# Experimental productivity rate optimization of rare earth element separation through preparative solid phase extraction chromatography

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## ABSTRACT

Separating individual rare earth elements from a complex mixture with several elements is difficult and this is emphasized for the middle elements: Samarium, Europium and Gadolinium. In this study we have accomplished an overloaded one-step separation of these rare earth elements through preparative ion-exchange high-performance liquid chromatography with an bis (2-ethylhexyl) phosphoric acid impregnated column and nitric acid as eluent. An inductively coupled plasma mass spectrometry unit was used for post column element detection. The main focus was to optimize the productivity rate, subject to a yield requirement of 80% and a purity requirement of 99% for each element, by varying the flow rate and batch load size. The optimal productivity rate in this study was 1.32 kg Samarium/(h m$^3_{column}$), 0.38 kg Europium/(h m$^3_{column}$) and 0.81 kg Gadolinium/(h m$^3_{column}$).

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## 1. Introduction

Rare earth elements (REE) are important components of many modern technological products [1]. They occur in many types of minerals. These minerals normally contain all REEs with varying concentrations of each [1,2]. The minerals are processed through extraction methods [2,3] and must be upgraded to high purity levels before being used for commercial purposes [2]. Separating individual REEs from a complex mixture with several elements is difficult [1,3,4], and achieving a high productivity rate for the separation process is problematic since large feed loads with high concentration results in difficulties with reaching sufficient purity levels.

The current industry standard is to employ liquid extraction methods due to their ability to handle large and highly concentrated feeds, and achieve purity levels above 90% [1–3]. Chromatography, as an alternative method, has the benefit of being able to achieve even higher purity levels. The expenditure of extractants is less demanding than for liquid extraction, and chromatography also offers possibilities of recovery and recycling of process media [2]. Furthermore, liquid extraction requires several process steps

whereas it is possible to reduce the separation to a single step through chromatography [2,5–7].

Since there are many apparent benefits for chromatography it would be of interest to determine if it is a commercially feasible separation method compared to liquid extraction. However, the details for either method are usually not disclosed in publication [2,3]. For this reason we have focused on finding the optimal chromatography operation point, in terms of productivity, for a REE separation case including the middle REEs: Samarium (Sm), Europium (Eu) and Gadolinium (Gd), which are particularly difficult to separate [4,8–10].

REE chromatography utilizes the differences in affinity elements have for a ligand to separate target elements from other elements [11,12]. The affinity will decide the order of elution, and the degree of separation between the elements can be controlled by adjusting the operating conditions. This includes changing mobile phase properties, such as media type and concentration, and column properties such as length, porosity and bead particle- and pore-size. The retention time of each element will also be decided by temperature, batch load size and composition, ligand concentration, flow rate and elution-gradient length [12,13].

Previous work has shown that bis (2-ethylhexyl) phosphoric acid (HDEHP) is a suitable extractant for liquid extraction of REEs [2,3]. HDEHP also makes it possible to separate all REEs in a single step since its affinity for a REE increases with atomic number. It has also been shown in analytical REE chromatography studies that

**Table 1**
Decision variables.

| Decision variable | Lower boundary | Upper boundary |
|---|---|---|
| Flow rate (ml/min) | 0.25 | 0.75 |
| Load (μl) | 150 | 220 |

HDEHP is a suitable ligand which enables separation with different mobile phases such as nitric acid [5,8,9,14,15], hydrochloric acid [8,15], and α-hydroxyisobuturic acid (α-HIBA) [16]. Recent work [5,6,17] has shown that it is possible to model both analytical and overloaded HPLC chromatography of REEs under demanding conditions with an acid involved. They have also highlighted the potential for chromatography as a large scale separation method through computer simulations. However, experimental studies of productivity optimization for overloaded HPLC chromatography with HDEHP as ligand and nitric acid as mobile phase has not been reported.

In this study we have experimentally shown that it is possible to accomplish a demanding and overloaded one-step separation of REEs through preparative ion-exchange high-performance liquid chromatography (IE-HPLC), and provided data regarding expected performance for chromatography as a REE processing method. This was done by focusing on finding the optimal operating point for a Monazite middle REE mixture containing Sm, Eu, Gd and impurities.

