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Separation of Gadolinium(III) from Terbium(III) by the Liquid-Liquid Extraction Method with Dibutyldithiophosphate as the Extractant

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Abstract

The purpose of this research is to separate gadolinium(III) from terbium(III), by the liquid-liquid extraction method, with the extractant dibutyl dithiophosphate. Gadolinium(III) and terbium(III) have been selected in this study to see if the two metallic ions still could be separated although they have only one difference in atomic number, and in fact, terbium ($_{65}$Tb) is the next to gadolinium($_{64}$Gd), in the lanthanide series. Also besides, the two metals have been found together in the same mineral such as gadolinite, and in some other minerals in Indonesia. Extraction parameters have been firstly selected and extraction conditions have been optimized as well, using the experimental design of Plackett Burman. Thus, experiments have been done to select which of the nine parameters (i.e. Gd(III) and Tb(III) concentrations, the concentration of the extractant (dibutyl dithiophosphate), pH, volume ratio of aqueous phase to the organic phase, extraction temperature, shaking rate, shaking time, resting time (after shaking), have their significant effect on the extraction efficiency and separation. The data resulted from this study show that there were five of the nine factors studied that determine the extraction efficiency and separation. They were (with its respective optimum value in the bracket): Gadolinium concentration [Gd(III)](5 ppm), terbium concentration [Tb(III)](5 ppm), pH(3.0), shaking time (10 minutes), and rest time after shaking (10 minutes)..

Keywords: gadolinium, terbium, dibutyl dithiophosphate, liquid-liquid extraction, experimental design, Plackett Burman

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1 Introduction

Rare-earth elements are ideal elements for their use in high technology. They have been used in several modern technologies such as permanent magnets, hybrid batteries, catalysts, generators, telephone, computers, televisions, and optic fibers [1]. It has also been reported by the same authors that (REEs) have also been used in data transmission, touch screens, and high-resolution imaging equipment/ instruments, making modern life easier. Other uses of rare-earth elements are in missile systems, light but strong alloys, wave tubes, and in energy industries, batteries, nuclear fuel, or its additive.

Based on the quantitative data on the REEs total distribution in the world, released by USG S, CSRE, and Roskill for the year 2010, the first rank is taken by Brazil (32.32%), followed by China (22.12%), CIS (11.68%), Vietnam (9.1%), Australia (8.25%), and America (7.25%) [2]. It has been reported also that Indonesia, although is not on the list, has a significant source of REEs. In fact, minerals containing these elements (associated with tin minerals) stretch from Karimun (Riau) in the north to Bangka and Pulau Belitung islands in the south, that is what is called "The Tin Belt". REEs are found mainly in zircon, monazite, and xenotime minerals [3].

REEs have similar physical and chemical properties, making them not easy to separate from one another. Separation and purification among REEs in the same group (Light-, Middle-, and Heavy REEs), are even relatively more difficult because of the very similar physical and chemical properties, which in turn due to the very small difference of atomic number or electron configuration. But many studies have been done to separate the elements in the middle group of REEs, using the common method of separation, i.e. the liquid-liquid extraction method with D2EHPA, which is considered to be the best extractant, so far [4].

The use of D2EHPA has been studied for the separation of Sm(III), Gd (III) ,and Dy(III) by extraction method [5], and for the separation of Gd (III) and Sm(III) [6], [7]. In the case of Gd (III) and Sm(III) separation, it has been shown that the two ionic metals could separated at pH 3.0 with a factor of α for Gd /Sm = 3.65; αSm / Gd = 0.27; % ESM = 49% and % EGd = 87.1%.

The extractant D2EHPA has been also studied as its mixture with other extractants to improve the separation by their synergic effect. Thus, Morais & Ciminelli [8] studied the separation of Eu from Gd by liquid-liquid extraction, using a mixture of D2EHPA and HEH (EHP) . They reported a better separation factor of αEu / Gd (1.48). In 2009, Fontana & Pietrelli [9] reported their work on the separation of using the liquid-liquid extraction with a mixture of 2 Ethylhexyl phosphonic and mono-2-ethyl hexyl-ester acids as extractants. Miranda & Zinner [10] also reported results of their research work on extraction using a settler mixer with the same mixture of ligands D2EHPA and mono-2-Ethylhexyl ester for the separation of Sm(III) and Gd(III).

