Optimization of Voltammetric Determination of Dysprosium (III) Using Plackett-Burman and RSM-CCD Experimental Designs

Santhy Wyantuti[1*]   **Zulida Setyorini[1]**   **Safri Ishmayana[1]**
Yeni Wahyuni Hartati[1]   **M. Lutfi Firdaus[2]**

[1]Department of Chemistry, Faculty of Mathematics and Natural Sciences, Universitas Padjadjaran, Bandung, Indonesia.
[2]Graduate School of Science Education, University of Bengkulu, Bengkulu, Indonesia
[*]Corresponding author: santhy.wyantuti@unpad.ac.id *,zulida14001@mail.unpad.ac.id, ishmayana@unpad.ac.id
yeni.w.hartati@unpad.ac.id,lutfi@unib.ac.id
[*]ORCID ID: https://orcid.org/0000-0002-4382-8372*, https://orcid.org/0000-0003-0885-4206, https://orcid.org/0000-0002-9825-4425, https://orcid.org/0000-0003-1463-6352, https://orcid.org/0000-0002-5627-5834

Abstract:

This study was aimed to develop an optimized Dy determination method using differential pulse voltammetry (DPV). The Plackett-Burman (PB) experimental design was used to select significant factors that affect the electrical current response, which were further optimized using the response surface method-central composite design (RSM-CCD). The type of electrolyte solution and amplitude modulation were found as two most significant factors, among the nine factors tested, which enhance the current response based on PB design. Further optimization using RSM-CCD shows that the optimum values for the two factors were 0.1046 M and 0.1082 V respectively. When the optimum conditions were applied for Dy determination good recovery and precision were achieved with values of 91.58%, and 99.80%, respectively. The detection limit and quantification limit of the method were 1.4322 mg/L and of 4.7741 mg/L, respectively.

Key words: Dysprosium, Experimental Designs, Optimization, Rare Earth Elements, Voltammetry.

Introduction:

Dysprosium (Dy) is one of the seventeen rare earth elements (REEs) that have identical physical and chemical properties and similar behavior in the environment. REEs are not rarely found in real terms from a geochemical perspective but are quite abundant in the earth's crust after Cu, Zn, and Pb. REEs have been categorized as light- and heavy-weight REEs based on their atomic number, chemical and physical properties. Dy is a REE which has similar properties to metal, has a silver sparkle, relatively stable in air at room temperature, but dissolves easily in dilute or concentrated acids (1, 2).

Different analytical methods using inductively coupled plasma-mass spectrometry (ICP-MS) (3, 4), inductively coupled plasma optical emission spectrometry (ICP-OES) (5), X-ray fluorescence (XRF) (6), and other methods have been reported for the determination of Dy (III) ions in various sample matrices. ICP-OES has become the most appropriate technique for determining REE but the detection limit of this method is not good

when the metal concentration is too low (5). On the other hand, ICP-MS has the detection power to determine elements under mg/L level, but there are problems with polyatomic isobaric interference and it is also very expensive and its maintenance is very difficult (4). So, for the determination of Dy, an alternative analysis method that is fast, efficient, sensitive, inexpensive and simple is required.

Voltammetry is an electro-analytic method for obtaining information about analytes by measuring electrical currents in electrochemical cells as a function of electrical potential. In addition, voltammetry is widely used for fundamental studies of oxidation and reduction processes in various media, surface adsorption processes, and electron transfer mechanisms on the surface of chemically modified electrodes (7, 8).

Differential pulse voltammetry (DPV) is based on the application of successive double potential pulses. This technique is one of the most suitable for characterizing electrochemical systems because it presents a peak shaped response with

significantly reduced non-Faraday contributions and Ohmic droplet effects compared to other voltammetric procedures, such as linear sweep voltammetry (9-11). In this study, the optimum condition was determined using statistical experimental design approach in order to reduce experiment run and chemicals used in the experiments as compared to one factor at a time experiment design.

