An experimental design approach for determination of rare earth elements as a complex with DTPA ligand by voltammetry method

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Abstract. A study related to fast and simultaneously method for detection of rare earth elements (REEs) is still challenging. The combination methods of voltammetric and experimental design are suggested to not only provide simple sample preparation and swift analysis time but also concurrently and low detection limit. In the present work, Samarium (Sm), Dysprosium (Dy) and Europium (Eu) were chosen as a sample of REE. Those metals were analyzed as a complex form with Diethylenetriamine Pentaacetic Acid ligand (DTPA). A Plackett-Burman experimental design was conducted to determine the important factors which were optimized by Box-Behnken. An optimum 5 factors, from total 11 factors, have the potential to be the main effect which are: the electrolyte solution NH_4Cl 0.10 M, the pH at 5.15, the scan rate of 0.05 V/s, the DTPA ligand concentration 267.67 mg/L and the pulse amplitude of 0.5489 V. Each REE and it`s mixture were analyzed under optimum condition. The detection limit for Sm, Dy and Eu were found as 27.44 mg/L, 27.63 mg/L, and 27.89 mg/L, respectively. The accuracy and recovery value for Sm = 96,80% and 97.88%; for Dy = 98,24% and 93.40%; and for Eu = 94,28% and 99.27%, respectively.

Keywords: rare earth elements, differential pulse voltammetry, experimental design, DTPA.

1 Introduction

Rare earth elements (REEs) which include the lanthanides, can be divided into two groups: the light rare earth elements (LREEs) which have lower atomic weight elements, lanthanum to europium, and the heavy rare earth elements (HREEs) which are gadolinium to lutetium and yttrium [1], [2]. Most REEs possess similar atomic radii and oxidation states. REEs are found in a wide range of mineral types, including halides, carbonates, oxides, phosphates and silicates. The abundance of REEs within Earth's crust varies widely across individual REEs, ranging from the most abundant at 66ppm of cerium (exceeding other important metals including copper −27ppm and lead −11ppm) to 0.28 ppm for thulium [3]–[5]. REE are rarely used in various industrial fields such as the nuclear industry, steel metallurgy, electronics, optics, superconductors, magnets, TV colour tubes and others. REE are very useful for the development of new materials and are commercial materials with high economic value [6]-[8].

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Minerals that contain REE in Indonesia are found in alluvial gold and tin mining activities which have the potential as a by-product. Tin resources are found in the territory of Indonesia starting from the Karimun Islands, Singkep to Bangka Belitung which contributes greatly to the fulfilment of domestic metal needs. Current world rare earth element production is around 80,000 tons with the main products bastnaesite and monazite [9]-[12].

The concentration of rare earth in monazite is usually determined using Inductively Coupled Plasma-Mass Spectrometry (ICP-MS), or Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES). The use of these instruments is sophisticated such as analyze many elements quickly and has a high sensitivity, but the performance of weak instruments is rarely due to the complexity of the emission spectrum and a number of interference from major elements. separation of matrices by cation exchange is usually needed [13]. This is one of the problems that not yet be solved in the analysis by ICP due to the molecular mass of each REE is close together [14].

Electrochemical techniques such as voltammetry can be used to determine rare earth metals because they have high detection limits and allow simultaneous determination. In addition, using this technique does not need to be separated or concentrated [15]-[17]. Currently, the application of graphite pencil as working electrode become popular because it is easy to obtain, inexpensive, can conduct electric current, is not toxic and has a wide potential range [18]-[21].

In the voltammetric analysis method, there are many factors that might have a significant impact on the response, interactions between factors also affect the response. Factors that really influence the analysis need to be selected and optimized for value. If you do one by one measurement to test each factor and each interaction between factors will be expensive and time-consuming. A method that is able to examine a large number of factors with a small number of measurements is the experimental design [22]-[25]

In this study, the experimental design was used for factor selection and looked for optimum conditions voltammetrically for the determination of the content of each REEs: Sm, Dy, Eu and its mixture through the formation of complexes with DTPA ligands. The addition of DTPA ligands is expected to produce a distinguished peak current for each element. DTPA ligands can form stable complexes with Gd forming Gd-DTPA which is used as contrast agents so that in this study, DTPA ligands were added to form complexes with Sm, Dy and Eu which are REEs such as Gd.

2 Materials and Methods

2.1 Chemicals and apparatus

The chemicals used in this study were used as received without further purification. Diethylenetriamine pentaacetic acid ligand (DTPA), Samarium (III), Dysprosium (III) and Europium (III) purchased from Sigma Aldrich, $K_3[Fe(CN)_6]$ and NH_4Cl purchased from Merck.