Different techniques and methods, or their combination with the extraction method have been used to separate the middle group of REEs. Thus, Rabie, Sayed, Lasheen, & Salama [11] separated europium from the other Middle REEs using a reduction-precipitation process, in which Eu(IV) was reduced to Eu(III) and then deposited as $Eu(SO_4)_4$. The separation of Eu(III) from Sm(III), Eu(III), and Gd(III) has also been studied by electrochemical reduction and liquid-liquid extraction. Takahashi, Abdel-Tawab, Nii, Yajima, & Kawaizumi [12], [13] reported separation of Sm and Gd by extraction using 5 and 2 stages mixer settlers.

This study is aimed at the separation of Gd(III) from Tb(III) by the method of liquid-liquid extraction using the extractant dibutyldithiophosphate (DBDTP). Parameters playing important role in the separation of Gd(III) from Tb(III) have been selected. The efficiency and effectiveness of the separation of Gd(III) from Tb(III) using the selected parameters based on the Plackett Burman design have also been determined roved that the Gd(III) can be separated from the Tb(III) with a separation factor (α) is determined in response.

2 Materials and Methods

2.1 Materials

The main chemicals used in this study consisted of: Gadolinium oxide (Gd_2O_3), CAS 12064-62-9, MW 362,50 [Sigma Aldrich]; terbium oxide (Tb_2O_3), CAS 12036-41-8, MW 365.85 [Sigma Aldrich]; n-butanol, No. 1.01990.1000; MW 74.12 [E. Merck]; *n*-hexane, ACS 1.04367.2500, MR 86.18 [E. Merck]; metanol, ACS ISO Reag. Ph; Eu 1.06009.2500, MW 32.04; P_2S_5 for synthesis 8.21024.1000, MW 222.28, Assay 27.8 – 28.8%;

2.2 Apparatus

The main apparatus used in this study consisted of general glass apparatus, pH meter, rotary evaporator Buchi R-210, UV-Vis spectrophotometer, JENWAY 6705, ICP-OES Agilent Technologies 700 Series, an oven, and a hot plate with stirrer.

2.3 Selection and optimization of the parameters for the Gd(III) and Tb(III) separation.

Selection and optimization of the separation to determine the parameters having main effects on the separation of Gd(III) and Tb(III) by the method of liquid-liquid extraction using the extractant dibutyldithiophosphate (DBDTP), were done by using the Plackett Burman experimental design. As a rule, the number of experiments in this study was made to be 4 N, with N = 1, 2, 3, 4, . etc., where N is a multiple of 4 but not a power of 2. Thus, the number of experiments was 12, and the number of parameters was 9 (4N-1). As shown in Table 1, there are nine parameters consisting of: pH, [Gd(III)], [Tb(III)], [extractant], volume ratio of aqueus phase to organic phase, temperature, stirring rate, stirring time, and rest time.

The addition of dummy experimens (2 dummies) to the experiments was intended to meet the Plackett-Burman requirements, which were 11 parameters (4N-1) for 12 experiments (4N). Furthermore, for the 9 parameters used in the Plackett-Burman experimental design, it is necessary to determine the upper (+1) and lower (-1) limits. This is shown in Table 2.

Table 1 Selected parameters for optimum extraction conditions in the separation of Gd(III) from Tb(III)

Run	Parameter	Unit	Min(-)	Max (+)
X1	Shaking Time	min	10.0	30.0
X2	Shaking Rate	rpm	150.0	250.0
X3	pH		3.0	4.0
X4	Rest.Time	min	10.0	15.0
X5	Organic phase: aqueous phase		1.0	2.0
X6	[Extractant]	%	0.1	0.2
X7	[Tb]	ppm	5.0	10.0
X8	[Gd]	ppm	25.0	50.0
X9	Temperature	°C	28.0	40.0
D1				
D2				

Note: D = Dummy

Table 2 The upper limit (+1) and the lower limits(-1) for the 9 parameters used, in Plackett-Burman experimental design.