## 2. Theory

### 2.1. Optimization

When optimizing a process step it is necessary to define the objective function in order to clarify what the optimization target is. The objective function will depend on several variables that can be divided into two groups, the decision variables and fixed parameters. The decision variables comprise the conditions that are being altered during the optimization, and the fixed parameters are kept constant. Finally, some constraints are normally introduced to make sure that the optimization results remain within a feasible region [18].

#### 2.1.1. Objective function

The objective function is the productivity, $P$, of component $i$ as given in Eq. (1)

$$P_i = \frac{L_i Y_i}{t_c V_{col}} \tag{1}$$

where the load, $L$, is defined as the product of the feed concentration of component $i$ and the feed volume, $t_c$ is the total cycle time and $V_{col}$ is the total column volume.

The yield, $Y$, of component $i$ is defined in Eq. (2)

$$Y_i = \frac{c_{pool,i} V_{pool,i}}{L_i} \tag{2}$$

where $c_{pool,i}$ is the product pool concentration and $V_{pool,i}$ is the product pool volume of component $i$.

#### 2.1.2. Decision variables

The decision variables are presented in Table 1.

**Table 2**
Composition of the mixture used in the experiments.

| REE | Nd | Sm | Eu | Gd | Tb |
|---|---|---|---|---|---|
| %(wt) | 4.6 | 58.2 | 12.0 | 24.3 | 0.9 |

#### 2.1.3. Constraints

A purity above 99% was required since this is a common commercial purity grade [2], and it was decided that an 80% yield for each component was necessary to avoid excessive waste.

## 3. Materials and methods

An Agilent 1200 series HPLC system (Agilent Technologies, Waldbronn, Germany) was used together with two different columns, Kromasil M3 and Kromasil H4 (Eka, Bohus, Sweden). The columns were delivered as is with a stationary phase of spherical silica particles coated with C18, a diameter of 16 μm and a pore size of 100 Å. HDEHP was used as ligand due to its versatile ability to separate REE [2,3,14,16,19] and each column was filled with HDEHP (Sigma–Aldrich, St. Louis, USA) to a 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. The length of the elution gradient was set to 5 column volumes in order to avoid diluted product pool concentrations while still enabling sufficient separation. Each elution was followed by a regeneration step of 2.5 column volumes 7 M nitric acid and a equilibration step of 2.5 column volumes water. An inductively coupled plasma mass spectrometry (ICP-MS) system (Agilent Technologies, Tokyo, Japan) was used for in-line post column REE detection due to its documented capability for this purpose [1,14,20].

### 3.1. Experimental study

The REE composition in this study is an approximation of a REE mixture from a Monazite ore [21] that has been pre-treated to isolate the Sm, Eu and Gd (SEG) part [2]. Neodymium (Nd) and Terbium (Tb) were introduced to make sure that other REE impurities would not interfere with the objective of producing pure SEG pools. Nd and Tb are specifically suitable for this purpose since Nd precedes Sm and Tb follows Gd in terms of affinity for HDEHP. The experiment feed composition is given in Table 2. The mixture was dissolved in nitric acid to reach a lanthanide concentration of 32.56 g/l and a final pH level of 1.51. The two variables that were investigated were the flow rate and the batch load size. A smaller scale up trial of close to optimal operating point conditions was also conducted. A summary of the experimental conditions is given in Table 3.

## 4. Results and discussion

### 4.1. Optimal flow rate

The load was set to 180 μl and the flow rate was varied. Fig. 1 and Table 4 show how the production rate, yield and pool concentration of each component varied with an increased flow rate. It can be seen that the best yield was achieved for the lowest flow rate and that it worsened with increasing flow rate. We believe that this is due to

**Table 3**
Summary of the experimental conditions. Experiments 1–3 were used in the flow optimization study, experiments 2 and 4–6 were used in the load optimization study, and experiments 2, 5, 7 and 8 were used in the scale-up study.

| Experiment | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
|---|---|---|---|---|---|---|---|---|
| Flow rate (ml/min) | 0.25 | 0.50 | 0.75 | 0.50 | 0.50 | 0.50 | 0.835 | 0.835 |
| Load (μl) | 180 | 180 | 180 | 150 | 200 | 220 | 300 | 333 |
| Column volume (ml) | 2.49 | 2.49 | 2.49 | 2.49 | 2.49 | 2.49 | 4.15 | 4.15 |