The apparatus was used in this study included various graphite pencil electrodes (Faber Castell 2B, Faber Castell HB, Pentel 2B and Pilot Eno 2B), Ag/AgCl as a reference electrodes, Pt wire as a counter electrodes, digital analytical balance and pH meter AL 204 (Mettler Toledo), ICP-OES 275 series (Agilent technologies), Metrohm® potentiostat μAutolab and analyzed by NOVA 7.0.0, and Design Expert 10.0.1 software.

2.2 Preparation of rare earth element stock solutions (Sm(III), Dy(III) and Eu(III))

A solid of 5.7369 g Dy(III), 1.3483 g Eu(III), and 4.9625 g Sm(III) were separately put into 50 mL beaker, then added 65% HNO_3 dropwise until submerged and stirred with a magnetic stirrer until homogeneous. The solution then dissolved using aquamilli-Q to obtain a concentration of Dy 10000 mg/L, Eu 2328 mg/L and Sm 30000 mg/L. The actual concentration is measured by ICP-OES.

2.3 Selection of graphite pencil electrodes

A 10 mM of $K_3[Fe(CN)_6]$ solution was put into voltammetry cells then the oxidation voltammetric currents were measured using Faber Castell 2B, Faber Castell HB, Pentel 2B and Eno 2B Pilot as a working electrode, Ag/AgCl as reference electrodes and Pt wire as counter electrodes.

2.4 Plackett Burman's experimental design

Sm solution was analyzed by the Plackett-Burman experimental design method with total of 12 times measurements. About 11 factors were tested which are deposition potential (-1.0 and -1.5 V), deposition time (80 and 40 s), stirring (yes or no), pretreatment (yes or no), supporting electrolytes (NH_4Cl 0.1 M and H_2O), DTPA ligand concentration (392.41 and 261.61 mg/L), potential range (-1.5 to +1.5 V and -1.0 to +1.0 V), scan rates (0.05 and 0.01 V/s), pulse amplitude (0.10 and 0.05 V) and pH (7 and 5). The total of 12 measurements times was performed using differential pulse voltammetry as shown in Table 1.

2.5 Box-Behnken's experimental design

The Selected factors of Plackett-Burman's design, which are supporting electrolytes, potential range, scan rate, ligand concentration, pH and pulse amplitude, were processed using the Design-Expert program along with the highest level (+) and lowest (-) then measured 41 times with the highest level (+), middle (0) and lowest (-).

2.6 Analysis of each rare earth element (Sm, Dy, Eu)

A 3 mL of Sm, Dy and Eu (with a concentration of 5, 10, 15, 20 and 25 mg/L) were added into 4 mL electrolyte solution in voltammetry cells then measured using the DPV method with condition: 60 s deposition time, pulse amplitude 0.5489 V, scan rate 0.05 V/s, DTPA ligand 267.67 mg/L, supporting electrolyte 0.1 M NH_4Cl, pH 5.15.

2.7 Analysis of mexed rare earth element

About 3 mL of Each mixture of 1 (contain Sm, Dy and Eu with a concentration of 25 mg/L) and a mixture of 2 (contain Sm 25 mg/L, Dy 0.34 mg/L and Eu 16.05 mg/L) was added into 4 mL electrolyte solution in voltammetry cells then measured using DPV with deposition conditions 60 s, pulse amplitude 0.5489 V, scan rate 0.05 V/s, DTPA ligand 267.67 mg/L, electrolyte supporting NH_4Cl 0, 1 M, pH 5.15, potential deposition -3.4477 V, and the potential range of the deposition potential up to +1.25 V.

2.8 Determination of Recovery

A solution of Sm 25 mg/L, Dy 20 mg/L and Eu 15 mg/L were analyzed by DPV with conditions of pulse amplitude 0.5489 V, scan rate 0.05 V/s, electrolyte supporting NH_4Cl 0.1 M, DTPA ligand 267,.7 mg/L, pH 5.15, deposition time 60 s, potential deposition -1.25 V (Sm); -3,4535 V (Dy); -1,2091 V (Eu), the potential range of deposition potential applications up to +1.25 V.

Table 1. A 12 times measurement conditions according to Plackett-Burman experimental design

Run	$\mathbf{X_1}$	$\mathbf{X_2}$	$\mathbf{X_3}$	$\mathbf{X_4}$	$\mathbf{X_5}$	$\mathbf{X_6}$	$\mathbf{X_7}$	$\mathbf{X_8}$	$\mathbf{X_9}$	$\mathbf{X_{10}}$	$\mathbf{X_{11}}$
1	+	+	-	+	+	+	-	-	-	+	-
2	-	+	+	-	+	+	+	-	-	-	+
3	+	-	+	+	-	+	+	+	-	-	-
4	-	+	-	+	+	-	+	+	+	-	-
5	-	-	+	-	+	+	-	+	+	+	-
6	-	-	-	+	-	+	+	-	+	+	+
7	+	-	-	-	+	-	+	+	-	+	+
8	+	+	-	-	-	+	-	+	+	-	+
9	+	+	+	-	-	-	+	-	+	+	-
10	-	+	+	+	-	-	-	+	-	+	+
11	+	-	+	+	+	-	-	-	+	-	+
12	-	-	-	-	-	-	-	-	-	-	-

