Model Calibration of Chromatographic Separation of Rare Earth Elements

Frida Ojala

Department of Chemical Engineering, Lund University

January 2010

Abstract

A calibration of models depicting separation of rare earth elements by ion-exchange chromatography has been conducted. The main calibration method was based on the preparative chromatograph simulator (PCS). An unexpected relation was found during the calibrations. Henry's constant and the maximum concentration of metal ions on the stationary phase were expected to be in direct variation, but appeared to have an exponential relation according to the simulations. An explanation to this phenomenon is that another model for describing the mobile phase should have been chosen. There may also be certain reversed phase effects to take into consideration in the calculations. Nevertheless, the calibrations have resulted in simulations that fit the current experiments very well. The values in the elaborated model are considered to be plausible, and are believed to be close to the real values.

Keywords: Calibration, Ion-exchange, Langmuir MPM, convective-dispersive model.

Introduction

The source of the rare earth elements are minerals consisting of oxides from several of the metals. As they do not appear individually, separation is essential to get clean components. The separation method studied here is ion-exchange chromatography. However, conducting enough experiments to be able to find the optimum separation conditions can be time consuming and expensive. This is where modelling and simulation enter the picture.

Calibrations are necessary to get an accurate model of the system. The calibrations done have been based on the preparative chromatograph simulator (PCS) developed by a group of PhD students lead by Professor Bernt Nilsson at the department of chemical engineering, Lund University. The focus in this report is separation of neodymium, samarium, europium and gadolinium.

Theory

The PCS was originally created to simulate separation of large peptides in ion-exchange columns. It is made up of models describing various fluid phenomena occurring in the chromatograph, such as dispersion, adsorption and desorption, but it also describes how to numerically solve the models including pre- and post processing of the data.

Adsorption Description

According to the Langmuir mobile phase modulator (MPM) model the concentration of each component on the surface of the stationary phase, q, changes per time unit, t, according to the following relation.

$$\frac{\partial q}{\partial t} = \left(H_{ref} \frac{\exp\left(\gamma(S/S_{ref})\right)}{(S/S_{ref})^{\nu}} c \cdot \left(1 - \sum_{j=1}^{n_{comp}} \frac{q_j}{q_{max}}\right) - q \right) k_{kin,ref} (S/S_{ref})^{\nu} \qquad (1)$$

S is the concentration of the acid, S_{ref} is the reference value for this concentration, γ describes the hydrophobicity of the stationary phase, ν is the number of sites that each ion will occupy and k_{kin} is a kinetic constant. n_{comp} is the number of components adsorbing on to the sites. Since the model describes an ion-exchange process, the hydrophobicity is set to zero. As all the elements have the same ionic charge it was assumed that they had the same value of ν. Henry's constant, H_{ref}, is a reference value describing how well the components are adsorbed to the surface at a certain pH. H_{ref} is proportional to q_{max} according to

$$H_{ref} = K_{eq} q_{max} \qquad (2)$$

The equilibrium constant, K_{eq}, is described by the following relation.

$$K_{eq} = \frac{k_{ads0}}{k_{des0}} \frac{\exp(-\gamma S_{ref})}{S_{ref}^v} \qquad (3)$$

k_{ads0} and k_{des0} are kinetic constants describing the adsorption and desorption.

q_{max} is the maximum concentration on the surface of the stationary phase. The value is proportional to the total concentration of binding sites, Λ, according to

$$q_{max} = \frac{\Lambda}{\sigma + v} \qquad (4)$$

where σ is the number of sites blocked by the ion. Since the components studied are small and without steric hindrance, σ was set to zero. As in the case of v, it was assumed throughout the calculations that because the elements all had the same charge, they had the same q_{max}. To get a relation between q_{max} for the different columns equation 5 was used. This is based on the equation deciding the retention time for gradient elution according to Perry and Green (1997, pp. 16-45).