Materials and Methods:
Materials and Instruments

The chemicals used in this study were analytical grade reagents. Ammonium chloride (NH_4Cl) was purchased from Merck while nitric acid (HNO_3) and dysprosium oxide (Dy_2O_3) were purchased from Sigma Aldrich. All solutions were prepared and diluted with Milli-Q water. The Instruments used in this study include various types of glassware, graphite pencil electrode (Faber-Castell grades HB and 2B with 0.5 mm in diameter), Ag/AgCl comparative electrode, platinum wire auxiliary electrode, 14 mL voltammetric cell, micro-pipette (Eppendorf), digital analytical balance (Sartorius), potentiostat μAutolab (Metrohm®) connected to a computer using NOVA 7.0.0 software from Metrohm, and Minitab 18 statistical software. .

Preparation of Solutions

The two main solutions which were used in this investigation were ammonium chloride and dysprosium stock solution. The ammonium chloride solution was prepared by dissolving the required amounts of the reagent in Milli-Q water to obtain final concentrations of 0.0793, 0.1000, 0.1500, 0.2000, and 0.2207 M. While dysprosium stock solution was prepared by firstly dissolving 0.2868 g dysprosium oxide in 50 mL Milli-Q water with dropwise addition of 65% nitric acid with heating (100°C) and stirring until the solid dissolved completely. The solution was made up to 250 mL with Milli-Q water in a volumetric flask to give a final concentration of ~1000 mg/L and this solution was diluted to give the required range of concentration in the experiment. The exact concentration of the dysprosium stock solution was determined with ICP.

Determination of Dysprosium Voltammetric Peak

As much as 5 mL of 0.2 M ammonium chloride solution was transferred into the voltammetric cell, followed by the addition of 5 mL of each of 1 and 25 mg/mL Dy solutions to give

final concentrations of 0.5 and 12.5 mg/mL, respectively. The cell was then connected to the three electrodes mounted with a potentiostat, and DPV measurements were carried out under the following experimental parameters: potential range of -3.5 V to +1.0 V, deposition potential -3.5 V, deposition time of 60 s, amplitude modulation of 0.05 V, and scanning rate of 0.05 V/s.

Screening of Significant Factors Using Plackett-Burman Design

To the voltammetric cell, 5 mL of 6 mg/mL Dy solution and 5 mL of Milli-Q water were added to give a final concentration of 3 mg/mL. This concentration was selected based on preliminary experiment which indicated that this concentration is the lowest concentration that give a clear peak (data not shown). The solution was then analyzed using DPV with the conditions described in Table 1 based on a Plackett-Burman design generated using Minitab 17. Two significant factors, determining the measured voltammetric response, resulted from the analysis of Plackett-Burman design were then used for further optimization using RSM-CCD.

Table 1. Selected levels for each factor of the Plackett–Burman design

Code	Factor	Highest (+1)	Lowest (-1)
X_1	Deposition potential (V)	-3.0	-3.5
X_2	Deposition time (s)	80	40
X_3	Pretreatment	Yes	No
X_4	Stirring	Yes	No
X_5	Supporting electrolyte solution	Yes (Ammonium chloride)	No
X_6	Potential range (V)	-3.0 to +0.5	-3.5 to +1.0
X_7	Scan rate (V/s)	0.1	0.05
X_8	Amplitude modulation (V)	0.1	0.05
X_9	Graphite pencil electrode grade	2B	HB
X_{10}	Dummy	-	-
X_{11}	Dummy	-	-

Optimization of Measuring Conditions Using RSM-CCD

Based on the Plackett-Burman Design, two factors, namely electrolyte solution, and amplitude modulation are the most significant factors that affect the measured diffusion current (will be discussed in the Results and Discussions section). Therefore, these two factors were further optimized using RSM-CCD. The levels of parameters used in RSM-CCD generated by Minitab 17 are presented in Table 2.

