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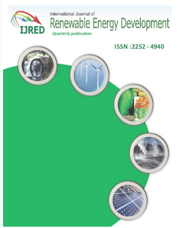

Research Article

Differential Pulse Voltammetry Study for Quantitative Determination of Dysprosium (III) in Acetonitrile Solution

Santhy Wyantuti*, Uji Pratomo, Shauvina A. Asyifadewi, Yeni Wahyuni Hartati, Husein Hernandi Bahti

Department of Chemistry, Faculty of Mathematics and Natural Sciences, Padjadjaran University. Jl. Raya Bandung Sumedang Km 21. Jatinangor, Sumedang 45363, Indonesia

ABSTRACT. Dysprosium has gained global interest due to its key application in renewable technology, such as wind power technology. The presence of this rare earth element (REE) can be determined by several spectroscopic methods. Recently, a voltammetry method has provided an alternative method for the simple and fast detection of REEs. However, to the best of our knowledge, this experiment is usually carried out in an aqueous solvent, and the response of the REE in an organic solvent by the voltammetry method has rarely been investigated. In this research, the quantitative detection of dysprosium and dysprosium mixtures with samarium, europium and gadolinium in acetonitrile is reported by differential pulse voltammetry. A Box-Behnken design was applied to predict the optimum condition of the measurements. Three factors, namely potential deposition, deposition time and amplitude modulation, were found to significantly influence the signal under optimal conditions, which are -1.0 V, 83.64 s and 0.0929 V, respectively. The surface characterization of dysprosium deposited on a Pt surface shows better deposition under 100% acetonitrile compared to a lower concentration of acetonitrile. The evaluation in this study shows a detection limit of 0.6462 mg•L^{-1} and a quantitation limit of 2.1419 mg•L^{-1}, with a precision value and recovery value of 99.97% and 93.62%, respectively.

Keywords: Acetonitrile, Box-Behnken design, Dysprosium, Differential Pulse Voltammetry, Chemometrics

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1. Introduction

In recent years, the depletion of fossil fuels has motivated many researchers to develop new technological approaches from renewable energy sources, such as wind power (Alonso *et al.,* 2012; Crawford, 2009; Demir & Taskin, 2013; Kalair *et al.,* 2020). Many devoted studies of wind power technology and its potential for clean electricity generation focus on the environmental impacts and the availability of resources to drive the wind turbine, especially dysprosium (Dy) (Elshkaki & Graedel, 2013; Elshkaki & Graedel, 2014; Garcia-Olivares *et al*., 2012; Gross *et al*., 2003).

Dysprosium is one of the rare earth elements (REEs) that has increased significantly in terms of application in modern technology, such as electronics, metallurgy, phosphorus, magnets, catalysts, lasers and ceramic (Zamani *et al*., 2013; Tian *et al*., 2013). The oxidation state of dysprosium is +3, and its reduction potential is about -2.30 V with the reaction: $Dy^{3+}_{(aq)} + e^- \rightarrow Dy^{2+}_{(aq)}$ (Krebs, 2006; Kushkhov *et al*., 2013).

The presence of Dy can be determined by various analytical methods, such as ICP-MS, ICP-AES and XRF methods. However, these methods are considered relatively expensive for most analytical laboratories (Bank *et al*., 2016; Chien *et al*., 2006; Rajendran *et al*., 2008; Taam *et al*., 2013; Schramm, 2016; Smoli *et al*., 2016).

As an alternative, a voltammetry technique provides an inexpensive, simple, fast, efficient and sensitive method. To obtain information about analytes, this electroanalytical method measures the current in an electrochemical cell as a function of potential (Ganjali *et al*., 2009; Markombe *et al*., 2018). It was reported that the presence of some REEs, including Gd, Sm, Dy and Eu, could be determined by voltammetric methods (Anwar, 2017; Harahap, 2018; Setyorini, 2018; Wyantuti *et al*., 2018a; Wyantuti *et al*., 2018b).

In our previous work, the detection of Dy in NH_4Cl electrolyte solution by differential pulse voltammetry was successfully investigated. However, the Dy signal could not be distinguished in mixtures with other REEs under such as NH_4Cl electrolytes (Wyantuti *et al*., 2019).

Among the many organic solvents, acetonitrile can be utilized as a solvent in a voltammetry method due to its wide potential window (-3.45 V to 2.35 V), which is suitable for metal deposition (Creager, 2007; Elgrishi *et*

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[*] Corresponding author: santhy.wyantuti@unpad.ac.id

al., 2018). It has been reported that dysprosium, cobalt, aluminium, nickel and silver could be deposited by an electroanalytical method using acetonitrile as a solvent (Lodermeyer *et al*., 2006; Koverga *et al*., 2017; Yanez *et al*., 2015; Suchacz *et al*., 2016). Therefore, acetonitrile was utilized as a solvent for the detection of Dy by the voltammetry method in this work.

