



# SAMARIUM(III) REMOVAL BY LIQUID-LIQUID AND SOLID-PHASE EXTRACTION. KINETICS AND THERMODYNAMICS ASPECTS

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The liquid-liquid and liquid-solid extractions of samarium(III) from aqueous nitrate solution using D2EHPA (di-2-ethylhexyl phosphoric acid) and chelating resin "Chelex 100" as extractants is investigated to recover samarium(III) from aqueous solution. The effect of operating parameters, such as time, nitrate ion, aqueous phase acidity, concentration of the extractant, resin mass, ion strength, temperature on the samarium extraction and various acid solutions on the metal stripping from the loaded organic phase and resin are investigated. The synergistic effect showed that addition of D2EHPA to TOP (Tri-iso-octyl-phosphate) extraction was obtained for the volume ratio 4.5/0.5. The thermodynamic functions like free energy ( $\Delta G$ ), enthalpy ( $\Delta H$ ) and entropy ( $\Delta S$ ) of extraction mechanism are discussed. Solid phase extraction is found to be more suitable than the liquid-liquid extraction for samarium(III) recovery. By liquid-liquid extraction the removed quantity was 93.26 mg g<sup>-1</sup>; for the liquid-solid extraction by Chelex 100 resin the removed quantity was 19 mg g<sup>-1</sup>. The stripping efficiency was found to be quantitative in HNO<sub>3</sub> and HCl 1 M. The robustness of the procedure is demonstrated by the average recoveries obtained (>99.6 %) for samarium(III).

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this purpose, solvent extraction and solid phase extraction are the most popular and versatile techniques.<sup>3</sup>

This paper describes the extraction of samarium(III) by liquid-liquid and liquid-solid using D2EHPA (di(2-ethylhexyl)phosphoric acid) diluted with dichloromethane and resin Chelex 100 as extracting agent.

Solvent extraction is widely applied to processes of metal ions recovery, ranging from aqueous solutions in hydrometallurgical treatment to environmental applications. It is also considered a useful technique to increase the initial concentration of the solute, commonly used in the separation processes of analytical applications.<sup>4</sup> Di-2-ethylhexyl-phosphoric acid (D2EHPA) is extensively used as an extractant for the extraction of Sm(III) from aqueous solutions.<sup>2</sup> Other applications of this popular extractant include the removal of Zn(II)<sup>5</sup>, Mn(II)<sup>6</sup>, Fe(III).<sup>7</sup>

Chelex-100, used in this work, is a polystyrene divinylbenzene copolymer incorporating iminodiacetate chelating groups. The iminodiacetate groups coordinate metals by means of oxygen and nitrogen bonds and the resins have a particularly strong affinity for trace metals. Its use was first proposed for the preconcentration of total trace metals from seawater. Chelex-100 retains free metal ions and loosely bound trace metals.<sup>8</sup> It has been used in numerous studies for the binding of several metals including Cr (III), Ni (II), Cu (II), Zn(II), Tl (III) and La (III).<sup>9-14</sup>

The objective of this study is to investigate the best conditions for samarium(III) extraction by D2EHPA and Chelex 100 by varying diverse parameters as shaking time, the initial samarium(III) ion concentration, initial pH of aqueous solution, ion strength and the temperature. The extraction mechanism is also investigated and the processes of liquid-liquid extraction or liquid-solid Extraction are compared.

## Introduction

The recovery of heavy metals by removal from dilute aqueous system has required the development of new technique for their concentration and separation.<sup>1</sup> In recent years, rare earth elements (REE) have been regarded as vitally important components from an industrial point of view. The major reason for this is the high application of the REE in many fields as these elements and their compounds find various commercial applications. Samarium is primarily used in the production of samarium-cobalt permanent magnets, which are used in lightweight electronic equipments where the size or space is a limiting factor, and where function at high temperature is of a great concern. Stable samarium titanate compounds with useful dielectric properties are suitable for coatings and in capacitors of microwave frequencies. The specific applications of samarium in different fields of technology have turned samarium into an industrial material of outstanding significance.<sup>2</sup>

Intricately similar in their chemical properties, lanthanides pose an exigent problem in their separation. Therefore, separation of trivalent lanthanides is still a very important and serious problem. Among the different methods used for