Information:
X_1 = Potential deposition
X_2 = Deposition time
X_3 = Pretreatment
X_4 = Stirring
X_5 = Supporting electrolyte
X_6 = Range potential
X_7 = Scan rate
X_8 = Ligand concentration
X_9 = pH
X_{10} = Pulse Amplitudo
X_{11} = Dummy

3 Results And Discussion

3.1 Selection of pencil graphite electrodes

The ability of a graphite pencil electrodes as a good working electrode is determined by testing their oxidation-reducing activities from a solution of $K_3 [Fe(CN)_6]$. The pencil graphite electrodes that we tested are taken from the several famous pencil companies included Faber Castell 2B, Faber Castell HB, Pentel 2B and Pilot Eno 2B. The higher peak current proves that the optimum electron transfer occurs between electroactive species $[Fe(CN)_6]^{3-}$ and the working electrode. The voltammogram results can be seen in Figure 1.

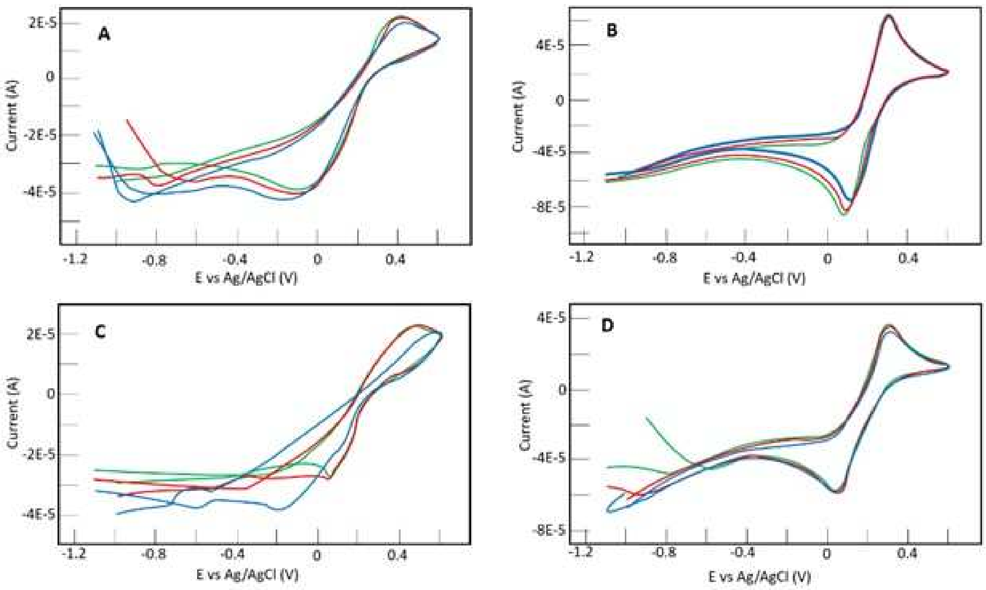

Figure 1. Cyclic voltammogram A) Faber Castell 2B; B) Faber Castell HB; C) Pentel 2B; D) Pilot Eno 2B in a 10 mM $K_3[Fe(CN)_6]$ solution with a scan rate of 0.05 V/s and a potential range of -1.10 to +0.60 V.

As shown in figure 1, the graphite pencil Faber Castell HB has the highest peak oxidation-reduction, so it was chosen as the working electrode in the study.

3.2 The selected factor from the result of Plackett-Burman's experimental design

In this study, we focus on the Plackett-Burman (PB) experimental design as a method of for determining the main influences on the voltammetry for detection of rare earth elements. At the first stage, Samarium (Sm) was chosen for analyzed by PB because the standard reduction potential is -1.77 V Vs Ag/AgCl, which is not too negative as Dysprosium (Dy) (-2.82 V) or not too positive like Europium (-0.57 V) [26]. Reduction potential Sm also is in the potential range which can be detected by graphite pencil electrodes.

Factors that may have a significant effect as the main influence on differential pulse voltammetry (DPV) analysis were selected. The overall factors and levels can be seen in Table 2. The selection of these factors is based on the condition of analysis that will be carried out in this study. The current, as a function of potential, is influenced by scan rate and diffusion coefficient where the analyte deposition on the electrode can occur due to diffusion, migration (difference in charge) and convection (stirring). The electrode is given a negative potential so that the positive species will move towards the electrode because there is a difference in charge. Supporting electrolytes can help those species to move so it is necessary to optimize the supporting electrolytes. In this study, NH_4Cl and H_2O supporting electrolyte were chosen because it does not produce the peak current as shown in Figure 2 so that it can be used as a background flow.