Table 2. Experimental ranges and levels of the independent parameters studied in CCD

Code	Parameters	Level				
		- α	-1	0	1	+ α
X_5	Supporting electrolyte solution (M)	0.039	0.050	0.075	0.100	0.110
X_8	Amplitude modulation (V)	0.039	0.050	0.075	0.100	0.110

Preparation of Calibration Curve

To the voltammetric cell, 5 mL of 4 mg/L Dy solution and 5 mL of 0.1046 M ammonium chloride solution (the concentration was obtained from optimization, final Dy concentration 2 mg/mL) were added and measured by DPV with the following conditions: amplitude modulation = 0.1082 V (based on optimization result, close to +α value), Faber-Castell HB graphite pencil as electrode (Ø = 0.5 mm), potential range used was -3.5 V to 1.0 V, deposition potential was -3.5 V, deposition time was 60 s, scanning rate was 0.1 V/s. The measurement was also performed using various concentrations of Dy with final concentration as follows: 2, 4, 6, 8, and 10 mg/L.

Determination of Precision

Precision is calculated using equation **3** after calculating the percentage of coefficient of variation (*%CV*) (equation **2**) of triplicate measurement of known Dy^{3+} concentration as described by Miller *et al*. (12).

$$SD = \sqrt{\frac{(\Sigma(x - \overline{x})^2}{n-1}} \quad \dots \text{ eq. } (1)$$

$$\%CV = \frac{SD}{\overline{x}} \times 100\% \quad \dots \text{ eq. } (2)$$

$$\%P = 100\% - \%CV \quad \dots \text{ eq. } (3)$$

Where SD = standard deviation of multiple measurement
x = value of concentration of individual measurement
$\overline{x}$ = means of concentration of measurement results
n = amount of measurement
$\%CV$ = coefficient of variation
$\%P$ = Precision

Determination of Recovery

For the determination of recovery, the same experiment as the preparation of the calibration curve was performed but the final concentration was fixed at 5 mg/mL and the measurement was conducted in triplicate. To calculate the recovery, equation **4** is used (12).

$$\%R = \frac{Cm}{Cr} \times 100\% \quad \dots \text{ eq. } (4)$$

Where $\%R$ = Recovery
Cm = Means of measured concentration
Cr = Real concentration of sample

Determination of Limit of Detection (LoD) and Limit of Quantitation (LoQ)

Limit of detection (LoD) and limit of quantitation (LoQ) were determined based on equation (**5**) and (**6**), respectively, as described by Miller *et al*. (12).

$$LoD = y_B + 3SD \quad \dots \text{ eq. } (5)$$

$$LoQ = y_B + 10SD \quad \dots \text{ eq. } (6)$$

Where LoD = Limit of detection
LoQ = Limit of quantitation
y_B = Analyte concentration giving signal equal to the blank signal
SD = Standard deviation of the intercept of linear regression of standard curve

Results and Discussion:
Determination of Dy Peak

A peak at potential less than -1.0 V was detected when measuring the background flow response. Therefore, determination of the Dy peak was performed by comparing the current response of the blank solution and the Dy solution with different concentrations. As a preliminary test, two different solvents, i.e. 0.1 M NH_4Cl and Milli-Q water, were trialed to measure Dy^{3+} (data not shown). The result indicated that when 0.1 M NH_4Cl applied it gave a higher and slimmer peak compared to Milli-Q water only as solvent. The result of the measurement is presented in Fig. 1. The peaks that are present in Fig. 1 indicate that the position of the peak does not appeared exactly in the same position, but the shift was not too large. Therefore, it can be concluded that the characteristic peak for Dy^{3+} is around -0.75 V. Thus, for the next stage the determination of the Dy peak is measured in the potential range of -1.0 V to -0.5 V.
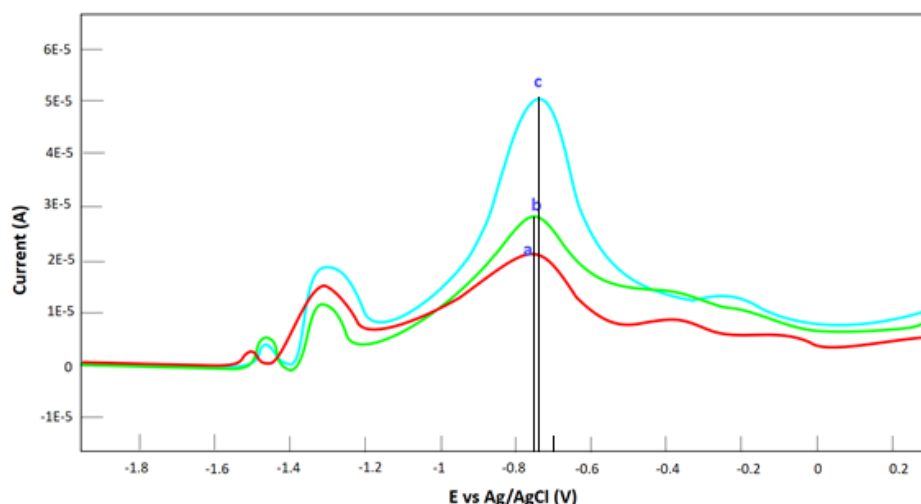
Figure 1. Voltammogram of Dy. (a) blank Ammonium chloride 0.1 M, (b) Dy 0.5 mg/L, (c) 12.5 mg/L. The measurement was performed with potential range -3.5 V s / d + 1.0 V, deposition potential -3.5 V, deposition time 60 s, amplitude modulation of 0.05 V, and scanning rate of 0.05 V / s.