## Materials and methods

### Chemicals and reagents

Samarium(III) nitrate hexahydrate is procured from Sigma (ALDRICH), Hydrochloric acid, used for adjusting pH of samarium(III) solutions, is from Stinnes chemicals, sodium thiosulfate (Sigma Aldrich). Tri-iso-octyl-phosphate (Alfa Aesar), tri-butyl-phosphate (Sigma Aldrich) and di (2-ethylhexyl) phosphate (Sigma Aldrich) were dissolved in dichloromethane (Sigma Aldrich) to achieve the required concentration. All other reagents such as buffer at pH = 4.0 (VWR Prolabo) and Arsenazo III (Alfa Caesar) were used for the analysis of the results by UV-Visible spectrometer (SPECORD 210 plus).

Chelex-100 (Bio-Rad Laboratories, CA, USA) is a chelating resin which uses ion exchange to bind transition metal ions. The resin is composed of polystyrene divinylbenzene copolymers containing paired iminodiacetate ions, which act as chelators for polyvalent metal ions (see Table 1).<sup>10</sup> This group can interact via its nitrogen and oxygen atoms with the samarium according a tridentate interaction.

**Table 1.** General description and some properties of resin

Type	Chelex 100
Ionic form	Na <sup>+</sup>
Functional group	Iminodiacetic acid
Matrix	Polystyrene-divinylbenzene
Structure	Macroporous
pH range	0–14
Bead size	0.3-1.0 mm
Capacity	0.4 mmol mL <sup>-1</sup>
Appearance	White, translucent

### Liquid-liquid and liquid-solid extractions and determination procedure for samarium(III)

General extraction and stripping experiments were carried out by contacting equal volumes (5 mL) of the aqueous (samarium(III) at 1 mmol L<sup>-1</sup>) and organic phases (D2EHPA at 2 mmol L<sup>-1</sup>) ( $V_{Aq}/V_{Org} = 1$ ) in reagent bottles. After equilibrium between two phases is established, the phases were separated by decantation.

The recovery of Sm(III) onto Chelex 100 resin was studied. An exactly weighted amount (0.1 g) of Chelex 100 in Na<sup>+</sup> form was mixed with 5 mL of (Sm(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O) solution at 1 mmol L<sup>-1</sup> initial concentration.

The removal of Sm(III) onto Chelex 100 resin in three different extractants D2EHPA, TBP and TOP was investigated as a function of contact time between 2 and 15 minutes at initial concentration of samarium(III) = 1 mmol L<sup>-1</sup>. The effect of solution pH on the equilibrium uptake of samarium(III) from aqueous solution by D2EHPA and Chelex 100 resin was investigated between initial pH 1.3 and 5.05. Dilute nitric acid was used to adjust the pH of samarium solutions using a pH meter (model WTW, pH 3310 SET 2).

Kinetic experiments were carried out by agitating 5 mL of samarium(III) solution of concentration ranging from 0.2 to 5.0 mmol L<sup>-1</sup> with 0.1 g of Chelex 100 resin and 5 mL of D2EHPA respectively in an Erlenmeyer flasks of 10 mL at 20 ± 1 °C, pH = 5.05 and at a constant agitation speed of 1000 rpm.

The effect of the ionic strength was studied with 5 mL of samarium(III) solution (1 mmol L<sup>-1</sup>) and varying concentration of sodium thiosulfate from 0.1 to 0.4 mol L<sup>-1</sup>. Under constant pH and constant concentrations of Chelex 100 resin and D2EHPA, samarium(III) extraction was enhanced by varying temperature in the range of 298–328 K. The concentration of Sm(III) in the aqueous phase was analyzed with a SPECORD 210 plus spectrophotometer using the method described in the literature.<sup>15</sup>

All procedures of the extraction liquid-liquid and liquid-solid were carried out at room temperature 298 K and stirring rate at 1000 rpm. In these experiments percentage extraction (%E) was determined as follows:

$$\%E = 100 \frac{C_0 - C}{C_0} \quad (1)$$

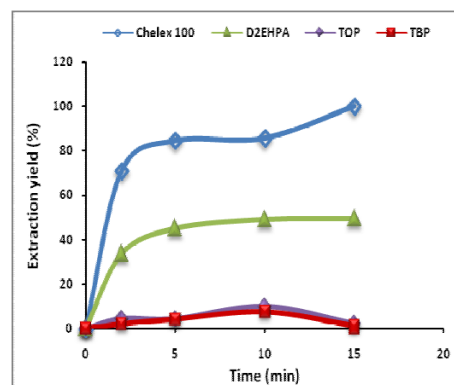
where  $C_0$  and  $C$  are the concentrations (mol L<sup>-1</sup>) of samarium ions before and after extraction, respectively.