$$V_r = V_{r,0} + \frac{1}{G}\left(GB \left(\frac{\Lambda}{z_{H_3O^+}}\right)^v (v+1) + \right.$$

$$\left. c_{H_3O^+,0}^{v+1} \right)^{\frac{1}{v+1}} - \frac{c_{H_3O^+,0}}{G} \qquad (5)$$

where V_r is the retention volume for the component, $V_{r,0}$ is the retention volume for the acid, G is the gradient slope, z is the charge of the hydronium ion, $c_{H_3O^+,0}$ is the initial concentration of the acid in the mobile phase and B is a lumped variable given by the following relation.

$$B = V_{col}(1 - \varepsilon_c)\varepsilon_p K_d K_{eq} \qquad (6)$$

V_{col} is the column volume, ε_c is the void in the column, ε_p is the porosity of the particle and K_d and K_{eq} is the exclusion and the equilibrium constant. The exclusion factor is set to 1 as it is believed that all of the ions can reach the entire pore. As can be seen in equation 5, B and Λ is not linearly independent. This means that the calculations cannot give a set value of Λ, but it can give a relation between the values for the three columns.

Mobile Phase
The convective-dispersive model used to describe the mobile phase is based on the assumption that the mass transfer resistance is not the decisive term. The concentration of each element in the mobile phase, c, changes per time unit according to

$$\frac{\partial c(z,t)}{\partial t} = D_{ax}\frac{\partial^2 c(z,t)}{\partial z^2} - v_{lin}\frac{\partial c(z,t)}{\partial z} + r_{ads} \qquad (7)$$

where z is the axial coordinate along the column and D_{ax} describes the axial dispersion. The linear velocity, v_{lin}, is calculated by

$$v_{lin} = \frac{F}{R^2 \cdot \pi} \frac{1}{\varepsilon_c + (1-\varepsilon_c)\varepsilon_p K_d} \qquad (8)$$

F is the flow rate and R is the column radius. The adsorption term is calculated by the following relation.

$$r_{ads} = -\frac{1-\varepsilon_c}{\varepsilon_c + (1-\varepsilon_c)\varepsilon_p K_d}\frac{\partial q(z,t)}{\partial t} \qquad (9)$$

Objective Function
When performing a calibration, it is important to make the right choice of objective function. To make all the experiments influence the minimisations to the same extent, the objective function was set to calculate the residual relative the total absorption for each experiment.

$$res = \left(\sum_{i=1}^{n_{exp}} \left(\frac{\sum_{j=1}^{n_{points}}|c_{exp,j} - c_{sim,j}|^2}{\sum_{k=1}^{n_{points}}|c_{exp,k}|^2} \right)_i \right)^{\frac{1}{2}} \qquad (10)$$

Here c_{sim} is the simulated concentration in the mobile phase and c_{exp} is the experimentally determined concentration.

Materials and method
The calculations in this thesis were based on the two steps used when conducting the experiments: injection and elution. A gradient elution had been used in order make the ions release from the stationary phase sooner. The gradient slope, the change of acid concentration per time unit, was varied in the experiments.

The stationary phase was assumed to consist of equally sized spheres with a diameter of 5 μm. It was made of silica gel, and the eluent was nitric acid. The ligand was di-(2-ethylhexyl) phosphoric acid (HDEHP), a specified functional group for separation of lanthanides. The amount of HDEHP per silica in the columns is just a hint of the real value as the preparation was made without assurance of the amount bound to the gel.

The acid concentration started at 0.007 M in all the experiments, and the elution time was 20 minutes. 50 μl was injected in each experiment, with a concentration of 500 ppm of component. The diameter of the columns was 4.6 mm. Data for the three columns used can be seen in Table 1.

Table 1. The columns differ in the percentage by weight of HDEHP per silica. The gradient slope was varied in the different experiments by changing the concentration in the end of the elution.