In this study, DTPA ligands were chosen because they can form stable complexes with lanthanide metal such as Sm. The mole ratio used of metal: ligand = 1: 2 (261.61 mg/L) and 1: 3 (392.41 mg/L). The higher mole ratio for ligands can help all Sm(III) to forms a stable complex with a ligand because the whole Sm binds to the ligand [27]. The Optimization of pH was carried out because the pH conditions affect the formation of complexes with metals. The selection of deposition potential in accordance with the Nernst equation where electrochemical analysis of the number of electrons affects the reduction potential, while the amplitude of pulses affects the resolution and sensitivity of measurements according to the modified Cottrel equation [15].

Table 2. Factors that have the potential as a major influence in the analysis of Sm-DTPA using differential pulse voltammetry.

No	Factor	Highest (+)	Lowest (-)
X_1	Deposition Potential	-1.00 V	-1.50 V
X_2	Deposition time	80 s	40 s
X_3	Pretreatment	Yes	No
X_4	Stirring	Yes	No
X_5	Supporting electrolytes	NH_4Cl	H_2O
X_6	Range potential	-1.5 to +1.5 V	-1.0 to +1.0 V
X_7	Scan rate	0.05 V/s	0.01 V/s
X_8	Ligand concentration	392.41 mg/L	261.61 mg/L
X_9	pH	7	5
X_{10}	Pulse amplitude	100 mV	50 mV
X_{11}	Dummy	-	-

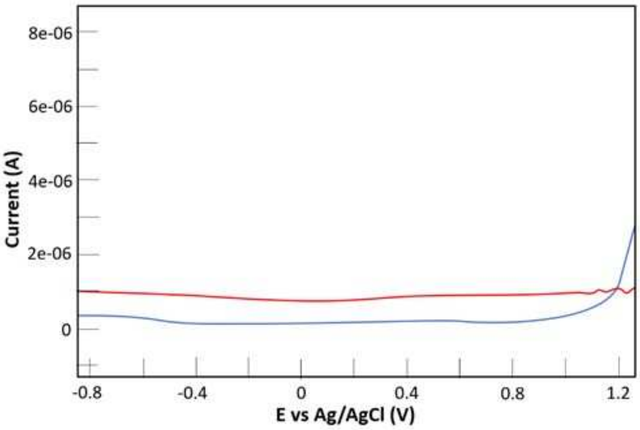

Figure 2. Voltogram of NH_4Cl (blue) and H_2O (red) supporting electrolyte solutions using DPV with potential deposition condition -1.0 V; potential range -1.0 to 1.5 V; scan rate 0.025 V / s; deposition time 60 s.

After 11 factors were selected, measurements were taken of the solution of Sm(III) 50 mg/L as much as *k* (s-1) +1 according to PB experimental design or 11 (2-1) = 12 runs using differential pulse voltammetry with conditions each measurement is in accordance with Table 3.

Table 3. Measurement Result according to Plackett-Burman's design

Run	**X_1**	**X_2**	**X_3**	**X_4**	**X_5**	**X_6**	**X_7**	**X_8**	**X_9**	**X_{10}**	**X_{11}**	**Respon (10^{-5} A)**
1	+	+	-	+	+	+	-	-	-	+	-	2.7899
2	-	+	+	-	+	+	+	-	-	-	+	0.4332
3	+	-	+	+	-	+	+	+	-	-	-	4.3360
4	-	+	-	+	+	-	+	+	+	-	-	0
5	-	-	+	-	+	+	-	+	+	+	-	1.0524
6	-	-	-	+	-	+	+	-	+	+	+	2.1971
7	+	-	-	-	+	-	+	+	-	+	+	1.3838
8	+	+	-	-	-	+	-	+	+	-	+	3.2711
9	+	+	+	-	-	-	+	-	+	+	-	0
10	-	+	+	+	-	-	-	+	-	+	+	0.9857
11	+	-	+	+	+	-	-	-	+	-	+	0.3029
12	-	-	-	-	-	-	-	-	-	-	-	0.4014

All the measurement response were processed using the Design Expert 10.0.1 program. The coefficient of the response function is obtained by using multiple linear equations:

$$Y = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_3 X_3 + \beta_4 X_4 + \beta_5 X_5 + \beta_6 X_6 + \beta_7 X_7 + \beta_8 X_8 + \beta_9 X_9 + \beta_{10} X_{10} + \beta_{11} X_{11}$$

where Y: response, X_i: factor and β: intercept.

The result of coefficient response in this study is shown in the following equations:

$$Y = 0{,}0032 - 0{,}0007X_1 - 3{,}1821\text{E-}005X_2 - 4{,}0214\text{E-}006X_3 - 0{,}0011X_4 + 0{,}0009X_5 - 0{,}0002X_6 + 0{,}0006X_7 + 0{,}0006X_8 + 0{,}0008X_9 + 0{,}0004X_{10} + 0{,}0003X_{11}$$

As shown in the above equation, it can be determined which factors that have a significant effect on the analysis of Sm-DTPA using the differential pulse voltammetry method, which are: X5 (supporting electrolytes), X7 (scan rate), X8 (ligand concentration), X9 (pH) and X10 (pulse amplitude). All the significant factor is labelled as a selected factor.