Most of the reported techniques for metal detection by the voltammetry method use a sophisticated technique but have not touched the factorial design as an approach to assess the significant factors that will influence the response. Chemometrics propounds an approach that can investigate this condition at the same time, with less experiment effort. Combining chemometrics for analytical method development would provide a comprehensive knowledge of a particular phenomenon (Morgan, 1997; Montgomery, 2001; Elazazy *et al*., 2018). The Box-Behnken design is one tool for chemometric analysis. It is a set of mathematical and statistical techniques that are useful for modelling and analysing problems when the observed response is influenced by several factors. The Box-Behnken design aims to optimize responsiveness in order to achieve the best system performance (Bezerra *et al*., 2008).

The current study implies a differential pulse voltammetry strategy for the determination of Dy in the organic solvent acetonitrile. The proposed strategy engages the Box-Behnken design as a screening tool for optimization of the condition. The surface analysis of the deposition of Dy on a Pt electrode is also reported.

2. Materials and Methods

2.1 Materials

The materials used in this study included distilled water, nitric acid 65% (HNO_3, Merck), acetonitrile (Merck), europium oxide (Eu_2O_3, 99.9%) (Sigma Aldrich), dysprosium oxide (Dy_2O_3, 99.9%) (Sigma Aldrich), gadolinium oxide (Gd_2O_3, 99.9%) (Sigma Aldrich) and samarium oxide (Sm_2O_3, 99.9%) (Sigma Aldrich).

The tools used in this study included 14 mL voltammetry cells, platinum working electrodes (Antam), dry-type Ag/AgCl reference electrodes (eDAQ), platinum wire counter electrodes (Antam), magnetic stirrers, a digital analytical balance (Sartorius), a Metrohm® μAutolab potentiostat connected to a computer with the ANOVA 7.0.0 program and the Minitab 17.1 program, and a scanning electron microscope (SEM) JEOL JSM-7500F.

2.2 Methods

2.2.1 Preparation of Stock Solution Dy_2O_3

The stock solution of 1000 mg·L^{-1} Dy_2O_3 was prepared by dissolving 0.2868 g Dy_2O_3 solid in a small amount of 65% HNO_3, stirring and heating on a hot plate until homogenous. Then, 250 mL distilled water was added to the solution and the mixture was stirred.

2.2.2. Measurement of Background Current

A total of 10 mL of acetonitrile was pipetted into a voltammetry cell. The three electrodes were connected with a potentiostat, and the measurement was conducted using differential pulse voltammetry under the following conditions: a potential range of −1.0 V to +1.0 V, potential deposition of −1.0 V, deposition time of 80 s, amplitude modulation of 0.1 V and scan rate of 0.05 V/s.

2.2.3. Measurement of Dy Current

In this process, 10 mL of a 10.0 mg L^{-1} Dy solution was pipetted into a voltammetry cell. The three electrodes were connected with a potentiostat, and the measurement was conducted using differential pulse voltammetry under the following conditions: a potential range of −1.0 V to +1.0 V, potential deposition of −1.0 V, deposition time of 80 s, amplitude modulation of 0.1 V and scan rate of 0.05 V/s. The measurement was repeated for various concentrations: 15.0, 20.0, 25.0 and 30.0 mg·L^{-1}.

2.2.4. Measurement of Dy Current in 50%, 75% and 100% Acetonitrile by Differential Pulse Voltammetry

A total of 10 mL of a 10.0 mg L^{-1} Dy solution in 50% acetonitrile was pipetted into a voltammetry cell. The three electrodes were connected with a potentiostat, and the measurement was conducted using differential pulse voltammetry under the following conditions: a potential range of −1.0 V to +1.0 V, potential deposition of −1.0 V, deposition time of 80 s, amplitude modulation of 0.1 V and scan rate of 0.05 V/s. The measurement was repeated for a 10.0 mg L^{-1} Dy solution in 75% and 100% acetonitrile.

2.2.5. Deposition Analysis of Platinum Working Electrode Surface by SEM

The surface morphology of the platinum working electrodes was observed before and after deposition with Dy in 50%, 75% and 100% acetonitrile. The electrodes had a length of around 1 cm and were attached to the sample specimen holder. The morphological features were then characterized using SEM (JEOL JSM-7500F).

