

Full Paper

Implementation of Steepest Ascent and Box-Behnken Approaches for Detecting Dysprosium in Acetonitrile Solution via Differential Pulse Voltammetry

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Abstract: Dysprosium (Dy) is considered an important Rare Earth Element (REE) material in modern technology. However, due to its analogous chemical properties to other REEs, differentiating it within mixtures proves to be a challenging endeavor. Voltammetry has emerged as an alternative method for Dy determination, offering heightened sensitivity and fast analysis time. The selection of acetonitrile as the solvent is based on its broad potential range and exceptional conductivity. Additionally, the pursuit of optimal conditions through experimental design plays a pivotal role in identifying specific targets within mixtures. The combination of these methods is assumed to provide a satisfactory detection result. In this study, the Steepest Ascent and Box-Behnken designs were employed to optimize the conditions for Dy determination. The parameters subject to optimization included deposition potential, deposition time, and amplitude modulation. The outcome of this optimization process revealed the optimal conditions for Dy measurement via differential pulse voltammetry which are a deposition potential of -1.5171 V, deposition time of 76.0898 s, and amplitude modulation of 0.0860 V. Under these optimum conditions, the determination of Dy yielded a recovery rate of 99.47%, an accuracy of 97.06%, and a precision of 95.19%. Furthermore, the detection limit and quantitation limit values were found to be 2.1223 mg/L and 7.0744 mg/L, respectively. Moreover, the qualitative voltammetry result provides an insight into distinguishing Dy from Eu in the mixture.

Keywords: Differential Pulse Voltammetry; Steepest Ascent; Box-Behnken; Dysprosium; Acetonitrile

1. INTRODUCTION

Voltammetric methods involve the application of a potential difference between a working electrode and a reference electrode in an electrochemical cell. By varying the applied potential, information about the electrochemical behavior of the analyte can be obtained [1,2]. This information includes the identity and quantity of species present, the reduction/oxidation potentials of the species, and the kinetics of the electron transfer reactions. Different voltammetric techniques, such as square wave voltammetry, cyclic voltammetry, and differential pulse voltammetry, can be used to investigate different electrochemical processes [3-5]. These techniques are widely used in many areas of research, including analytical chemistry, materials science, and biochemistry, for the detection, identification, and quantification of analytes. The versatility and sensitivity of voltammetric techniques make them a valuable tool in many scientific fields [6,7].

To the best of our knowledge, the voltammetric method has also given alternative tools for scientists for the detection of Rare Earth Elements (REE's) [8-10]. As we know, the similarity in properties between each element in REEs makes their determination even more difficult and complicated. This can be exacerbated if there is a mixture with other REEs. Several analytical methods can be used to analyze the mixture, such as ICP-MS [11], ICP-AES [12], RLS [13], capillary electrophoresis [14], and XRF [15]. However, this method requires a long analysis time and is relatively expensive [16, 17]. Thus, the voltammetric method is developed to determine the REE element in a mixture without chemical separation.

Dysprosium (Dy) is considered as an important REE since its application involves magnet [18], nuclear reactors [19], lighting [20], catalyst [21], glass and ceramics [22], and data storage [23]. It is important to note that while dysprosium has these valuable applications, but its availability can be limited. So far, the Dy determination using voltammetry has been carried out. Determination of dysprosium using aquamili-Q with NH_4Cl as the electrolyte solution by DPV but Dy in the REE mixture could not be determined because the standard reduction potential value was the same as the other medium group REEs. The determination of Dy by differential pulse voltammetry with the organic solvent acetonitrile and the Box-Behnken experimental design has been carried out but has not been able to determine dysprosium in mixtures of other rare earth elements [24,15].

In the analysis using voltammetry, the analyte was analyzed in an acetonitrile solvent. Acetonitrile is an organic solvent with a wide potential range, and high dielectric constant, which allows it to dissolve metals, and is commonly used in electrochemical systems for electrodeposition of nickel or other metals [26]. Acetonitrile has a potential range of -2.6 V to +3.5 V, providing a potential window of 6.1 V [27]. When compared to methanol, DMSO, and DMF, acetonitrile is more polar with better electrodeposition results [28].