Column no.	HDEHP per Silica (wt-%)	End Acid Conc. (M)
1	2	0.75, 1.0
2	5	0.25, 0.5, 0.75, 1.0
3	10	0.25, 0.5, 0.75, 1.0

When evaluating the experimental data, it was soon discovered that the measured concentrations and thus the areas were inconsistent. In an ideal situation, a certain total concentration of a component corresponds to a certain area. This was not the case in the experimental data acquired. The problem was solved by calculating the areas for each component in the experiments individually. The areas were calculated using the trapezoidal method in MATLAB. The start and end point for each peak was estimated manually.

When solving differential equations ode15s was used, capable of solving stiff problems with fairly good accuracy. A three point central finite volume method was used in the simulations. The inlet boundary was set to be Dirichlet and the outlet was a homogenous Neumann condition.

Results and Discussion

To be able to set the values of q_{max} for the columns, overloaded experiments are necessary. At the moment all the executed experiments has been conducted in the area where the relation between c and q is close to linear. This makes it impossible to decide where q_{max} is located. Without knowing the maximum load capacity of the column the optimal operating point for the system cannot be found.

However, according to the experiments 125 mg (0.336 mmol) of ligand was added to column number two. Assuming that the entire amount of ligand added stayed on the stationary phase and that ε_p was 0.6 and ε_c is 0.4, Λ and q_{max} for column number two can be calculated. Using the ratio calculated with equation 5 and 6, the values for all three columns could be determined. The result is seen in Table 2

Table 2. Results from calculations on the total concentration of binding sites and maximal concentration of metal ions on the surface on the stationary phase.

Column no.	Λ (mol HDEHP/m^3 silica)	q_{max} (mol metal ions/m^3 silica)
1	330	140
2	370	160
3	1080	450

After this the experiments was used to set Henry's constant for the compounds. The result was very satisfying. Experimental and simulated values for column number two can be seen in Figure 1. The fit between experiments and simulations was very good. The values in the elaborated model are considered to be plausible, and are believed to give a good idea of in what order of magnitude the real values will be found. Henry's constant for the three columns is seen in Table 3.

Table 3. Henry's constant for Samarium, Europium and Gadolinium in the three first columns.

Column no.	Sm	Eu	Gd
1	0.35	0.51	0.67
2	0.56	0.84	1.1
3	20	34	47

The calibration gave a ν of 2.4 mol ligand per mol metal ion. The expected value was around 3 as the charge of the ions is +3. The result is therefore considered to be plausible.

H_{ref} was believed to be proportional to q_{max} according to equation 2 but when calculating the relation between Henry's constant for the three columns using the column number one as reference, the results show differently, see Table 4.

Table 4. Relation between q_{max} and H_{ref} for the components, using the value of column number one as reference.