3.3 The optimum condition of the results of the Box-Behnken experiment design

The Selected factors were optimized using the Box-Behnken experimental design to find the optimum condition of the Sm analysis by differential pulse voltammetry. These factors are supporting electrolytes (X1), scan rate (X2), ligand concentration (X3), pH (X4) and pulse amplitude (X5). The box-Behnken design was chosen to determine the relationship between response functions and factors using a sequence designed experiments to get the optimal response. About 3 levels of Box-Behnken designed is used: low level (-), middle level (0) and high level (+). The value of each level is shown in Table 4.

Table 4. Factors and a level analysis of Sm(III) using DPV

Factor	**Level**		
	-	**0**	**+**
X_1	H_2O	NH_4Cl 0.05 M	NH_4Cl 0.1 M
X_2	0.01 V/s	0.03 V/s	0.05 V/s
X_3	261.61 mg/L	326.50 mg/L	392.41 mg/L
X_4	5	6	7
X_5	50 mV	75 mV	100 mV

Based on the Design Expert program, the number of measurements taken for 5 factors and 3 levels is 41 measurements. The measurement response is entered into the Design Expert program and then processed so that the coefficient of the response function is obtained to predict the desired response, namely the maximum current. From the results of data processing, a regression equation was obtained as:

$$Y = -1{,}1874E\text{-}08 + 4{,}2818E\text{-}06X_1 - 7{,}4863E\text{-}07X_2 + 1{,}5607E\text{-}06X_3 + 1{,}4588E\text{-}06X_4 + 2{,}4839E\text{-}06X_5 + 3{,}8112E\text{-}06X_1X_2 - 2{,}0785E\text{-}06X_1X_3 - 2{,}3357E\text{-}06X_1X_4 + 6{,}0369E\text{-}06X_1X_5 + 2{,}7937E\text{-}06X_2X_3 + 1{,}0149E\text{-}05X_2X_4 + 1{,}4901E\text{-}06X_2X_5 - 4{,}0256E\text{-}06X_3X_4 + 5{,}4010E\text{-}06X_3X_5 - 8{,}3554E\text{-}06X_4X_5 + 7{,}5049E\text{-}06X_1^2 + 4{,}2063E\text{-}06X_2^2 + 6{,}7054E\text{-}06X_3^2 + 8{,}6525E\text{-}06X_4^2 + 3{,}3577E\text{-}06X_5^2$$

The actual response value and response value predicted by the program can be seen in Figure 3.

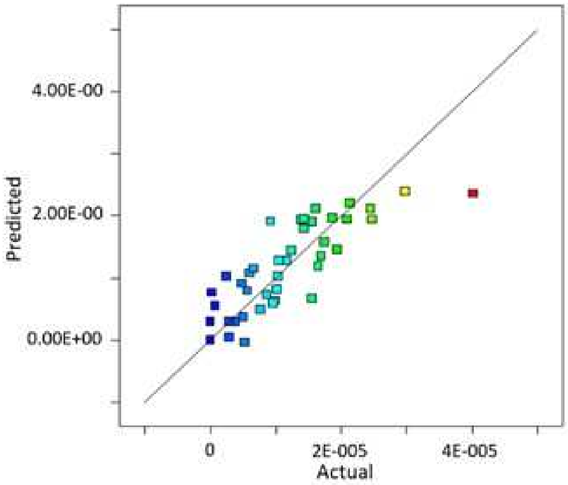

Figure 3. Linear regression curve between the actual response value and the program predictive response value.

The ANOVA Box-Behnken results in the Quadratic Design Expert program shows the value of P = 0.0379, the $P < 0.05$ (significant) means that the factor variable influences the response variable. In the Box-Behnken design, there are 100 optimum formula values for each factor with different desirability function (df) values. If the value of df is close to 1 means that the higher the value of the accuracy of the optimization was obtained. The criteria for the factor used are between the highest and lowest levels (in range) while the response criteria are the desired target in the form of the highest current among 41 measurements. From the 100 optimum alternative formula conditions provided by the Design Expert program, there are 75 formulas with df = 1, so that one of the optimum formula conditions can be selected, which are: scan rate 0.05 V / s, ligand concentration 267.67 mg / L, pulse amplitude 0.5489 V, supporting electrolyte 0.1 M NH_4Cl and at pH 5.15. This condition is the optimum condition of the results of the Box-Behnken experiment design used for the analysis of each REE and its mixture.

