)}{\partial \theta}^t \right)^{-1} \quad (6)$$

with $\tilde{\theta}_N = \hat{\theta}_N - \theta$ and n , the number of parameters to estimate.

A typical covariance matrix obtained from the study of the basin of attraction for the parameter vector $\hat{\theta}_N = [\hat{q}_s \quad \hat{b}_1 \quad \hat{b}_2 \quad \hat{k}_1^{rel} \quad \hat{k}_2^{rel}]$ is given by (Grosfils, 2004):

$$\begin{pmatrix} 1.17e-8 & 2.46e-9 & 5.7e-9 & -2.8e-9 & 8.69e-7 \\ 2.46e-9 & 1.25e-9 & 1.48e-9 & 2.38e-9 & 2.29e-7 \\ 5.7e-9 & 1.48e-9 & 2.95e-9 & -8.77e-10 & 4.15e-7 \\ -2.8e-9 & 2.38e-9 & -8.77e-10 & 2.22e-6 & -5.05e-8 \\ 8.69e-7 & 2.29e-7 & 4.15e-7 & -5.05e-8 & 1.6e-4 \end{pmatrix}$$

It is observed that the correlation between the parameters is not negligible. Moreover, the variances of the mass transfer coefficients are larger than the variances of the isotherm parameters. This can be explained by the differences in the magnitude of the sensitivities. However, the variances are so small that the confidence interval at 99% of $\hat{\theta}_N(i)$ does not contain $\theta(i)$, $i=1, \dots, n$, which is the parameter used for the generation of the fictitious measurements. The explanation of this observation requires further investigation to check whether the assumptions behind (6) are fulfilled.

7. CONCLUSION

An identification procedure for determining the isotherm parameters as well as the mass transfer coefficients of a kinetic SMB model with competitive Langmuir isotherms from SMB experiments is proposed. The main contributions of this paper are a systematic identifiability study and the examination of the basin of attraction to determine the influence of local minima. Both studies allow to verify that the parameters are structurally identifiable, to select the appropriate measurements and to set up an identification procedure. In future work, other

isotherm equations should be considered and the procedure should be tested on experimental data.

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9. REFERENCES

- Altenhöner U., M. Meurer, J. Strube, H. Schmidt-Traub, 1997, Parameter estimation for the simulation of liquid chromatography, *Journal of Chromatography A*, 769, 59 – 69
- Dose EV, S. Jacobson, G. Guiochon, 1991, Determination of isotherms from chromatographic peak shapes, *Analytical Chemistry*, 63, 833 - 839
- Felinger A., A. Cavazzini, G. Guiochon, 2003, Numerical determination of the competitive isotherm of enantiomers, *Journal of Chromatography A*, 986, 207-225
- Grosfils V., C. Levrie, 2004, Rapport technique, Projet Movida, février 2004, ULB – FPMs
- Grosfils V., 2004, SMB processes model identification from SMB processes data, *Technical Report*, ULB
- Guiochon G., S. Golshan-Shirazi, A. M. Katti, 1994, *Fundamentals of Preparative and Nonlinear Chromatography*, Academic Press.
- Luenberger D. G., 1969, *Optimization by vector space methods*, John Wiley and sons, NY.
- Point N., A. Vande Wouwer and M. Remy, 1996, Practical Issues in distributed parameter estimation: gradient computation and optimal experiment design, *Control Engineering Practice*, vol. 4, 11, 1553 – 1562.
- Powell M.J.D., 2000, UOBYQA: unconstrained optimization by quadratic approximation, *Report DAMTP 2000/NA14*
- Seber G.A.F. and C. J. Wild, 1989, *Nonlinear regression*, John Wiley & Sons, New York
- Seidel-Morgenstern A., 2004, Experimental determination of single solute and competitive adsorption isotherms, *Journal of Chromatography A*, 1037, 255 - 272
- Toumi A., S. Engell, 2004, Optimization-based control of a reactive simulated moving bed process for glucose isomerization, *Chemical Engineering Science*, 59, 3777 – 3792
- Vande Wouwer A., N. Point, S. Porteman, M. Remy, 2000, An approach to the selection of optimal sensor locations in distributed parameter systems, *Journal of Process Control*, 10, 291 – 300
- Walter E. and L. Pronzato, 1997, *Identification of parametric models from experimental data*, Springer, London
- Zimmer G, G. Dünnebier and K.U. Klatt, On-line parameter estimation and process monitoring of simulated moving bed chromatographic separation processes, *Proceedings of the European Control Conference*, Karlsruhe, Germany, 1999