No.	X1	X2	X3	X4	X5	X6	X7	X8	X9	D1	D2	R(α)
1	1	1	-1	1	1	1	-1	-1	-1	1	-1	
2	1	-1	1	1	-1	1	1	1	-1	-1	-1	
3	-1	-1	1	-1	1	1	-1	1	1	1	-1	
4	1	-1	-1	-1	1	-1	1	1	-1	1	1	
5	-1	1	-1	1	1	-1	1	1	1	-1	-1	
6	-1	1	1	1	-1	-1	-1	1	-1	1	1	
7	-1	-1	-1	1	-1	1	1	-1	1	1	1	
8	1	1	-1	-1	-1	1	-1	1	1	-1	1	
9	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1	
10	1	1	1	-1	-1	-1	1	-1	1	1	-1	
11	1	-1	1	1	1	-1	-1	-1	1	-1	1	
12	-1	1	1	-1	1	1	1	-1	-1	-1	1	

The selected nine variables were expected to have major influences or effects on the separation factor (α), and were determined in this reseach works. The variables introduced into the experimental design of Plackett Burman, without coding for the 12 experiments carried out in this study are shown in Table 3.

Table 3. Plackett Burman Design consisting of 9 factors and 2 dummies, for 12 experiments.

No.	X1	X2	X3	X4	X5	X6	X7	X8	X9	D1	D2	R(α)
1	30	250	3	15	2	0.2	20	25	5	1	-1	
2	30	150	4	15	1	0.2	40	50	5	-1	-1	
3	10	150	4	10	2	0.2	20	50	10	1	-1	
4	30	150	3	10	2	0.1	40	50	5	1	1	
5	10	250	3	15	2	0.1	40	50	10	-1	-1	
6	10	250	4	15	1	0.1	20	50	5	1	1	
7	10	150	3	15	1	0.2	40	25	10	1	1	
8	30	250	3	10	1	0.2	20	50	10	-1	1	
9	10	150	3	10	1	0.1	20	25	5	-1	-1	
10	30	250	4	10	1	0.1	40	25	10	1	-1	
11	30	150	4	15	2	0.1	20	25	10	-1	1	
12	30	250	4	10	2	0.2	40	25	5	-1	1	

2.4 Experimental Design

Plackett Burman design was made and is shown in Table 1. The factors of the parameters which were expected to give their response to the separation factor (α), are shown in Table 3, in which the upper (+1) and lower (-1) limits requirements for the Plackett Burman design (Table 2), are given. The parameters for the optimum separation conditions of Gd(III) from Tb(III) were obtained from the data from the experimental design of Plackett Burman and then processed. The coefficient of the response function was obtained by using the multiple linear equations 1.

$$Y=\beta_0+\beta_1X_1+\beta_2X_2+\beta_3X_3+\beta_4X_4+\beta_5X_5+\beta_6X_6+\beta_7X_7+\beta_8X_8+\beta_9X_9+\beta_{10}X_{10}+\beta_{11}X_{12}$$

(Equation 1)

Where Y: is the response.
Xi: factors affecting the response.
β: Intercept.

3 Results and Discussion

3.1 Separation of Gd(III) from Tb(III)

As has mentioned before, in this study, the separation of Gd(III) from Tb(III) by liquid-liquid extraction has been carried out by using the Plackett Burman experimental design. The effects of the selected 9 parameters on the separation factor of Gd(III) from Tb(III) were determined. The results of the determination are shown in Table 4.

3.2 Plackett Burman Design

The Plackett Burman design is a first-order design that serves to select the influencing factors. The data were processed and the coefficient of the response function was obtained using the multiple linear equations because it has more than one independent variable to predict the desired response, namely the separation factor (a) with and without the maximum coding. The separation factors are shown in Table 5.

Table 4 Experimental data resulted from liquid-liquid extraction for Gd(III) separation from Tb(III).