2.2.6. Box–Behnken Experimental Design

A total of 10 mL of a 10.0 mg L^{-1} Dy solution was pipetted into a voltammetry cell. The three electrodes were connected with a potentiostat, and the measurement was conducted using differential pulse voltammetry under the selected factors: potential deposition, deposition time and amplitude modulation. The selected factors were then optimized by the Box–Behnken experimental design. The Box–Behnken experimental design was set in three levels (−1, 0, +1), with up to 15 measurements conducted using the Minitab program 17.1.

Table 1
Optimization of factors and analysis levels of Dy in differential pulse voltammetry

Symbol	Factor	Level		
		-1	0	+1
X1	Potential deposition / V	-2.0	-1.5	-1.0
X2	Deposition time / s	40	80	120
X3	Amplitude modulation / V	0.05	0.075	0.1

2.2.7. Measurement of Current Response of Dy, Eu and Gd under Optimum Conditions

Solutions of 6.0 mg·L^{-1} Dy, 1.0 mg·L^{-1} Eu, 10.0 mg·L^{-1} Gd and 30.0 mg·L^{-1} Dy in acetonitrile were pipetted into a voltammetry cell. The three electrodes were connected with a potentiostat, and the measurement was conducted using differential pulse voltammetry under the following conditions: a potential range of −1.0 V to +1.0 V, potential deposition of −1.0 V, deposition time of 83.64 s, amplitude modulation of 0.092 V and scan rate of 0.05 V/s.

2.2.8. Preparation of Dy Calibration Curve

A total of 10 mL of a 2.0 mg · L^{-1} Dy solution was pipetted into a voltammetry cell. The three electrodes were connected with a potentiostat, and the measurement was conducted using differential pulse voltammetry under the optimum conditions obtained from the Box–Behnken experimental design results: a potential range of −1.0 V to +1.0 V, potential deposition of −1.0 V, deposition time of 83.64 s, amplitude modulation of 0.092 V and scan rate of 0.05 V/s. The measurement was repeated for various concentrations: 3.0, 4.0, 5.0 and 6.0 mg L^{-1}.

2.2.9. Determination of Precision

Precision is calculated using equation 3, after calculating the percentage of the coefficient of variation (*%CV*) (equation 2) of triplicate measurement of known Dy^{3+} concentration, as described by Miller *et al.* (2018).

$$SD = \sqrt{\frac{(\Sigma(x-\bar{x})^2}{n-1}} \qquad (1)$$

$$\%CV = \frac{Stdev}{\bar{x}} \times 100\% \qquad (2)$$

$$\%P = 100\% - \%CV \qquad (3)$$

Where
Stdev = Standard Deviation of multiple measurements
x = Concentration value of individual measurement
$\bar{x}$ = Mean of individual concentration results
n = Number of measurements
%CV = Coefficient of variation
%P = Precision

2.2.10. Determination of Recovery

For the determination of recovery, the same experiment was performed as for the preparation of the calibration curve, but the final concentration was fixed at 5 mg·mL^{-1}, and the measurement was conducted in triplicate. To calculate the recovery, equation 4 is used (Miller *et al.*, 2018).

$$\%R = \frac{Cm}{Cr} \times 100\% \qquad (4)$$

Where
%R = Recovery
Cm = Mean of measured concentrations
Cr = Real concentration of sample

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

The limit of detection (LoD) and limit of quantitation (LoQ) were determined based on equations (5) and (6), respectively, as described by Miller *et al.* (2018).

$$LoD = y_B + 3SD \qquad (5)$$

$$LoQ = y_B + 10SD \qquad (6)$$

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

2.2.12. Randles–Sevcik Equation

In a voltammetry method using working electrodes such as graphite, gold and platinum, the Randles-Sevcik equation is applied (equation 7). The equation describes the effect of scan rate on the peak current ip (Bard & Faulkner, 2001; Zanello, 2003).

$$ip = 0.4463\, nFAC\sqrt{\frac{nFvD}{RT}} \qquad (7)$$

Where
ip = Current maximum in amps
n = Number of electrons transferred in the redox reaction
A = Electrode area in cm^2
F = Faraday Constant in C · mol^{-1}
D = Diffusion coefficient in cm^2 s^{-1}
C = Concentration in mol cm^{-3}
v = Scan rate in V s^{-1}
R = Gas constant in J · mol^{-1} K^{-1}
T = Temperature in K

3. Result and Discussion

3.1. Current Response of Acetonitrile and Dysprosium in Acetonitrile

At first, the current response of acetonitrile only and Dy in acetonitrile was investigated by using differential pulse voltammetry. The result of this experiment is shown in Figure 1.