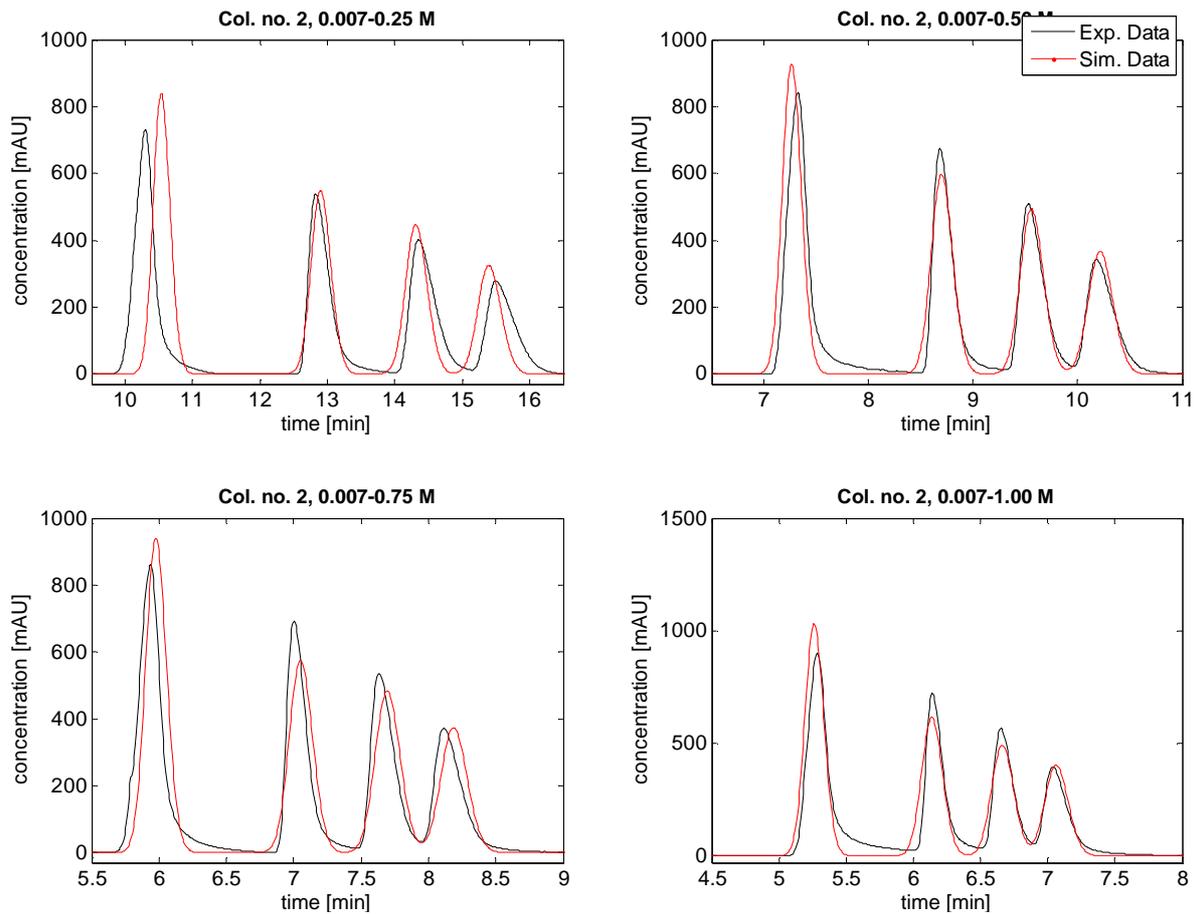| Column no.	Relative q_{max}	Relative H_{ref}
1	1	1
2	1.2	1.6
3	3.3	64

Figur 1. Comparison between experimental and simulated data for different gradient slopes on column number two. The four peaks are Nd, Sm, Eu and Gd.

It can be seen in that the difference between Henry's constants for the three components gets larger as the ligand concentration increases. It looks as though Henry's constant is changing exponentially instead of linearly. Three possible reasons for this are as follows:

1. The relation is linear. The results are only based on nine experiments and give inaccurate points.
2. The column has certain reversed phase effects, why the hydrophobicity should be included in equation 1.
3. Instead of the Langmuir mobile phase modulator, the steric mass actions model should have been used to explain the stationary phase. This model includes the interaction between the acid in the mobile phase and the stationary phase. Instead of equation 2, Henry's constant would be calculated according to

$$H_{ref} = K_{eq} \cdot q_{max}^{\nu} \qquad (11)$$

To find out if one of these theories is the correct one, or if the reason is found in some other explanation, more experiments has to be conducted. In these experiments, it would be recommended to use other columns with the same kind of particles, but with varying ligand concentrations. There is a big gap between the values from column number two and three. It would be interesting to get some more points in between these to get the true shape of the curve.

All the simulations made during this assignment have been based on very few experiments. This makes validation of the results difficult. Since it is hard to do experiments completely flawless, it is important to remember that small error in the experimental data can result in an invalid model unless a statistically sufficient amount of experiment is used. To produce a more reliable model, additional experiments have to be conducted and evaluated.

References

Perry, R. H., & Green, D. W. (1997). *Perry's Chemical Engineers' Handbook* (7 ed.). USA: McGraw-Hill.