## Results and discussion

### Effect of contact time

The kinetic of extraction that describes the solute uptake rate governing the residence time of the sorption reaction is one of the important characteristics that define the efficiency of sorption.

In order to establish equilibrium time for maximum uptake and to know the kinetics of extraction process; the sorption of Sm(III) for initial concentrations 1 mmol L<sup>-1</sup> by Chelex 100 resin in three different extractants D2EHPA, TBP and TOP is shown in Figure 1.



**Figure 1.** Effect of contact time on the ion exchange of Sm(III) using Chelex 100 resin, D2EHPA, TBP and TOP. Initial concentration of Sm(III) 1 mmol L<sup>-1</sup>,  $T = 20 \pm 1$  °C, stirring speed 1000 rpm and initial pH 5.05.

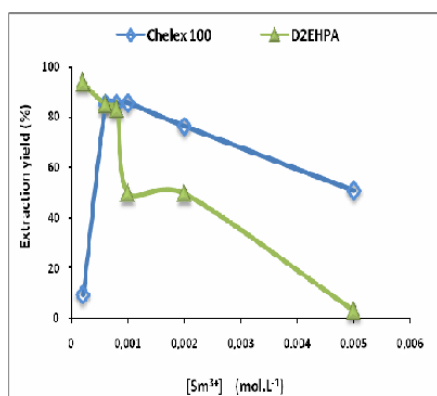
The results in Figure 1 suggest that the maximum extraction is achieved in Chelex 100. The curve suggests that the % extraction increases after 10 minutes reaching the highest value in 15 min. The next better extractant is D2EHPA. It is to be noted that in this case the maximum extraction is obtained in the first 10 minutes which rises slowly to reach the maximum in 15 min. The extraction in TOP and TBP is almost parallel reaching maximum at 10 min beyond which the extraction touches minimum at 15 min.

The amount of Sm(III) adsorbed onto Chelex 100 increased with increase in contact time, the maximum percentage of Sm(III) extraction was 85.67 % at 10 min for initial concentration of Sm(III) 1 mmol L<sup>-1</sup> which is used as a suitable contact time for samarium(III) adsorption. Thereafter, attained equilibrium at 15 min. This is apparent from the fact that the Chelex 100 has a large number of vacant surface sites available for adsorption during the stage of extraction of samarium(III).

Also, Fig. 1 shows the effect of time on the extraction of samarium(III) by D2EHPA, TBP and TOP. It is observed that 15 min is the maximum of sorption of samarium corresponding to 49.53 % was obtained by D2EHPA. However, the maximum percent Sm(III) extraction were 9.86 and 7.7 % obtained at 10 min by TOP and TBP respectively, Thereafter, becomes slower.

#### Effect of samarium concentration

Several experiments were made to study the effect of the initial samarium concentration on its percent removal. The initial Sm(III) concentrations tested were 0.2, 0.6, 0.8, 1, 2 and 5 mmol L<sup>-1</sup> at an amount of adsorbent of 0.1 g of Chelex 100 and at an initial D2EHPA concentration 2 mmol L<sup>-1</sup>.



**Figure 2.** Effect of initial concentration of Sm(III) sorption using Chelex 100 resin and D2EHPA.  $T = 20 \pm 1^\circ\text{C}$ , stirring speed 1000 rpm and initial pH 5.05, contact time 10 min for Chelex 100 and 15 min for D2EHPA.