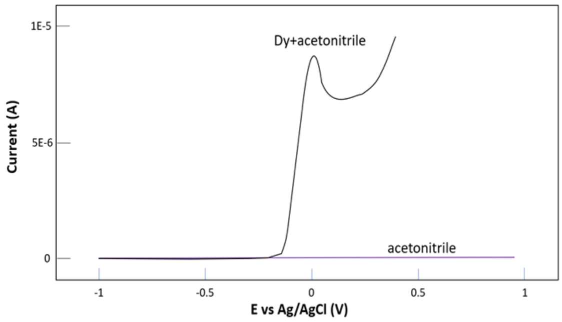

Fig 1. Voltammogram of acetonitrile as a solvent and 6 mg L^{-1} Dy in acetonitrile (potential range of −1.0 V to +1.0 V, deposition potential of −1.0 V, deposition time of 80 s, amplitude modulation of 0.1 V and scan rate of 0.05 V/s).

As shown in Figure 1, acetonitrile does not produce any response during measurement by differential pulse voltammetry, so it was assumed that acetonitrile will not interfere with the voltammogram of Dy. In contrast, the voltammogram result of 6 mg L^{-1} Dy in acetonitrile shows a high current response at 0.05 V vs. Ag/AgCl. Thus, the investigation of the current response of Dy under 50%, 75% and 100% of acetonitrile solvent was conducted.

3.2. Dy response under the various concentrations of acetonitrile

The electrochemical behaviour of Dy in 50%, 75% and 100% acetonitrile was carried out using differential pulse voltammetry. The result of this experiment is shown in Figure 2. It can be seen that 30 mg·L^{-1} Dy under 100% acetonitrile produces the highest current response at a potential around 0.05 V, while the same concentration of Dy in 75% and 50% acetonitrile shows the lower and lowest current responses at a potential around 0.07 and 0.09 V, respectively. This result indicates that Dy could be easily reduced and deposited on the Pt working electrode under 100% acetonitrile.

3.3. Characterization of Platinum Electrode Surfaces

To discover the inherent character of the platinum electrode surfaces, an investigation was carried out using a SEM instrument with a 4300x magnification. The analysis was carried out before and after the deposition of Dy in acetonitrile on the platinum electrode to investigate the changes in the surface profile.

The surface profile of the bare platinum electrode surface is shown in Figure 3A, while the surface profiles of the platinum electrode after Dy deposition under 50%, 75% and 100% acetonitrile are shown in Figures 3B, 3C and 3D, respectively. The SEM images in Figure 3B-D show the distribution of white spot microparticles (size around 1 µm) on the platinum electrode and indicate that the Dy has been successfully deposited. Moreover, the highest distribution of white spot Dy microparticles are shown on the platinum electrode under 100% acetonitrile conditions (Figure 3D). This result concluded that the deposition of Dy in 100% acetonitrile onto the platinum surface is considerably more convenient than lowering the concentration of acetonitrile.

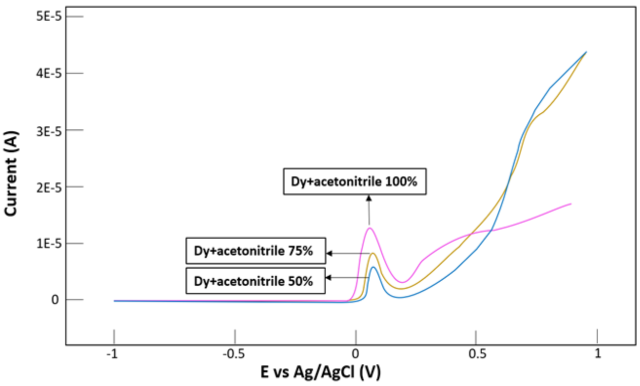

Fig 2. Voltammogram of 30 mg L^{-1} Dy in 50%, 75% and 100% acetonitrile (potential range of −1.0 V to +1.0 V, deposition potential of −1.0 V, deposition time of 83.64 s, amplitude modulation of 0.0929 V and scan rate of 0.05 V/s).

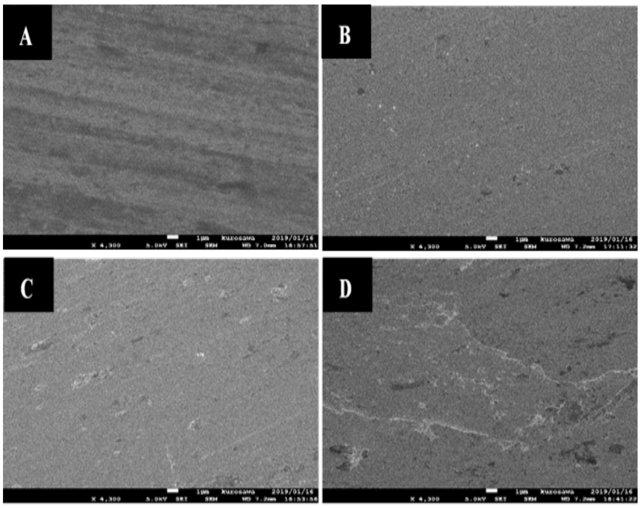

Fig. 3. SEM analysis of the platinum electrode surface (4300× magnification) (A) blank, (B) after deposition of Dy in 50% acetonitrile, (C) after deposition of Dy in 75% acetonitrile, (D) after deposition of Dy in 100% acetonitrile.