To achieve the optimal conditions for Dysprosium (Dy) determination, the rigorous optimization process targeting key factors, namely deposition potential, deposition time, and

amplitude modulation. This optimization endeavor leveraged the Steepest Ascent and Box-Behnken experimental designs. The Steepest Ascent approach was instrumental in pinpointing the most favorable conditions. It employs a gradient-based methodology, directing us toward conditions deemed optimal [29]. On the other hand, the Box-Behnken design was employed to harness the synergistic interactions between these parameters while maintaining a shorter processing time [25,30,31]. Notably, the Box-Behnken design necessitates fewer experimental trials compared to the Central Composite Design method, rendering it a more efficient choice [32].

In this research, the determination of Dy using differential pulse voltammetry (DPV) in conjunction with acetonitrile as the solvent was carried out. Moreover, the Box-Behnken and Steepest Ascent designs were employed to establish the optimal conditions for accurately measuring Dy within a mixture. The outcomes of this study are expected to offer valuable insights into enhancing the detection of REEs in complex mixtures.

2. EXPERIMENTAL SECTION

2.1. Materials and Apparatus

The materials used in this study included nitric acid 65% (HNO₃, Merck), acetonitrile (Merck), dysprosium oxide (Dy₂O₃, 99.9%, Aldrich), europium oxide (Eu₂O₃ 99.9%, Aldrich), gadolinium oxide (Gd₂O₃ 99.9%, Aldrich), and samarium oxide (Sm₂O₃ 99.9%, Aldrich). The tools used in this study included various glassware, Pt working electrodes, Ag/AgCl reference electrodes, Pt wire auxiliary electrodes, magnetic stirrers, digital analytical balances (Sartorius), potentiostats (Metrohm® µAutolab type III) connected to a computer with ANOVA 7.0.0 and Minitab 17.1 programs, RStudio program, and SEM-EDX (Hitachi TM3030 Swift ED3000).

2.2. Methods

2.2.1. Preparation of Dysprosium Oxide (Dy₂O₃) Stock Solution at 1000 mg/L

A solid mass of 0.11473 g of Dy₂O₃ was dissolved in a 50 mL beaker glass with the gradual addition of 65% nitric acid, while continuously stirring with a magnetic stirrer. The mixture was heated on a hot plate until homogeneity was achieved. The Dy₂O₃ solution in the acid was then transferred to a 100 mL volumetric flask and diluted with deionized water to approximately half of the flask's volume, followed by thorough mixing. Additional deionized water was added to reach the calibration mark, and the solution was homogenized. This process resulted in a Dy stock solution of 1000 mg/L, which would later be further diluted using acetonitrile to create various concentration levels.

2.2.2. Background Current Measurement

A 10 mL volume of acetonitrile was prepared into the voltammetry cell. The three electrodes were connected to a potentiostat, and differential pulse voltammetry (DPV) measurements were performed over a potential range of -1.5 V to +1.0 V, with a deposition potential of -1.5 V, a deposition time of 80 s, an amplitude modulation of 0.10 V, and a scan rate of 0.05 V/s.

2.2.3. Dysprosium Current Measurement

A 10 mL portion of the 20 mg/L Dy solution in acetonitrile was pipetted and introduced into the voltammetry cell, with the three electrodes connected to a potentiostat. The DPV measurements were conducted over the potential range of -1.5 V to +1.0 V, using a deposition potential of -1.5 V, a deposition time of 80 s, an amplitude modulation of 0.10 V, and a scan rate of 0.05 V/s.

2.2.4. Deposition of Dy in Acetonitrile onto Platinum (Pt) Surface

The deposition of 30.0 mg/L Dy solutions in 50%, 75%, and 100% acetonitrile, onto the Pt electrode was accomplished via cyclic voltammetry. The deposition was carried out under the specific conditions: a deposition potential of -1.5 V, a deposition time of 80 s, a potential range of -1.5 V to +1.0 V, an amplitude modulation of 0.10 V, and a scan rate of 0.05 V/s.