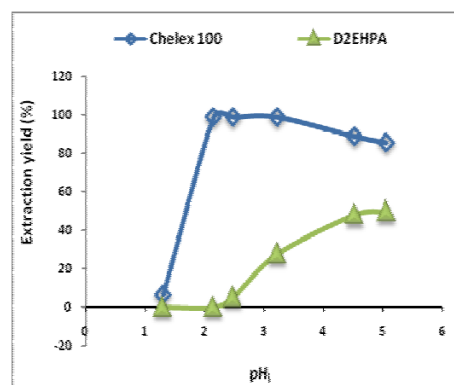
The results shown in Fig. 2 indicate that the removal of the samarium(III) is optimum at the low concentration beyond which the % removal diminishes continuously and it becomes almost zero in case of D2EHPA at 0.005 M samarium (III). removal is initial samarium concentration dependent and the necessary initial samarium concentration

to reach quantitative sorption is in the range of 0.6 to 1 mmol L<sup>-1</sup> and at 0.2 mmol L<sup>-1</sup> for removal of samarium by Chelex 100 resin and D2EHPA, respectively.

#### Effect of initial pH

In the adsorption the solution pH plays an important role for controlling the high sorption capacity and selectivity of the target lanthanide ions.<sup>16-18</sup> This is partly because hydrogen ions themselves compete strongly with adsorbents.<sup>19</sup>

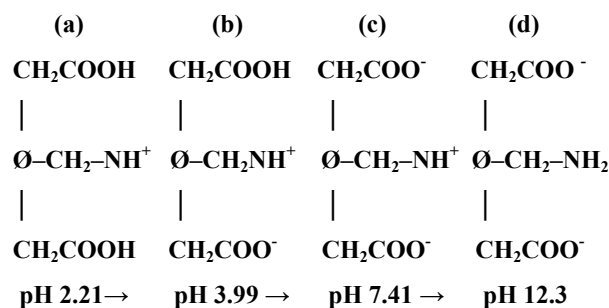
To determine the optimum pH for the adsorption of Sm(III) ions onto Chelex 100 resin and D2EHPA, the percentage removal of Sm(III) ion as a function of hydrogen ion concentration was examined at an initial concentration of samarium = 1 mmol L<sup>-1</sup>.



**Figure 3.** Effect of initial pH for efficient extraction of samarium ion by Chelex 100 resin and D2EHPA.  $T = 20 \pm 1^\circ\text{C}$ , stirring speed 1000 rpm, contact time 10 min for Chelex 100 and 15 min for D2EHPA.

The results shown in Figure 3 suggests that the sorption is strongly pH-dependent. For Chelex 100 the equilibrium sorption capacity is minimum at pH 1.3 (6.35 %) and increases with the pH reaching the maximum value between pH 2.15-3.22 (99 %). It then decrease thereafter. The corresponding sorption in D2EHPA, however, continuously increased with increasing pH acquiring a maximum value around pH 5.

The nature of the functional groups of the resin at different pH are shown in Figure 4. The functional groups shown under (a) predominate at pH<sub>i</sub> between pH 2.15- 3.22.

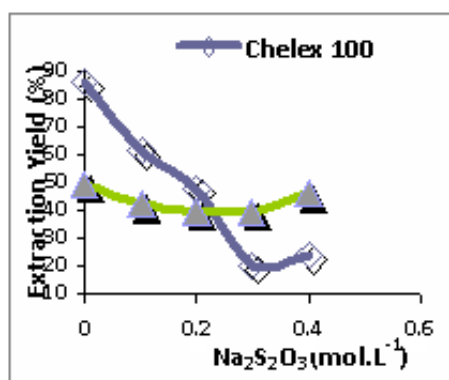


**Figure 4.** Different forms of the resin Chelex 100 depending on the pH.

The sorption capacity of D2EHPA to remove Sm(III) is lowest at lower pH conditions because hydrogen ions occupy most of sites on the surface of D2EHPA. However, with increasing pH of the solution, the competition by hydrogen ions is weakened because of the low hydrogen ion concentration and therefore Sm(III) ions occupy the sites more easily that results in the higher rate of removal of Sm(III) ions. The optimum pH for the maximum percentage (49.5 %) removal of Sm(III) in presence of D2EHPA is found to be pH 5.05.

### Effect of ionic strength

The effect of ionic strength on samarium(III) sorption was studied by stirring Chelex 100 resin and D2EHPA with increasing  $\text{Na}_2\text{S}_2\text{O}_3$  concentration in the aqueous solutions from 0.1 to 0.5  $\text{mol L}^{-1}$ .