Screening of Significant Factors Affecting Current Reading

The Plackett-Burman design is used to select the significant factors with factors N-1, where N is the number of experiments which are multiplication of 4. The experimental design with 8 and 12 experiments can be used for 7 to 11 factors, but if the number of the factors is smaller than N-1, dummy factors are included and can act as an estimated imaginary factor that can be used to interpret the effect of factors statistically (13, 14).

There are 11 factors (including 2 dummies) which were analyzed using Minitab 17. Measurements of current response were carried out with 3 repetitions. The response of the current obtained was further analyzed and the ANOVA Table is presented in Table 3 while the mathematical function is presented on equation **7**, where Y is the current response (µA), while Xs are factors that influence the response. A Pareto chart of the factors is also presented in Fig. 2.

Table 3. Analysis of variance (ANOVA) for model fitting the experimental results of Plackett-Burman design.

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Model	13	1476.64	113.588	5.21	0.000
Blocks	2	9.38	4.690	0.22	0.808
Linear	11	1467.26	133.387	6.11	0.000
Deposition potential (V)	1	23.52	23.517	1.08	0.310
Deposition time (s)	1	9.41	9.413	0.43	0.518
Pretreatment	1	33.99	33.991	1.56	0.225
Stirring	1	0.50	0.503	0.02	0.881
Supporting electrolyte	1	636.35	636.353	29.17	0.000
Potential range (V)	1	43.86	43.859	2.01	0.170
Scan rate (V/s)	1	142.73	142.733	6.54	0.018
Amplitude modulation (V)	1	338.01	338.008	15.50	0.001
Graphite pencil electrode grade	1	44.07	44.072	2.02	0.169
Dummy	1	43.84	43.843	2.01	0.170
Dummy	1	150.97	150.967	6.92	0.015
Error	22	479.89	21.813		
Total	35	1956.53			