3.4 Analysis of Sm(III)

A series of Sm(III) solutions with concentrations 5, 10, 15, 20 and 25 mg / L were measured using differential pulse voltammetry with optimum conditions resulting from the Box-Behnken experimental design. The potential deposition that uses for Sm(III) is -1.25 V. The voltammogram results of various concentration of Sm(III) can be seen in Figure 4.

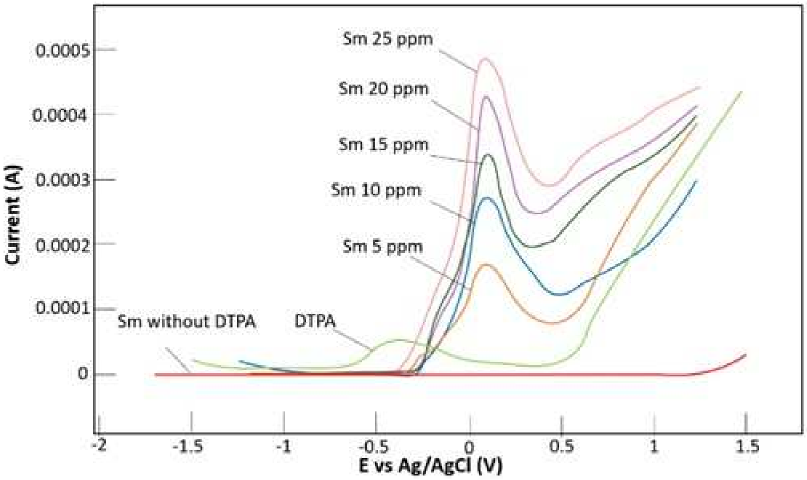

Figure 4. Voltammogram of the Sm-DTPA complex from the DPV analysis with the condition of pulse amplitude 0.5489 V; scan rate 0.05 V / s; electrolyte supporting NH_4Cl 0.1 M; DTPA ligand 267.67 mg / L and pH 5.15.

The Sm-DTPA complex is reduced at a potential of +0.0763 V, while Sm(III) without the ligand is reduced at a potential of around -1.50 to -1.55 V and DTPA ligand is reduced at a potential of -0,3989 V. The Sm(III) produces voltammograms with poor resolution, very small peak currents and are difficult to observe. The addition of DTPA ligands, to form Sm-DTPA complex, causes a more positive potential and produces a voltammogram with good resolution.

The higher the concentration of Sm(III), the higher the peak current response, according to the Randles-Sevcik equation where the current is proportional to the concentration of the analyte.

3.5 Analysis of Dy(III)

Dy(III) solutions with concentrations of 5, 10, 15, 20 and 25 mg / L were measured using differential pulse voltammetry with the same optimum conditions as Sm(III), but the deposition potential applied was different because the reduction potential of Dy(III) was different from Sm(III). The deposition potential used is -3.4891 V (5 mg / L); -3.4713 V (10 mg / L); -3,4069 V (15 mg / L); -3.4535 V (20 mg / L) and -3.4477 V (25 mg / L). The deposition potential of Dy(III) is calculated according to the Nernst equation. Dy(III) analysis voltograms can be seen in Figure 5.

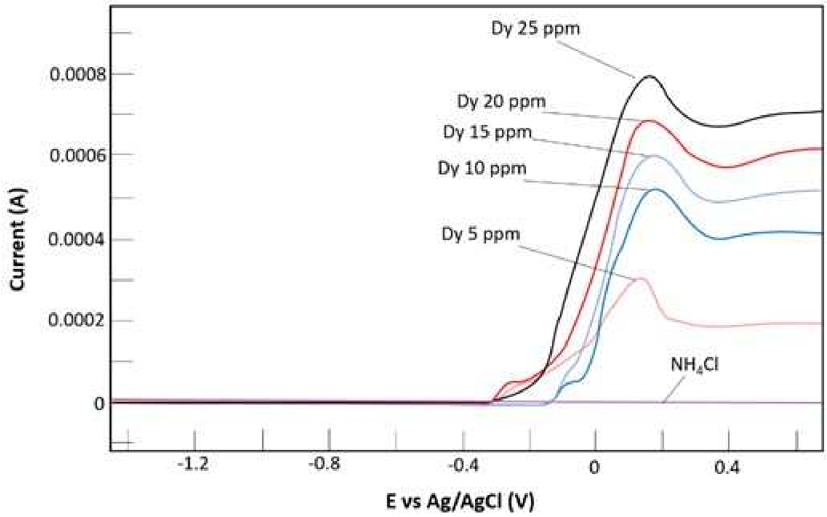

Figure 5. Dy-DTPA voltammogram from DPV analysis with conditions of pulse amplitude 0.5489 V; scan rate 0.05 V / s; supporting electrolyte NH_4Cl 0.1 M; DTPA ligand 267.67 mg / L and pH 5.15.

The Dy-DTPA complex is reduced to a potential of +0.1892 V while the Dy(III) without a ligand at a potential of -2.82 V Vs Ag / AgCl [26].