Experiment Number	[Gd] (ppm) org. phase	[Gd] (ppm) aques phase	Kd_{Gd}	[Tb] (ppm) org. phase	[Tb] (ppm) aques phase	Kd_{Tb}	Separation Factor (α)
1	7.58	25	2.30	0.19	2	9.53	0.24
2	4.10	50	11.20	0.09	2	21.22	0.53
3	2.81	50	16.79	0.05	4	79.00	0.21
4	23.12	50	1.16	0.72	2	1.78	0.65
5	29.43	50	0.70	0.82	4	3.88	0.18
6	21.38	50	1.34	0.58	2	2.45	0.55
7	16.24	25	0.54	0.44	4	8.09	0.07
8	30.37	50	0.65	0.74	4	4.41	0.15
9	19.85	25	0.26	0.61	2	2.28	0.11
10	11.30	25	1.21	0.33	4	11.12	0.11
11	21.29	25	0.17	0.65	4	5.15	0.03
12	24.28	25	0.03	0.70	2	1.86	0.02

Table 5 Parameter for optimal condition separation factor (α) with coding level

Experiment number	X1	X2	X-3	X4	X5	X6	X7	X8	X9	D1	D2	R(α)
1	1	1	1	1	1	1	-1	-1	-1	-1	-1	0.24
2	1	-1	1	1	1	-1	1	1	-1	-1	-1	0.53
3	-1	-1	1	-1	1	1	-1	1	1	1	-1	0.21
4	1	-1	-1	-1	1	-1	1	1	-1	1	1	0.65
5	-1	1	-1	1	1	-1	1	1	1	-1	-1	0.18
6	-1	1	1	1	-1	-1	-1	1	-1	1	1	0.55
7	-1	-1	-1	1	-1	1	1	-1	1	1	1	0.07
8	1	1	-1	-1	-1	1	-1	1	1	-1	1	0.15
9	1-	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1	0.11
10	1	1	1	-1	-1	-1	1	-1	1	1	-1	0.11
11	1	-1	1	1	1	-1	-1	-1	1	-1	-1	0.03
12	-1	1	-1	1	1	1	1	-1	-1	-1	1	0.02

$$Y = 0{,}2375 + \mathbf{0{,}0475X_1} - 0{,}0292X_2 + \mathbf{0{,}0042X_3} + \mathbf{0{,}0292X_4} - 0{,}0158X_5 - 0{,}0342X_6 + \mathbf{0{,}0225X_7} + \mathbf{0{,}1428X_8} - 0{,}1125X_9$$

(Equation 2)

The expected response in this study is to produce a maximum separation factor (a) while the other responses are minimum, so the mathematical equation was applied for the response to the separation factor (a). The mathematical equation for the response to the separation factor (a) has been made? be determined from Plackett Burman's design or manually, as equation 2.

In equation 2, the factors selected and give a positive effect are X1 (stirring time), X3 (pH of separation), X4 (rest time), X7 [Tb(III)] ,and X8 [Gd(III)].

Apart from being based on the above equation, it can also be seen that the factor selection using an expert design program where each variable is analyzed by ANOVA, one by one. The ANOVA model used can be selected according to what is suggested by the program, namely the model that has the highest desirability function (df) or close to number 1 where DF is the optimization value that shows the program's ability to fulfill the desires based on the criteria set in the final result. Besides that, it also resulted in ANOVA significance value and non-significance on the lack of fit. The results of ANOVA analysis and the regression coefficient are shown in Table 6 and Table 7.

Table 6 Results of Plackett Burman's ANOVA analysis with the response to the separation factor (α).

Source	SS	df	MS	F	P	Notes
Model	0.43	5	0.885	5.79	0.0271	Significant
X1	0.027	1	0.27	1.83	0.02246	
X3	0.00021	1	0.00021	0.0014	0.09094	
X4	0.010	1	0.010	0.69	0.4377	
X7	0.15	1	0.15	10.28	0.0185	
X8	0.24	1	0.24	16.11	0.0070	
Residu	0.089	6	0.015			
Core Total	0.52	11				

Notes: SS (Sum of Square), df (degree of freedom), MS (Mean Square), F (F test value), P (significance value).