$$Y = 11.2 + 3.23\,X_1 + 0.0256\,X_2 + 0.972\,X_3 + 0.118\,X_4 + 4.204\,X_5 + 1.104\,X_6 - 79.6\,X_7 + 122.6\,X_8 - 1.106\,X_9 - 1.104\,X_{10} - 2.048\,X_{11} \ldots \text{eq. }(\mathbf{7})$$
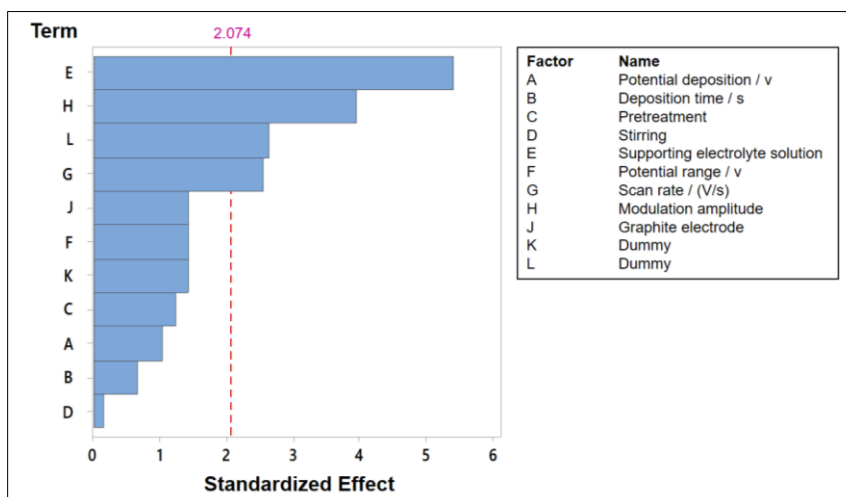
Figure 2. Pareto chart for Plackett–Burman design for current response of the factors tested in the present study.

Equation 7 can explain how the factors influence the current response in the determination of Dy with DPV. When the coefficient has positive (+) sign, it indicates that increasing of these factors will also increase the current response. On the other hand, coefficients with negative (-) sign indicates that increasing these factors will reduce the current response. As mentioned earlier, there are four factors that have significant effect on the current read ($p < 0.05$). The pareto chart also shows that there are 4 factors significantly affecting current read, i.e. supporting electrolyte solution, modulation amplitude, one of the dummy factors and scan rate. In the present experiment only two factors that significantly influence the current response the most were chosen. Factors with the lowest p-value were chosen for further optimization, i.e. supporting electrolyte ($p < 0.001$) and amplitude modulation ($p = 0.001$). Scan rate has higher p-value (0.018) and dummy cannot be optimized therefore omitted in the optimization step using RSM-CCD. Consequently, supporting electrolyte solution and modulation amplitude was further optimized.

Optimization of Factors for Dy Measurement

CCD is a technique from the second order response surface methodology (RSM) for optimization of a process (15, 16). CCD is also an alternative experimental design that is quite effective by getting more data, but with fewer experiments (17-19). In this study, the concentration of electrolyte solution (X_5) and amplitude modulation (X_8) were selected based on Plackett-Burman result and were further optimized using CCD. The levels used in CCD (-α, -1, 0, +1, and +α) is presented in Table 2.

The number of experiments carried out was 13 runs with 2 replicates (2 blocks) and the current response was measured. A 10 mg/L Dy solution was used for the experiment in order to get a clear and sharp signal for the current response. The result of the experiment is presented on Table 4.

From the data presented in Table 4, an ANOVA was performed and the result is presented in Table 5. A mathematical equation for the current response is also generated using the data and presented as equation **8**, where Y is the current response (μA), while X is a factor that influences the response.

Table 4. DPV experiments generated by CCD and corresponding responses. The experiment was performed in duplicate and the data presented is based on standard run generated by Minitab 18.

Electrolyte concentration (M)	Amplitude modulation (V)	Current (μA)	
		Experiment 1	Experiment 2
0.050	0.050	2.0243	2.7634
0.100	0.050	2.2079	2.5452
0.050	0.100	0.0000	8.5262
0.100	0.100	3.7537	4.8828
0.040	0.075	1.5228	1.9721
0.110	0.075	5.5237	6.5829
0.075	0.040	0.7645	0.0000
0.075	0.110	5.6652	7.1320
0.075	0.075	5.8777	4.2107
0.075	0.075	2.4200	4.0445
0.075	0.075	4.5280	2.3682
0.075	0.075	3.4437	4.5245
0.075	0.075	6.4209	6.2561

Table 5. Analysis of variance (ANOVA) for model fitting the experimental results of CCD.