**Figure 5.** Effect of  $\text{Na}_2\text{S}_2\text{O}_3$  concentration on the extraction yield. Initial concentration of samarium(III) 1  $\text{mmol L}^{-1}$ ,  $T = 20 \pm 1^\circ\text{C}$ , stirring speed 1000 rpm, initial pH = 5.05, contact time 10 min and 15 min for Chelex 100 and D2EHPA[RNM1] respectively.

Results, summarized in Fig. 5, show that the sorption of samarium by Chelex 100 is greatly influenced by the ionic strength whereas the ionic strength does not appreciably influence the sorption in the presence of D2EHPA. It is evident in Fig. 5, that there is a negative and null impact on increasing of extraction yield of Sm(III) by Chelex 100 and D2EHPA at concentration of  $\text{Na}_2\text{S}_2\text{O}_3$  from 0.1 to 0.5  $\text{mol L}^{-1}$ , respectively.

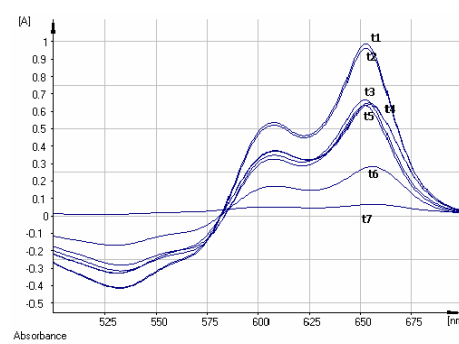
### Elution

Desorption of adsorbed samarium ions from Chelex 100 was evaluated by distilled water,  $\text{HNO}_3$  and HCl acid treatment. 5 mL of  $\text{HNO}_3$  and HCl solution at (0.5 – 1 – 2 M) concentrations were added at 0.1g of saturated resin on Samarium(III) respectively; the mixture was stirred for 1 h. After this time, the two phases were separated, then the samarium(III) present in the aqueous phase was determined by UV-Visible.

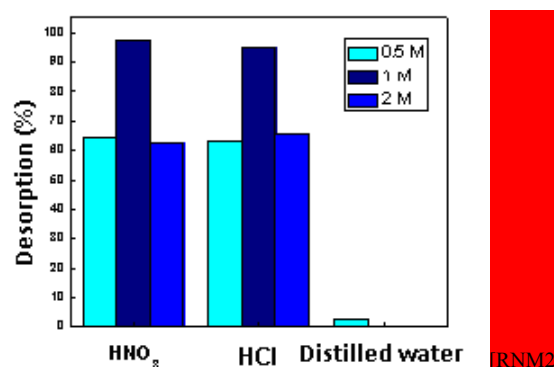
The extraction yield of elution was determined by the equation:

$$\text{Yield}(\%) = 100 \frac{\text{absorption of the aq. phase after elution}}{\text{absorption of the initial treated solution}} \quad (2)$$

Good regeneration properties of the adsorbent and reversibility of the adsorption process was obtained (Fig. 6). From these results it can be concluded that the Chelex 100 can be used repeatedly for the removal of samarium ions from aqueous solution.



**Figure 6.** Evolution of the absorbance on the desorption of Sm(III) at different time ( $t_1=5$  min,  $t_2=10$  min,  $t_3=15$  min,  $t_4=20$  min,  $t_5=30$  min,  $t_6=45$  min and  $t_7=60$  min).



**Figure 7.** Effect of the eluent concentration on the desorption;  $V=5$  mL ;  $t = 60$  min ;  $m = 0.1$  g.

The Fig. 7 shows that a solution of HCl or  $\text{HNO}_3$  (1.0 M) is sufficient for the elution of more than 95 % of Sm(III) retained on the Chelex 100 resin. The ratio between the aqueous volume (acid solution) and the mass of the saturated resin is taken equal to 50  $\text{g mL}^{-1}$ ; and that the desorption of the  $\text{Sm}^{3+}$  ions was insignificant (2.5 %) during the use of the distilled water without acid.

### Thermodynamic studies

Thermodynamic parameters, such as the Gibbs energy ( $\Delta G^\circ$ ), enthalpy ( $\Delta H^\circ$ ), and entropy ( $\Delta S^\circ$ ) changes are determined by using the following equations:

$$K_d = \frac{q_e}{C_e} \quad (3)$$

where

$q_e$  ( $\text{mg g}^{-1}$ ) was the adsorption capacity at equilibrium time and

$C_e$  was the concentration capacity at equilibrium time.