Table 7 Plackett Burman regression coefficient with separation factor response (α)

Source	Expected Coefficient
Intercept	0.24
X1	0.047
X3	0.0042
X4	0.0029
X7	0.14
X8	0.11
Standard Deviation	0.12
C.V.%	51.18
R2	0.8282
Adj-R2	0.6850
Pre-R2	0.3128
Precission degree	7.097

While the results of the Plackett Burman design selection obtained 20 alternative formulas for the recommended conditions for Gd(III) separation parameters from Tb(III), as shown in Table 8.

The table of the results of the Plackett Burman design (Table 8) explains that the parameter conditions in the first formula give the highest DF value or close to the number 1 (1.000). Thus, so that the parameter conditions in formula number 1 are chosen to then be optimized using the Central Composite Design. The parameter conditions in the experiment suggest that the selected factors are X1, X3, X4, X7 ,and X8, because other factors do not affect the optimization results, this is consistent with the results of calculations based on multiple linear mathematical equations. The parameter conditions in the experiment without coding were obtained: X1 (Shaking time = 10 minutes), X3 (pH = 3), X4 (Rest time = 10 minutes)), X7 ([Gd] = 5 ppm) and X8 ([Tb] = 5 ppm).

Table 8 Alternative Formula for Separation Parameters Gd(III) from Tb(III).

Number	X_1	X_2	X_3	X_4	X_5	X_6	X_7	X_8	X_9	R_1	DF	
1	10.00	150.00	3.00	10.00	1.00	0.10	5.00	25.00	28.00	0.128	1.000	Selected
2	10.00	180.96	3.00	10.00	1.97	0.19	5.00	25.00	35.65	0.128	1.000	
3	10.01	151.83	3.00	10.00	1.00	0.11	5.00	25.00	35.82	0.128	1.000	
4	10.00	188.76	3.00	10.00	1.93	0.19	5.01	25.01	38.62	0.128	1.000	
5	10.00	238.45	3.00	10.01	1.84	0.11	5.00	25.00	31.54	0.128	1.000	
6	10.00	231.73	3.00	10.00	1.68	0.10	5.00	25.05	30.19	0.128	1.000	
7	10.00	159.22	3.00	10.00	1.66	0.11	5.01	25.00	32.17	0.129	1.000	
8	10.02	240.86	3.00	10.01	1.22	0.11	5.02	25.00	33.94	0.128	0,999	
9	10.00	173.18	3.00	10.00	1.22	0.10	5.04	25.00	32.13	0.127	0.998	
10	10.00	219.41	3.00	10.05	2.00	0.14	5.00	25.00	38.64	0.129	0.998	
11	10.01	202.03	3.00	10.06	1.15	0.13	5.00	25.00	38.12	0.129	0.998	
12	10.00	163.02	3.00	10.00	1.69	0.20	5.00	25.45	36.24	0.133	0.996	
13	10.00	218.17	3.02	10.02	1.83	0.12	5.00	25.00	40.00	0.129	0.995	
14	10.00	180.43	3.00	10.00	1.36	0.20	5.00	25.74	34.98	0.127	0.994	
15	10.00	195.08	3.01	10.00	1.51	0.20	5.00	25.83	39.62	0.137	0.992	
16	10.16	159.98	3.03	10.00	2.00	0.18	5.04	25.03	38.63	0.138	0.991	
17	10.87	249.99	3.00	10.00	1.17	0.19	5.00	25.00	37.67	0.132	0.991	
18	10.00	249.93	3.00	10.06	1.21	0.13	5.00	25.04	39.78	0.141	0.989	
19	10.00	151.99	3.00	10.00	1.36	0.13	5.27	25.00	30.71	0.116	0.989	
20	10.03	181.73	3.00	10.30	1.03	0.20	5.00	25.06	35.73	0.132	0.987	

4 Conclusions

Gadolinium(III) could be separated from terbium(III) by the liquid-liquid extraction method, with the extractant dibutyl dithiophosphate, with extraction parameters selected and optimized using the Plackett Burman experimental design. The parameters determining significant effects on the separation of the two metallic ions (with their respective figure give in the bracket) were found to be: pH of the extracted solution (3.0), the concentration of gadolinium(III) (5.0 ppm), the concentration of terbium(III) (5.0 ppm), shaking time (10 minutes), and rest time after shaking (10 minutes).

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6 Conflicts of Interest

The authors declare no conflict of interest.

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