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Model	6	58.259	9.7099	2.71	0.045
Blocks	1	5.226	5.2257	1.46	0.242
Linear	2	47.328	23.6638	6.61	0.007
Electrolyte concentration (EC)	1	9.386	9.3858	2.62	0.122
Amplitude modulation (AM)	1	37.942	37.9417	10.60	0.004
Square	2	5.703	2.8517	0.80	0.465
EC*EC	1	1.528	1.5279	0.43	0.521
AM*AM	1	4.784	4.7837	1.34	0.262
2-Way Interaction	1	0.003	0.0026	0.00	0.979
EC*AM	1	0.003	0.0026	0.00	0.979
Error	19	68.039	3.5810		
Lack-of-Fit	11	49.335	4.4850	1.92	0.182
Pure Error	8	18.704	2.3380		
Total	25	126.298			

$$Y = -10.76 + 96\ EC + 211\ AM - 253\ EC*EC - 715\ AM*AM - 437\ EC*AM \dots \text{eq. (8)}$$

The p-value of lack of fit is 0.182, which is higher than 0.05, so it can be concluded that lack of fit is not meaningful or the linear model produced is appropriate. This lack of fit indicates a deviation or inaccuracy of the linear model, so that tests are carried out to detect whether the linear model is appropriate. Of the two factors, which is quite influential by increasing the response is amplitude modulation because it a p-value less than 0.05.

Furthermore, to check the interaction between the two factors one can use 3D surface response and also contour plot as shown in Fig. 3

From the 3D surface response and contour plot, the current response generated increases by increasing concentration of ammonium chloride solution and amplitude modulation. The more electrolyte ions that move freely, the more electrons from the oxidation-reduction reaction can be carried so that the measured diffusion current also increases. While the greater the amplitude modulation value will lead to increase of current response generated because the amplitude modulation value is directly proportional to the current response (19).
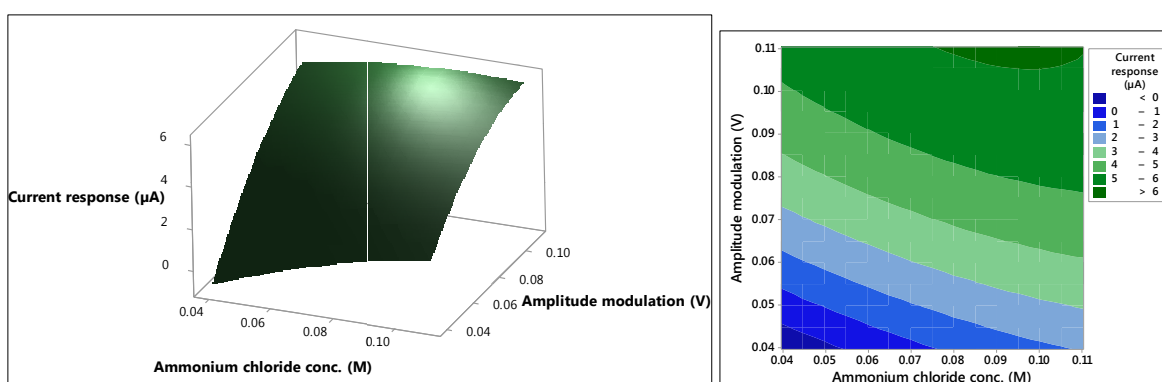

Figure 3. A 3D surface response diagram and contour plot of the current response and amplitude modulation

The optimum condition was analyzed using Minitab 17 for the factors and the value for ammonium chloride concentration and amplitude modulation was 0.1046 M and 0.1082 V, respectively, with the predictive response was 8.5262 µA. This predictive response value was compared to the actual response value at optimum

condition. The actual current response value is 7.9934 µA. The difference of the predictive and experimental value is common in a model developed using an RSM design. The difference indicates that the model obtained is not 100% accurate. Based on the result obtained, the predictive and actual response value deviation was

only 4.1%, which is close to an acceptable value for an RSM model (20).

Preparation of Dy Calibration Curve

The calibration curve was prepared using the optimum value obtained from the RSM-CCD results, i.e. the concentration of electrolyte solution (0.1046 M) and amplitude modulation (0.1082 V). While other factors are fixed i.e. potential range - 3.5 V to +1.0 V, deposition potential - 3.5 V, deposition time 60 s, scanning rate 0.1 V/s, and graphite pencil working electrode used is Faber-

Castell HB ($\emptyset$ = 0.5 mm). The concentration used for the preparation of calibration curves were 2, 4, 6, 8, and 10 mg/L, which was found to be the best range for calibration curve (11).