3.5 Analysis of Eu(III)

Eu(III) solutions with concentrations of 5, 10, 15, 20 and 25 mg / L were measured using differential pulse voltammetry with the same optimum conditions as Sm(III), but the applied deposition potential was different because the Eu(III) reduction potential was different from Sm(III). Potential deposition used is -1.2374 V (5 mg / L); -1,2196 V (10 mg / L); -1,2091 V (15 mg / L); -1,2017 V (20 mg / L) and -1,1960 V (25 mg / L). The voltammogram of Eu(III) can be seen in Figure 6.

The Eu-DTPA complex is reduced at a potential of +0.1068 V, while Eu(III) without ligand at a potential of -0.57 V Vs to Ag / AgCl [26]. On the voltammogram, there are 2 peak currents but the second peak current has a reduction potential that varies with each concentration. The appearance of 2 peak currents can be caused by inappropriate analysis conditions, because the experimental design of determining optimum conditions is only done on the element Sm(III).

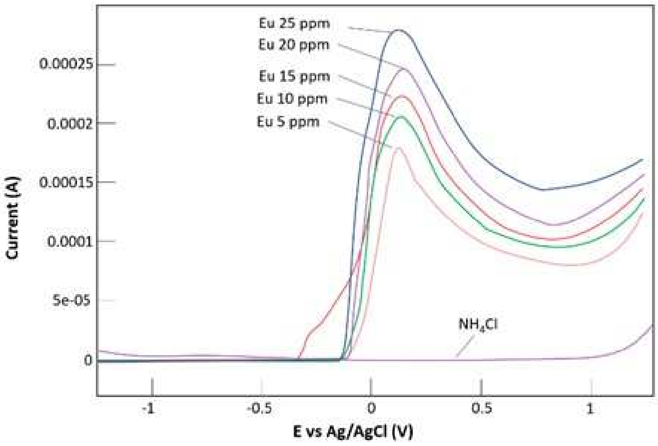

Figure 6. Eu-DTPA complex voltammogram from DPV analysis with conditions of pulse amplitude 0.5489 V; scan rate 0.05 V / s; electrolyte supporting NH 4Cl 0.1 M; DTPA ligand 267.67 mg / L and pH 5.15.

3.6 Analysis of Sm(III), Dy(III) and Eu(III) in the mixture

In this study, Sm(III), Dy(III) and Eu(III) in the mixture are also analyzed using DPV. There are 2 kinds of the mixture were prepared, namely mixture 1 with the concentration of each REE 25 mg / L and mixture 2 followed the composition of medium REE (Sm(III) 25 mg / L, Dy(III) 0.34 mg / L and Eu(III) 16.05 mg / L). The optimum condition was used but the value of potential deposition applied was the Dy(III) deposition potential because the most negative (-3.4477 V). The concentration of ligand used was 381.23 mg / L for mixtures 1 and 215.56 mg/L for mixtures 2. The voltammogram result can be seen in Figure 7.

Mixture 1 has a higher peak current than that mixture 2 because the concentration in mixture 1 is higher in which the current is proportional to the concentration. The peak currents of each Sm(III), Dy(III) and Eu(III) are 25 mg / L, higher than the mixtures 1 and 2. This is probably due to the competition of the complex formation with ligands so that electron transfer in the working electrode decreases and causes lower currents. The three elements when analyzed independently have voltammogram patterns that are similar to each other with adjacent reduction potential so that it is difficult to separate.

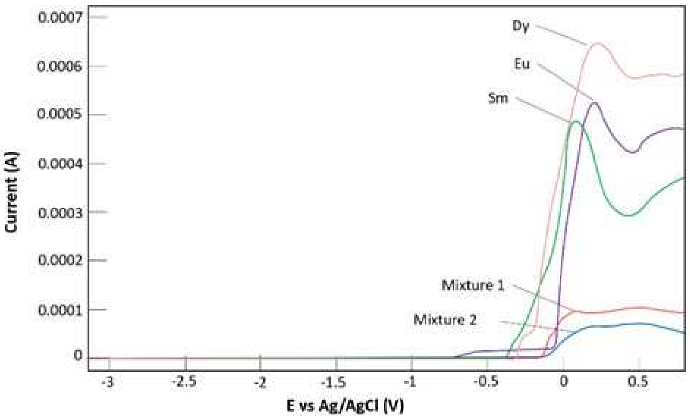

Figure 7. Voltammogram of DPV analysis with conditions of pulse amplitude 0.5489 V; scan rate 0.05 V/s; supporting electrolyte NH_4Cl 0.1 M; DTPA ligand 381.23 mg/L (mixture 1) and 215.56 mg/L (mixture 2) and pH 5.15.

