



Multi-objective optimization of chromatographic rare earth element separation



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ARTICLE INFO

Article history:

Received 15 June 2015

Received in revised form 20 August 2015

Accepted 3 September 2015

Available online 7 September 2015

Keywords:

Rare earth elements

Chromatography

Multi-objective optimization

Pareto optimal surface

Parameter estimation

ABSTRACT

The importance of rare earth elements in modern technological industry grows, and as a result the interest for developing separation processes increases. This work is a part of developing chromatography as a rare earth element processing method. Process optimization is an important step in process development, and there are several competing objectives that need to be considered in a chromatographic separation process. Most studies are limited to evaluating the two competing objectives productivity and yield, and studies of scenarios with tri-objective optimizations are scarce. Tri-objective optimizations are much needed when evaluating the chromatographic separation of rare earth elements due to the importance of product pool concentration along with productivity and yield as process objectives. In this work, a multi-objective optimization strategy considering productivity, yield and pool concentration is proposed. This was carried out in the frame of a model based optimization study on a batch chromatography separation of the rare earth elements samarium, europium and gadolinium. The findings from the multi-objective optimization were used to provide with a general strategy for achieving desirable operation points, resulting in a productivity ranging between 0.61 and 0.75 kg Eu/m³ column³ h⁻¹ and a pool concentration between 0.52 and 0.79 kg Eu/m³, while maintaining a purity above 99% and never falling below an 80% yield for the main target component europium.

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1. Introduction

Rare earth elements (REE) are used in many modern technological industries [1–7], and their increasing importance has made them strategic commodities in many countries [4,6–8]. The elements are found in varying types of minerals at sites around the world [1–5,7,9], and before the REEs can be utilized for commercial applications they must be upgraded to adequate purity [1,3,4]. This is normally achieved through liquid–liquid extraction methods [1–4,7], but several studies have highlighted chromatography as an alternative with considerable benefits [1,5,10–16].

In order to investigate the performance of chromatography as a REE processing method, we have previously conducted a demanding preparative chromatographic batch separation of the middle REE group, samarium (Sm), europium (Eu) and gadolinium (Gd), with focus on optimizing productivity [11]. The experimental study indicated that a single objective optimization of productivity was not sufficient when considering a comprehensive purification strategy. Productivity is desirable for optimizing output, but yield also

needs to be considered for minimizing waste, and an optimal pool concentration is important for minimizing the downstream processing costs. Therefore, a multi-objective optimization (MOO) including productivity, yield and product pool concentration was needed for further investigation.

In order to proceed with this we decided to employ computer modeling, since it has proven to be a powerful and cost efficient tool for performance evaluation and optimization of chromatographic systems [10,13,14,17–21]. MOO studies of preparative chromatography normally investigate the two competing objectives productivity and yield, but tri-objective MOO studies are scarce.

A previous study [20] has presented a tri-objective MOO approach with soft objective metrics for purification of a ternary protein mix, where the focus was on the later eluting component. This makes the mix binary from an optimization point of view, since the first two components essentially can be lumped into one component. Our study differs from this as the middle eluting component, Eu, is heavily prioritized over the other eluents due to its high commercial value [2,7]. Targeting the intermediately eluting component will result in an effective separation of the neighbouring eluents from a processing point of view. However, it also has the implication of making the pooling cut-time

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optimization more complex, since the mix will be ternary from an optimization point of view.

The optimization problem of a chromatography system is normally cast in a bi-level framework [22]. The upper level incorporates the impact of the decision variables, such as load and elution gradient slope, that governs the chromatogram, and the lower level constitutes the pooling strategy that decides the cut-times for the product pooling. We are introducing an optimization strategy that keeps the optimization objective intact for all levels of the bi-level optimization problem. Further, the proposed MOO strategy incorporates firm objective values when evaluating the tri-objective optimization problem, and we provide with a general strategy for achieving desirable operation points for the studied system.