3.4. Studies of Optimization Conditions for Measurement of Dy in Acetonitrile with Box–Behnken Experimental Design

The Box-Behnken design was chosen with the objective of achieving an effective optimization process that could shorten the analysis time. In this research, the main factors selected in the Box-Behnken design are the potential deposition, deposition time and amplitude modulation. The Box-Behnken design used 3 factors and 3 levels and obtained 15 measurements in total, which are listed in Table 2. The measurements were carried out by differential pulse voltammetry. The current response generated by each measurement was processed and analysed using the Minitab 17 program in order to obtain the optimum value. The optimum value is important to predict the desired current response.

The results from data processing are a regression equation that helps us to determine the positive or significant effect of the factors affecting the Dy analysis by differential pulse voltammetry. The regression equation is obtained as follows:

$$\begin{aligned} Y = {} & -0.000003 + 0.000003X_1 + 0.000000X_2 + 0.000237X_3 \\ & + 0.000000(X_1)^2 - 0.000000(X_2)^2 \\ & - 0.001352(X_3)^2 + 0.000000X_1X_2 \\ & - 0.0000015X_1X_3 - 0.000000X_2X_3 \end{aligned} \tag{8}$$

Where Y = Current response
X_1 = Potential deposition
X_2 = Deposition time
X_3 = Amplitude modulation

In equation 8, a positive coefficient means an increase in response, while a negative coefficient means a decrease in response. The potential deposition (X_1) and amplitude modulation (X_3) have a positive coefficient value, which indicates that these factors could increase the current response. Although deposition time (X_2) has a positive coefficient, the value is about 0.000000, which means that this factor only shows a little effect on increasing the current response.

Table 2
Current response of Dy in acetonitrile under various conditions

Run	Potential deposition / V	Deposition time / s	Amplitude modulation / V	Current / µA
1	-1.5	120	0.100	6.5804
2	-1.5	80	0.075	6.9616
3	-1.0	40	0.075	8.2181
4	-1.0	80	0.050	5.4199
5	-1.5	80	0.075	7.1082
6	-1.5	80	0.075	6.9380
7	-1.0	120	0.075	8.8030
8	-2.0	80	0.050	4.4601
9	-1.5	40	0.100	7.4405
10	-1.0	80	0.100	7.6019
11	-1.5	120	0.050	3.5718
12	-2.0	80	0.100	7.3853
13	-2.0	120	0.075	3.8593
14	-1.5	40	0.050	4.3818
15	-2.0	40	0.075	4.7108

3.5. Statistical Analysis

Statistical analysis was carried out to study whether the model of equation 8 is sufficient to describe the actual results. Theoretically, the smaller the *p*-value, the more significant the model. The proposed models can be considered as statistically significant at 95% if $p<0.05$ (Montgomery, 2001; Van Tran *et al.*, 2020a; Van Tran *et al.*, 2020b; Nguyen *et al.*, 2020. The ANOVA table is shown in Table 3.

As shown in Table 3, the *p*-value of the potential deposition and amplitude modulation factors are less than 0.05 (0.035 and 0.021, respectively). This indicates that these factors are significant for increasing the current response. In contrast, the *p*-value of the deposition time is 0.588, which indicates that the deposition time has an insignificant effect on the resulting current response. These predictions were in reasonable agreement with the model indicating that the potential deposition and amplitude modulation factors (X_1 and X_3) could influence the responses, while the deposition time (X_2) would only slightly impact the current response.

It is note that the "lack of fit" test value was found to be 0.004. These outcomes reveal that the model is significantly relevant to pure errors at a 95% significance level (α=0.05), because the value is less than 0.05. As shown in Table 3, the *p*-value of the square of each factor (X_1^2; X_2^2; X_3^2) and the interaction between each factor (X_1X_2; X_1X_3; X_2X_3) is higher than 0.05, which means that these factors are insignificant. It is therefore assumed that the low "lack of fit" *p*-value is influenced by these factors.