2.2.5. Analysis of the Pt Surface Using Scanning Electron Microscopy-Energy Dispersive X-Ray (SEM-EDX)

The working electrode, on which Dy was deposited in 50%, 75%, and 100% acetonitrile, underwent analysis using the Hitachi TM3030 Swift ED3000 instrument for EDX analysis. The surface morphology of the platinum working electrode with Dy deposits was observed under a voltage of 15 kV and at a magnification of 120 times.

2.2.6. Dysprosium Measurement with Optimization Results from Steepest Ascent and Box-Behnken

The factors identified as influential—deposition potential, deposition time, and amplitude modulation—showed a positive effect on the peak current response of Dysprosium. These selected factors were then optimized using the Steepest Ascent method. A 10 mL volume of the 20 mg/L Dy solution in acetonitrile was pipetted into the voltammetry cell, and analysis was conducted over the Steepest Ascent result range, considering factors such as deposition potential (-2.0 V to -1.0 V), deposition time (40 s to 120 s), and amplitude modulation (0.05 V to 0.1 V). Subsequently, the Steepest Ascent result range was further optimized using the Box-Behnken design, as shown in Table 1.

Table 1. Three different levels of factors selected for Box-Behnken Design optimization

Factors	Level		
	-1	0	+1
Deposition potential / V	-1.5171	-1.5168	-1.5165
Deposition time / s	76.0591	76.1315	76.2040
Amplitude modulation / V	0.0858	0.08592	0.08603

2.2.7. Determination of Dy in a Mixture Containing Sm, Eu, and Gd

A 10 mL aliquot of the mixture containing Sm, Eu, Gd, and Dy in acetonitrile was pipetted and introduced into the voltammetry cell. This yielded a 10 mL solution of the Sm, Eu, Gd, and Dy mixture, which was subjected to differential pulse voltammetry (DPV) measurements. The three electrodes were connected under the optimum conditions established for Dy using the Box-Behnken design, encompassing a potential range of -1.5 V to +1.0 V, a deposition potential of -1.51712 V, a deposition time of 76.0892 s, an amplitude modulation of 0.086032 V, a potential step of 0.02 V, and a scan rate of 0.05 V/s.

2.2.8. Calibration Curve

A 10 mL volume of a 20 mg/L Dy solution in acetonitrile was pipetted into the voltammetry cell, and DPV measurements were conducted while connecting the three electrodes under the established optimum conditions for Dy using the Box-Behnken design. This process was repeated for Dy solutions of 30, 40, 50, and 60 mg/L. Additionally, a 10 mL aliquot of a 30 mg/L Dy solution in acetonitrile was pipetted into the voltammetry cell, and cyclic voltammetry measurements were performed over a potential range of -1.5 V to +2.0 V, with a scan rate of 0.05 V/s. This procedure was repeated for Dy solutions of 40, 50, 60, and 70 mg/L.

3. RESULTS AND DISCUSSION

3.1. Investigation of Acetonitrile and Dy current response

This study examines the current response of acetonitrile and Dy within a specified potential range of -1.5 V to +1.0 V, a deposition potential of -1.5 V, a deposition duration of 80.0 s, a potential step of 0.02 V, and a scanning rate of 0.05 V/s. The primary objective is to ascertain whether acetonitrile exerts any influence on the current response of dysprosium. As shown in Fig.1, within this designated operational range, it is evident that acetonitrile fails to elicit any discernible peaks, with only the dysprosium current response exhibiting peaks. This observation suggests that acetonitrile, under these operational conditions, does not undergo a redox reaction, thus remaining devoid of any current response peaks.

Furthermore, the dysprosium solution demonstrates a current response of 4.4985 A at a potential of -0.68039 V. While the Nernst equation predicts a reduction potential for Dy at -3.45346 V, it is important to note that the background current and measurements for dysprosium were conducted at a potential of -1.5 V. This choice of potential was motivated by its ability to yield a significantly higher current response during experimentation.