1.1. Scope of this study

The main focus of this study was to perform a tri-objective MOO of chromatographic REE separation with respect to productivity, yield and pool concentration. In this context, an experimentally validated process model was used to generate the process system response. This model was produced through parameter estimation of a previous experimental study [11]. The results from the MOO were used to formulate a general operation point strategy for the separation.

1.2. Outline of article

This work is divided into two parts. Part 1 includes process description, chromatographic modeling, parameter estimation and the resulting model. Part 2 includes the multi-objective optimization problem formulation, optimization method and results including a desirable operation point strategy.

2. Part 1: Chromatography model and parameter estimation

2.1. Process description

The chromatography model used in this study is based on a previous experimental study [11] with focus on providing operation conditions for maximum productivity when separating a mix of Sm, Eu and Gd through batch chromatography. In the study [11], an Agilent 1200 series HPLC system (Agilent Technologies, Waldbronn, Germany) was used together with a Kromasil M3 (Eka, Bohus, Sweden) column. The column dimensions were 150 mm × 4.6 mm, and the stationary phase consisted of spherical silica particles coated with C18, a diameter of 16 μm and a pore size of 100 Å. Bis(2-ethylhexyl) phosphoric acid (HDEHP) was used as ligand and each column had a HDEHP (Sigma–Aldrich, St. Louis, USA) concentration of 342 mM. Nitric acid was used as eluent, and the elution concentration gradient was varied between 6 and 13 vol% of 7 M acid over an elution gradient length of 5 column volumes. An inductively coupled plasma mass spectrometry (ICP-MS) system (Agilent Technologies, Tokyo, Japan) was used for in-line post column REE detection.

2.2. Chromatography model

A kinetic dispersive model [23] with a Langmuir mobile phase modulator isotherm [13,14,18,19] was used to describe the column separation. The model equations, defined in the spatial, $z \in [z_0, z_f]$, and temporal, $t \in [t_0, t_f]$, domains are:

$$\frac{\partial c_\alpha}{\partial t} = -\frac{\partial}{\partial z} \left(c_\alpha v_{\text{int}} - \mathcal{D}_{\text{app},\alpha} \frac{\partial c_\alpha}{\partial z} \right) - \frac{(1 - \varepsilon_c)}{\varepsilon_c + (1 - \varepsilon_c)\varepsilon_p} \frac{\partial q_\alpha}{\partial t}, \quad (1)$$

$$\frac{\partial q_\alpha}{\partial t} = k_{\text{kin},\alpha} \left(c_\alpha K_{\text{eq},\alpha} q_{\text{max},\alpha} \left[1 - \sum_{\gamma \in \{\text{Sm, Eu, Gd}\}} \frac{q_\gamma}{q_{\text{max},\gamma}} \right] - q_\alpha c_s^{1/\alpha} \right), \quad (2)$$

where c_α and q_α are the mobile and solid phase concentration of component $\alpha \in \{\text{Sm, Eu, Gd, S}\}$, v_{int} is the quotient of superficial velocity over total porosity, $\mathcal{D}_{\text{app},\alpha}$ the apparent dispersion coefficient, and ε_c and ε_p the column and particle void fractions. Here, c_s denotes the concentration of the modifier (i.e. nitric acid), $k_{\text{kin},\alpha}$ a parameter describing the kinetics, $K_{\text{eq},\alpha}$ the equilibrium constant regarding adsorption and desorption, v_α a parameter describing the ion-exchange characteristics, and $q_{\text{max},\alpha}$ the maximum concentration of adsorbed components. The model does not consider modifier ions on the solid phase, therefore Eq. (2) and its associated part in Eq. (1) are omitted (i.e. $\partial q_\alpha / \partial t \equiv 0$) when $\alpha = \text{S}$. Eq. (1) is complemented with Danckwert boundary conditions [24]:

$$c_\alpha(t, z_0) v_{\text{int}} - \mathcal{D}_{\text{app},\alpha} \frac{\partial c_\alpha}{\partial z}(t, z_0) = \begin{cases} c_{\text{load},\alpha} v_{\text{int}} \Pi(t, t_0, \Delta t_{\text{load}}) & \text{if } \alpha \in \{\text{Sm, Eu, Gd}\}, \\ c_{\text{mix},\text{S}} v_{\text{int}} & \text{if } \alpha = \text{S}, \end{cases} \quad (3)$$

$$\frac{\partial c_\alpha}{\partial z}(t, z_f) = 0, \quad \forall \alpha \in \{\text{Sm, Eu, Gd, S}\} \quad (4)$$

where $c_{\text{load},\alpha}$ is the injected load concentration, and $\Pi(t, t_0, \Delta t_{\text{load}}) \in \{0, 1\}$ a rectangular function in the temporal horizon $[t_0, \Delta t_{\text{load}}]$. The dynamics of the modifier concentration in the upstream mixing tank, $c_{\text{mix},\text{S}}$, are given by:

$$\frac{dc_{\text{mix},\text{S}}}{dt} = \frac{1}{\tau_{\text{mix}}} (u(t) - c_{\text{mix},\text{S}}), \quad (5)$$

$$u(t) = \begin{cases} u_0, & \text{if } t \leq \Delta t_{\text{load}} + \Delta t_{\text{wash}}, \\ u_0 + \Delta u(t - (\Delta t_{\text{load}} + \Delta t_{\text{wash}})), & \text{if } t > \Delta t_{\text{load}} + \Delta t_{\text{wash}}, \end{cases} \quad (6)$$

where τ_{mix} is the residence time, u is the elution gradient described by the initial value, u_0 , and the slope of the linear elution gradient, Δu , expressed as $\Delta u = \frac{u_f - u_0}{t_f - (\Delta t_{\text{load}} + \Delta t_{\text{wash}})}$.

In this study, the first-order spatial derivative in Eq. (1) was approximated using a method-of-lines and finite volume method with 100 grid points where $z_k = k\Delta z$ is the discretized spatial coordinate and $k \in [1 \dots 100]$. The first order derivative was approximated as a two-point backward difference, and the second-order derivative was approximated as a three-point central difference.

2.3. Parameter estimation

Model parameters were estimated through non-linear parameter estimation by means of the Levenberg–Marquardt algorithm through MATLAB's *lsqcurvefit* wrapper with forward finite differences to estimate the Jacobian. The algorithm minimizes the weighted sum of the deviations between the observed, \hat{c} , and predicted, c , system responses, expressed as:

$$\min. \sum_{j=1}^{N_j} [\hat{c}(\hat{t}_j, z_f) - c(\hat{t}_j, z_f, \mathbf{p}_j, \boldsymbol{\beta})]^T \mathbf{W}_j [\hat{c}(\hat{t}_j, z_f) - c(\hat{t}_j, z_f, \mathbf{p}_j, \boldsymbol{\beta})], \quad (7a)$$

$$\text{w.r.t. } \boldsymbol{\beta} \in \mathbb{R}^{N_\beta},$$

$$\text{s.t. } \dot{\mathbf{x}} = \mathbf{F}(t, \mathbf{x}(t), \mathbf{p}, \boldsymbol{\beta}), \quad \mathbf{x}(t_0) = \mathbf{x}_0, \quad (7b)$$

$$\boldsymbol{\beta}_L \leq \boldsymbol{\beta} \leq \boldsymbol{\beta}_U, \quad (7c)$$

where j indicates the experiment index, $\boldsymbol{\beta}$ is a vector containing the parameters $[q_{\text{max}}, K_{\text{eq},\alpha}]$ being estimated, $\mathbf{x} = (c_\alpha, q_\alpha, c_{\text{mix},\text{S}}, c_s)$,

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