Table 3
Current response of Dy in acetonitrile under various factors

Factor	*p*-value
Constant	0.000^a
Potential deposition (X_1)	0.035^a
Deposition time (X_2)	0.588^b
Amplitude modulation (X_3)	0.021^a
Potential deposition * Potential deposition (X_1^2)	0.927^b
Deposition time * Deposition time (X_2^2)	0.330^b
Amplitude modulation * Amplitude modulation (X_3^2)	0.228^b
Potential deposition * Deposition time (X_1X_2)	0.570^b
Potential deposition * Amplitude modulation (X_1X_3)	0.984^b
Deposition time * Amplitude modulation (X_2X_3)	0.766^b
Lack of fit	0.004^a

^{a} *significant at $p<0.05$*
^{b} *insignificant at $p>0.05$*

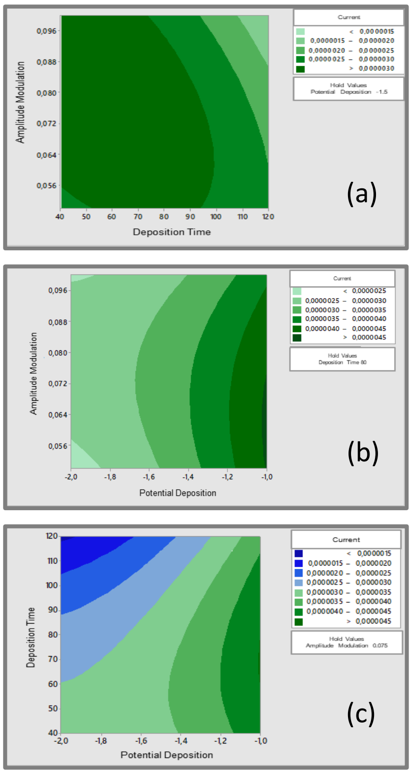

Fig 4. 2D contour plot current response of (a) deposition time and amplitude modulation; (b) potential deposition and amplitude modulation; (c) potential deposition and deposition time.

To make these interactions more visual, we created a 2D contour plot, as shown in Figure 4. The contour plot current response of deposition time and amplitude modulation, as shown in Figure 4(a), shows the optimum condition of deposition time around 83 s and amplitude modulation of 0.0926 V. Figure 4(b) reveals the influence of two factors to the current response: potential deposition and amplitude modulation. The optimum condition of potential deposition was observed at -1.0 V, while the optimum condition for amplitude modulation was 0.092 V. Finally, the 2D contour plot of potential deposition and deposition time is shown in Figure 4(c), highlighting the optimum condition of the potential deposition and deposition time at -1.0 V and 83 s, respectively. Hence, the optimum value of each factor was obtained; namely, the potential deposition of -1.0 V, the deposition time of 83 s and the amplitude modulation of 0.0929 V.

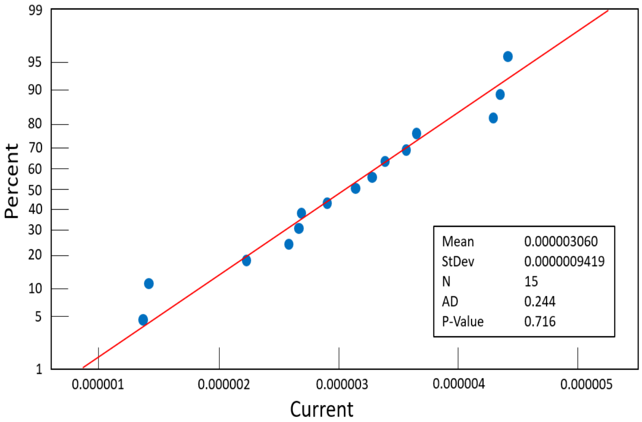

Fig 5. Normal probability plot of Box-Behnken design

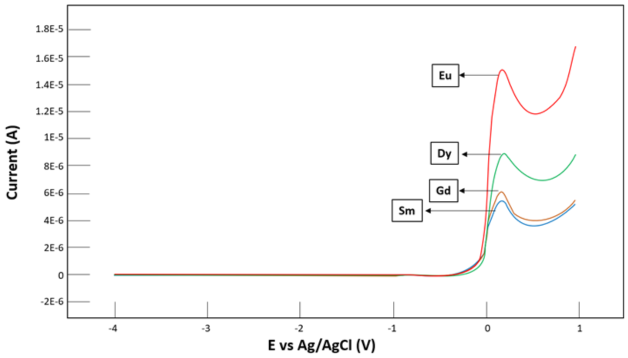

Fig 6. Voltammogram of the individual current response of Eu under conditions of 74.56 s, amplitude modulation 0.125 V and potential deposition -0.20 V; Dy under conditions of 83.64 s, amplitude modulation 0.10 V and potential deposition -1.32 V; Gd under conditions of 64.64 s, amplitude modulation 0.10 V and potential deposition -1.32 V; Sm under conditions of 60 s, amplitude modulation 0.05 V and potential deposition -1.50 V