Figure 4 shows that Dy peak is characteristic at potential -0.7473 V, and the current response increases with increasing concentration due to the increasing number of electroactive analyte ions (Dy^{3+}) being reduced or deposited at the working electrode because diffusion currents also increase.
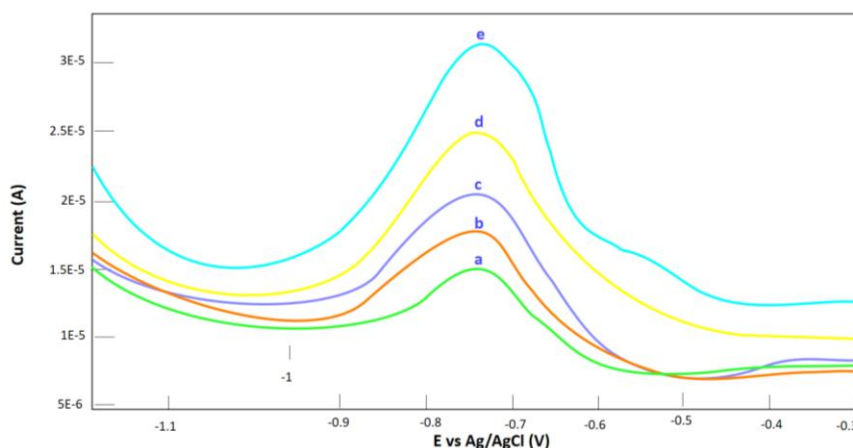

Figure 4. Voltammogram of Dy with concentration of (a) 2 mg/L, (b) 4 mg/L, (c) 6 mg/L, (d) 8 mg/L and (e) 10 mg/L. The condition of measurement were potential range of -3.5 V to +1.0 V, deposition potential -3.5 V, deposition time 60 s, scanning rate of 0.1 V/s.

The given negative potential produced negatively charged graphite working electrode. Dy ion which has a charge of 3+ will be reduced to Dy^{2+} on the surface of the working electrode. According to Fig. 5, higher Dy concentration leads to higher peak which is caused by reduction or deposition of Dy^{3+} on working electrode due to increasing current diffusion and following the Rendless-Sevcik equation where current is directly proportional to concentration of analyte (21). Dy

peak was observed at -0.75 V, and reduction of Dy^{3+} to Dy^{2+} has reduction potential of -2.30 V (21), and therefore the reaction in the present experiment most likely produce Dy^{2+}. Our previous work has succeeded to separate Dy and Eu from Sm and other rare earth elements by modifying the condition of voltammetric measurement (manuscript under review), and the present report further optimizes the measurement of Dy.
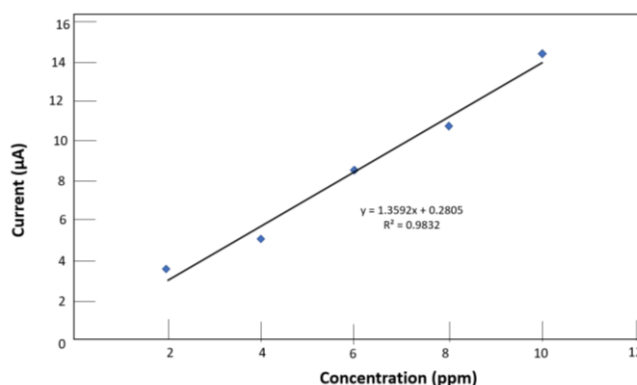

Figure 5. The Dy calibration curve variation of concentration, with a potential range of -3.5 V to +1.0 V, deposition potential -3.5 V, deposition time 60 s, scanning rate of 0.1 V/s, Ammonium chloride 0.1046 M and amplitude modulation of 0.1082 V.