**Table 2.** Gibbs free energy, enthalpy and entropy changes for Sm(III) sorption on Chelex 100 and D2EHPA.

Resin	$\Delta H^\circ$ kJ mol <sup>-1</sup>	$\Delta S^\circ$ J K <sup>-1</sup> ·mol <sup>-1</sup>	$\Delta G^\circ$ (kJ mol <sup>-1</sup> )			
			313 K	318 K	323 K	328 K
Chelex 100	-40.6	-106.17	-7.37	-6.84	-6.31	-5.78
D2EHPA	-15.0	-52.2	+1.07	+1.33	+1.6	+2.12

$$\Delta G^\circ = -RT \ln K_d \quad (4)$$

$$\ln K_d = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (5)$$

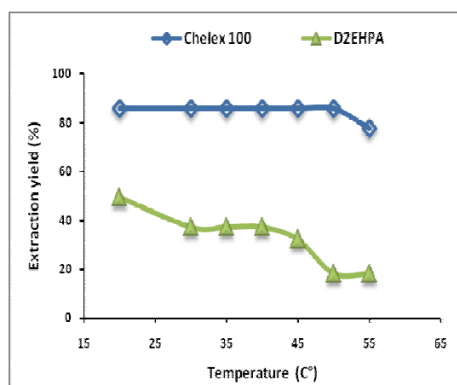
where

$R$  (8.3145 Jmol<sup>-1</sup> K<sup>-1</sup>) is the ideal gas constant,

$T$  (K) is the absolute temperature and

$K_d$  is the thermodynamic equilibrium constant.

The values of changes of enthalpy ( $\Delta H^\circ$ ) and entropy ( $\Delta S^\circ$ ) are calculated from the slopes and intercepts of the plot of  $\ln K_d$  vs.  $1/T$  by using Eq. (5).<sup>2</sup>



**Figure 8.** Effect of temperature on extraction of samarium(III). Initial concentration of samarium(III) 1 mmol L<sup>-1</sup>,  $T = 20 \pm 1^\circ\text{C}$ , stirring time 1000 rpm, initial pH=5.05, contact time 10 min for Chelex 100 and 15 min for D2EHPA.

The relative parameters and correlation coefficient calculated from Eqs. 2–4 are listed in Table 2. The negative  $\Delta G^\circ$  values show that, the sorption of ions of samarium by Chelex 100 occurs spontaneously in 298–328 K, while it is not spontaneous in case of D2EHPA system as indicated by the positive sign of  $\Delta G^\circ$ .

The enthalpy of the sorption,  $\Delta H^\circ$ , is a measure of the energy barrier that must be overcome by reacting molecules.<sup>16</sup> The value of  $\Delta H^\circ$  for sorption of Sm<sup>3+</sup> by Chelex 100 and D2EHPA is negative, indicating that the extraction procedure of samarium is exothermic in nature. The negative value of entropy for two extractants indicates the formation of a stable complex which makes the extraction system more ordered resulting in the decrease of entropy value.

## Conclusions

Sorption of samarium(III) by the Chelex 100 resin and D2EHPA were performed. The methods were optimized using various parameters such as contact time, the initial samarium(III) ion concentration, initial pH of aqueous solution, ion strength and the temperature.

The maximum sorption of samarium(III) by Chelex 100 took place in the initial pH 2.15 to 3.22 and the initial concentration of metal 1 mmol L<sup>-1</sup> with a equilibrium time equal to 10 min.

D2EHPA is shown to be a good and stable extractant. It is more selective for recovery of Sm<sup>3+</sup> from aqueous media. It should be noted that at pH 5.05, maximum extraction efficiency is obtained with 2 mmol L<sup>-1</sup> D2EHPA in kerosene at initial concentration of Sm<sup>3+</sup> 1 mmol L<sup>-1</sup>. D2EHPA extracts Sm<sup>3+</sup> very rapidly. Equilibrium was reached within 15 min.

Thermodynamic functions of extraction reaction were calculated and discussed. The reaction of extracting samarium(III) was found to be spontaneous by Chelex 100 resin and not spontaneous by D2EHPA extractant.

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