Apart from the lack of fit test, we performed a normal distribution analysis to assess whether the model obtained is equally distributed in linear regression (Montgomery, 2001). The Anderson-Darling test was chosen to demonstrate the adequacy of the model. The hypothesis used for the normality test is as follows:

H_0: Residuals are normally distributed if the *p*-value is ≥5%

H_1: Residuals are not normally distributed if the *p*-value is <5%

As shown in Figure 5, the normal probability plot shows the following result: mean = 0.000003060, stdev = 0.0000009419, AD = 0.244 and R^2 = 87.11%. The Anderson-Darling test value from the normal probability plot shows a *p*-value of 0.716, which is higher than 0.05, and it could be concluded that H_0 is accepted or is normally distributed. According to this result, the adequacy of the model was considered good, because the data could be distributed well to the line. Therefore, it is suggested that the model can be used.

3.6. Determination of Dy in Mixtures with Sm, Eu and Gd, under Optimum Conditions

An investigation of the current response of the Sm, Eu, Gd and Dy elements by differential pulse voltammetry under optimum conditions was conducted to determine whether the presence of other REEs would disturb the voltammogram of Dy in acetonitrile. As shown in Figure 6, the voltammogram of the individual current response of Dy, Gd, Eu and Sm in acetonitrile was determined by differential pulse voltammetry under optimum conditions.

The Dy and Gd simulations were carried out using a 3:5 ratio of Dy and Gd concentrations using the optimum conditions for Dy. The voltammogram for this simulation is shown in Figure 7(A). Here, the current peak of individual Gd is greater than the individual current peak of Dy. The voltammogram profile of the Gd and Dy mixture shows that there is a change of current intensity for both characteristic peaks. This result indicates that there is a correlation between Dy and Gd that influences each current.

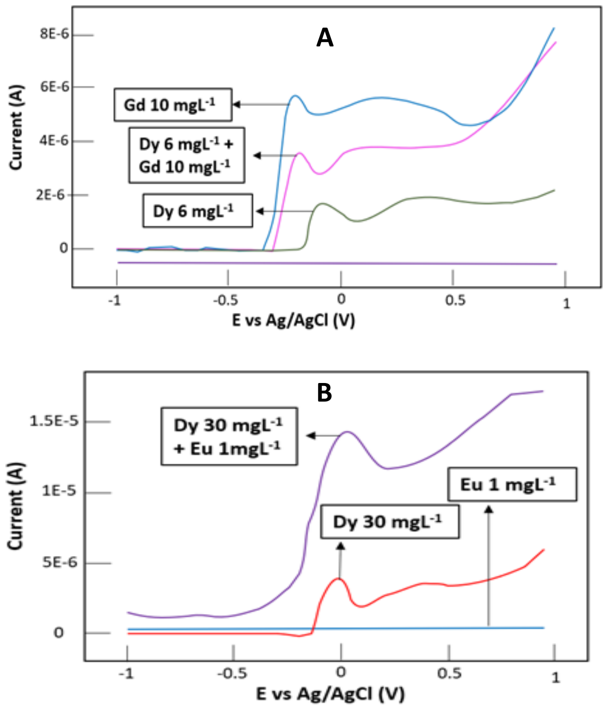

Fig 7. Voltammogram of (A) mixture of 10 mg L^{-1} Gd and 6 mg L^{-1} Dy, (B) mixture of 30 mg L^{-1} Dy and 1 mg L^{-1} Eu, potential range of −1.0 V to +1.0 V, deposition potential of −1.0 V, deposition time of 83.64 s, amplitude modulation of 0.0929 V and scan rate of 0.05 V/s

The simulation experiment between Dy and Eu was carried out with a concentration ratio of 1:30 Eu to Dy (Dy 30 mg L^{-1} and Eu 1 mg L^{-1}) using the optimum conditions for Dy. The result is shown in Figure 7(B); only an individual Dy peak was produced in the voltammogram. This result indicates that an individual Dy peak could be distinguished from an individual Eu peak. Although the peak current of the Eu and Dy mixture produces the highest current compared to the individual currents, the current peak of Eu could not be observed.

3.7. Calibration Curve of Dy

The calibration curve for Dy was obtained by determining the current peak of various concentrations of Dy in acetonitrile: 2, 3, 4, 5 and 6 mg·L^{-1} under the optimum value of Dy by differential pulse voltammetry. As shown in Figure 8, the concentration is correlated with the peak current. This is due to the number of Dy^{3+} ions being reduced or deposited on the Pt working electrode and is in accordance with the Randles-Sevcik equation, where the current is proportional to the concentration of the analyte.