3.7 Analytical parameters

The calibration curve of the Sm(III), Dy(III) and Eu(III) is made by determining the peak currents of each rare earth element for concentrations 5, 10, 15, 20 and 25 mg/L in the medium NH_4Cl 0.1 M. Measurements were carried out with optimum conditions of experimental design results. The calibration curve of Sm(III), Dy(III) and Eu(III) can be seen in Figure 8.

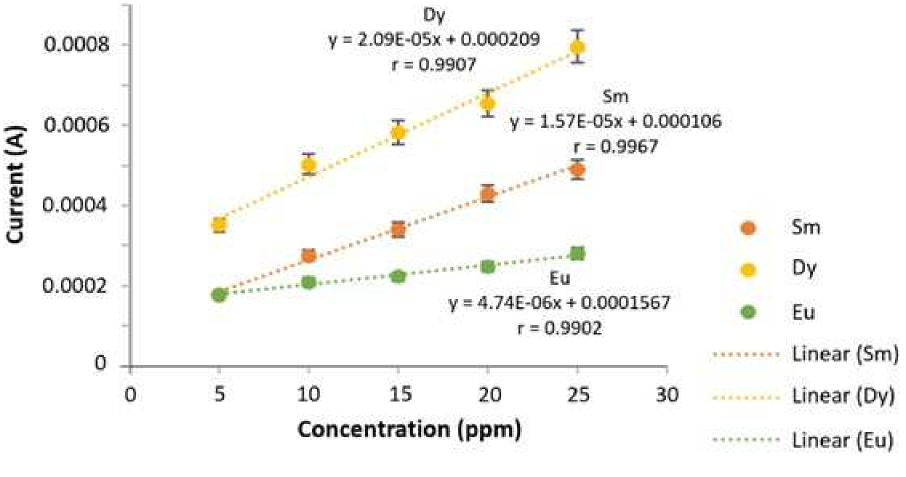

Figure 8. The calibration curve of the solution Sm(III), Dy(III) and Eu(III) for concentrations 5, 10, 15, 20 and 25 mg/L which are complexed with DTPA 267.67 mg/L.

The correlation coefficient (r) for Sm is 0.9967 while Dy is 0.9907 and Eu is 0.9902. Each element has a strong correlation between response and concentration. Sm(III) has the highest correlation coefficient which means the variable relationship is very strong. The linear regression equation from the standard curve of the solution Sm(III), Dy(III) and Eu(III) can be used to determine the analytic parameters, namely the detection limit, quantitation limit, accuracy and precision.

The limit of detection (LoD) is the smallest concentration that can be measured regardless of accuracy and precision and can be distinguished by blank. Detection limits are obtained by making five concentrations close to zero. The LoD of Sm(III) is 27.44 mg / L while Dy(III) 27.63 mg / L and Eu(III) 27.89 mg / L.

The quantitation limit (LoQ) is the smallest concentration that can still be measured according to the tolerance of accuracy and precision. The LoQ of Sm(III) is 91.47 mg / L while Dy(III) 90.91 mg / L and Eu(III) 92.83 mg / L.

In this study accuracy was determined by comparing the average value of measured concentrations of rare earth elements with actual values, whereas the precision value is measured as the coefficient of variation in where the smaller the standard deviation means the higher of precision. As shown in Table 5, the value of accuracy (accuracy) in this study is in the range of 94.28% to 98.24% while the precision (accuracy) is 95.67% to 98.61%.

Table 5. Data on the accuracy and precision of rare earths Sm(III), Dy(III) and Eu(III).

Element (C/mgL^{-1})	Current (10^{-4} A)	Concentration observed (mg/L)	Sb	KV	Accuracy	Precision
Sm (25)	4.90	24.46				
	4.80	23.82				
	4.88	24.33				
average		24.20	0.34	1.40 %	96.80 %	98.61 %
Dy (25)	7.96	25.45				
	7.85	24.93				
	8.06	25.93				
average		25.44	0.5	1.97 %	98.24 %	98.03 %
Eu (25)	1.79	25.11				
	1.67	27.19				
	1.70	26.98				
average		26.43	1.30	4.92 %	94.28 %	95.08 %

4 Conclusion

From the results of the study, it can be concluded that the factors selected as the main influences using Plackett-Burman's experimental design are scan rate, ligand concentration, pulse amplitude, supporting electrolytes, and pH. Selected factors optimized using the Box-Behnken experiment design produce optimum conditions where the scan rate is 0.05 V/s, the concentration of a ligand is 267.67 mg/L, pulse amplitude is 0.5489 V, electrolyte supporting NH_4Cl 0.1 M and pH 5, 15. The limit of detection and quantitation for Sm is 27.44 mg/L and 91.47 mg/L; for Dy 27.63 mg/L and 90.91 mg/L; for Eu 27.89 mg/L and 92.83 mg/L, respectively . The accuracy value of Sm is 96.80%, Dy 98.24% and Eu 94.28% while the precision value is Sm 98.60%, Dy 98.03% and Eu 95.08%.

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