The current value from the measurement of varying concentration of Dy was then plotted to generate calibration curve as presented in Fig. 5. The value graphed was obtained from the NOVA 7.0.0 software, calculated from the baseline of the graph. The linear regression equation for the calibration curve was $y = 1.3592 x + 0.2805$ with $R^2 = 0.9832$. The linear regression equation obtained from this calibration curve was tested to check whether it passes zero or not. From the calculation of the actual intercept range, the value of the range that passes the zero point is obtained so that the linear equation from the calibration curve becomes $y = 1.3974x$. From this data, calculations can be made to determine detection limits, and limit of quantitation (22). Detection limit value obtained was 1.4322 mg/L, while the quantitation limit was 4.7741 mg/L (23).

A synthetic solution with known concentration of Dy was measured by DPV at the optimum condition. Based on calculations, the precision and recovery of the current method was 99.83% and 91.58%, respectively. The precision of the method is acceptable according to the requirement as described by Miller *et al*. (12). The recovery result obtained fulfill the acceptable percentage, which require that recovery should fall within 80-110% range (24). So, in conclusion the method is adequate for determination of Dy. Our group is still optimizing measurement of rare earth elements using voltammetric method. Therefore, further application for real samples such as geological samples need to be optimized since the presence of other rare earth elements may interfere the measurement.

Conclusion:

In summary, based on Plackett-Burman design results, factors that have significant influence on current response in Dy determination using DPV are ammonium chloride electrolyte solution, amplitude modulation and scan rate. Optimization of the two factors using RSM-CCD, the optimum condition for Dy measurement are 1046 M and 0.1082 V for ammonium chloride concentration and amplitude modulation, respectively. The recovery of the method using the optimum condition is 91.58%, while precision, detection limit and quantitation limit are 99.83%, 1.4322 mg/L, and 4.7741 mg/L, respectively.

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Authors' declaration:
- Conflicts of Interest: None.
- We hereby confirm that all the Figures and Tables in the manuscript are mine ours. Besides, the Figures and images, which are not mine ours, have been given the permission for re-publication attached with the manuscript.
- Ethical Clearance: The project was approved by the local ethical committee in Universitas Padjadjaran.

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التقدير الفولتامتري الامثل للديسبروسيوم (III) باستخدام التصاميم التجريبية بلاكيت بورمان و- RSM-CCD

سانتي ويانتوتي [1] *   زوليدا سيتوريني[1]   سفري إشمايانا[1]   يني وحيوني هارتاتي[1]

م لطفي فردوس[2]

[1] قسم الكيمياء، كلية الرياضيات والعلوم الطبيعية، جامعة بادجادجاران، باندونج، إندونيسيا.

[2] مدرسة الدراسات العليا للعلوم، جامعة بنجكولو، بنجكولو، إندوني

الخلاصة:

هدفت هذه الدراسة إلى تطوير طريقة مثلى لتقدير Dy باستخدام قياس الجهد النبضي التفاضلي (DPV). تم استخدام التصميم التجريبي (Plackett-Burman (PB لتحديد العوامل الهامة التي تؤثر على الاستجابة للتيار الكهربائي، والتي تم تحسينها بشكل أكبر باستخدام تصميم المركب المركزي لطريقة الاستجابة (RSM-CCD). حيث وجد ان نوع المحلول الالكتروليتي وتعديل السعة عاملين مهمين من بين العوامل التسعة التي تم اختبارها ، والتي تعزز استجابة التيار بناءً على تصميم PB. علاوة على ذلك تلاحظ ان الامثلية باستخدام RSM-CCD أن القيم المثلى للعاملين كانت 0.1046 م و 0.1082 فولت على التوالي. عندما تم تطبيق الظروف المثلى لتقدير Dy ، تم الحصول على استعادية ودقة جيدة مع قيم 91.58٪ و 99.80٪ على التوالي. كان حد الكشف والحد الكمي للطريقة 1.4322 ملغم / لتر و 4.7741 ملغم / لتر على التوالي.

الكلمات المفتاحية: الديسبروسيوم، التصاميم التجريبية، الامثلية، عناصر النادرة الارضية، فولتامتري.