The voltammetry process involves three electron transfer processes: diffusion, migration and convection. The diffusion current mechanism occurs when a negative potential is given, which will cause the platinum working electrode to be negatively charged so that the positively charged Dy^{3+} will be deposited on the platinum working electrode, or a reduction reaction occurs, thus becoming Dy^{2+}. Migration and convection were minimized by not stirring and by keeping a constant temperature so that only the diffusion current process occurs.

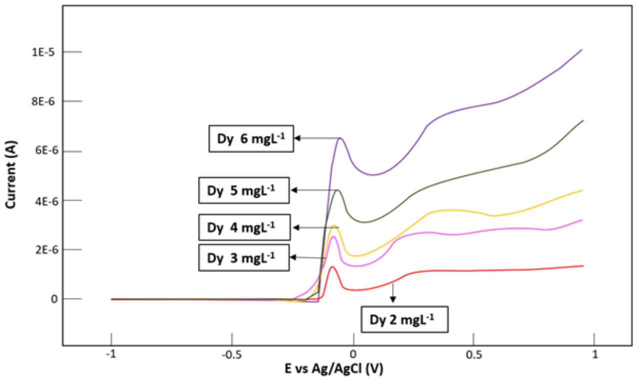

Fig 8. Voltammogram of various concentrations of Dy in acetonitrile, from 2 to 6 mg L^{-1} (potential range: −1.0 V to +1.0 V, deposition potential: −1.0 V, deposition time: 83.64 s, amplitude modulation: 0.0929 V, and scan rate: 0.05 V/s).

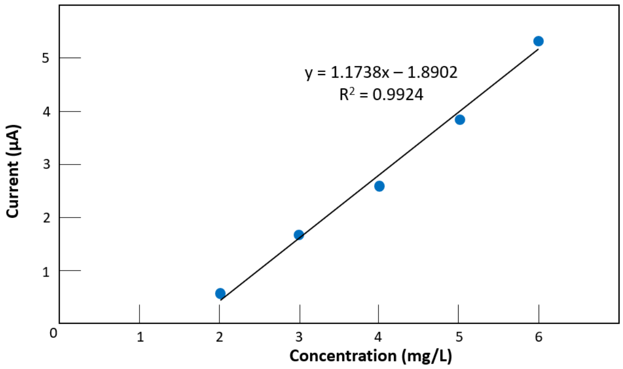

Fig 9. Calibration curve of Dy in acetonitrile from 2 to 6 mg L^{-1} (deposition potential: −1.0 V, deposition time: 83.64 s, amplitude modulation: 0.0929 V, and scan rate: 0.05 V/s).

Table 4
Result comparison with the previous works

Method	Result
A Study of Green Electro-Analysis Conducted by Experimental Design Method for Detection of Samarium as Complex with Diethylenetriamine Penta Acetic Acid (DTPA) (Wyantuti *et al.*, 2018a)	LoD: 24.44 mg L^{-1} LoQ: 91.53 mg L^{-1} Solvent: NH_4Cl Not yet selectively distinguish the current of Sm, Eu and Dy
Application of Experimental Design by Differential Pulse Voltammetry for Determination of Rare Elements as Complexes with Diethylenetriaminepentaacetic Acid (DTPA) (Wyantuti *et al.*, 2019)	LoD: 27.11 mg L^{-1} LoQ: 92.33 mg L^{-1} Solvent: NH_4Cl Not yet selectively distinguish the current of Sm, Eu, Dy
This Work	LoD: 0.6462 mg L^{-1} LoQ: 2.1419 mg L^{-1} Solvent: CH_3CN Not yet selectively distinguish the current of Eu and Dy

As shown in Figure 9, the current response is obtained by calculating the linear regression, producing the equation y = 1.1738x - 1.8902. The correlation coefficient (R) is 0.9924, which indicated that the linear regression equation could be used for the determination of analytical parameters. The analytic parameters could then be determined, namely accuracy, precision, LoD and LoQ.

Determination of the analytical parameters is carried out to ensure and confirm that the voltammetric method is suitable and can be used for analysis. The average value for precision was 99.97%, while the LoD and LoQ values were 0.6426 mg L^{-1} and 2.1419 mg L^{-1}, respectively. The recovery (%R) of Dy was 93.62%.

4. Conclusion

The optimum potential deposition, deposition time and amplitude modulation conditions for determining Dy by differential pulse voltammetry, based on the Box-Behnken design, are -1.0 V, 83.64 s and 0.0929 V, respectively. The performance of the Pt electrode for the determination of Dy by differential pulse voltammetry in the range concentration of 2 to 6 mg L^{-1} shows a recovery value of 93.62% and an average precision value of 99.97%, while the LoD value was 0.6426 mg L^{-1} and the LoQ was 2.1419 mg L^{-1}.

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