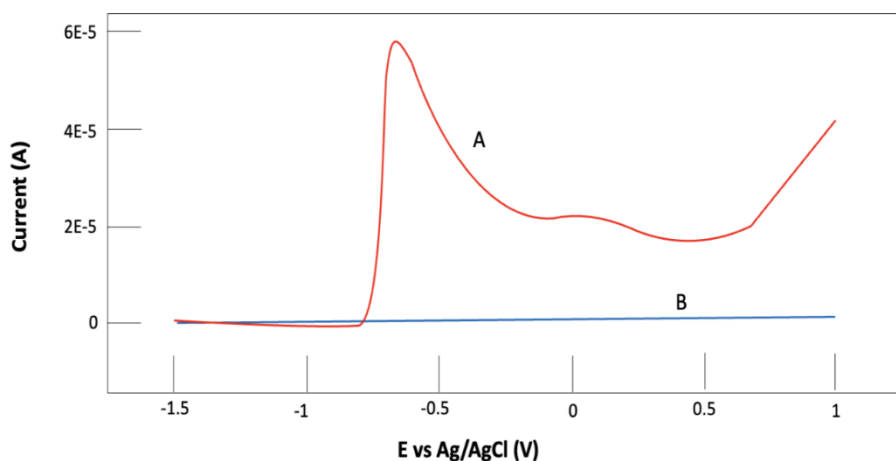


Figure 1. Voltammogram of Solution (A) Dy 20.0 mg/L and (B) Acetonitrile under Differential Pulse Voltammetry (DPV) conditions within the potential range of -1.5 V to +1.0 V, deposition potential -1.5 V, deposition time 80 s, potential step 0.02 V, and scanning rate 0.05 V/s.

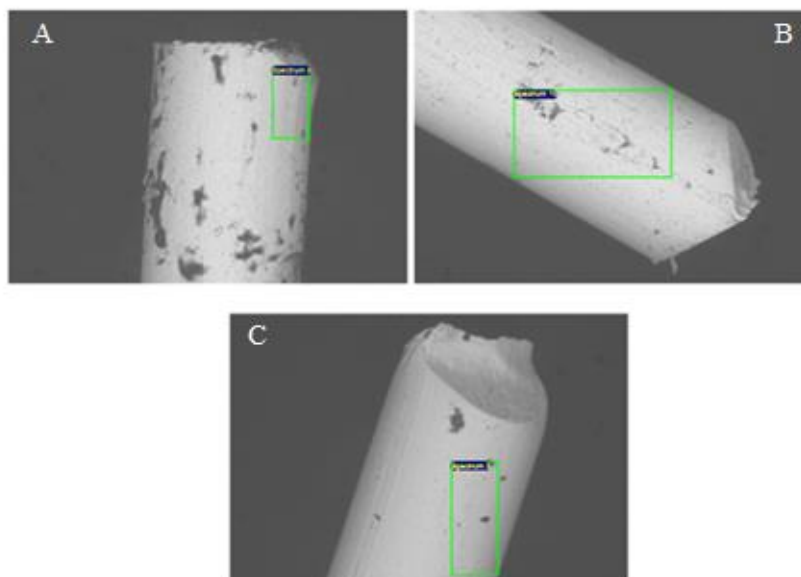


Figure 2. SEM results Pt surface at 120x magnification of (A) Dy with 50% acetonitrile, (B) Dy with 75% acetonitrile, and (C) Dy with 100% acetonitrile

3.3. Optimization of the analysis factors with the steepest ascent.

The steepest ascent method was carried out in this research due to the preliminary study confirmi that the lack-of-fit value > 0.05 . Then, the range is selected for deposition potential factor (-2.0 V to -1.0 V), deposition time (40 s to 120 s), and amplitude modulation (0.05 V to 0.1 V). From the steepest ascent, eleven measurement designs of 20 mg/L Dy in acetonitrile were produced and measured by DPV, as shown in Table 2. The current response obtained was plotted as shown in Figure 4.

Table 2. Current response of selected condition by steepest ascent

No	Deposition potential (V)	Deposition time (s)	Amplitude modulation (V)	Current (μA)
1	-1.5180	76.42	0.08500	3.6147
2	-1.5177	76.348	0.08520	3.7375
3	-1.5174	76.276	0.08541	3.8587
4	-1.5171	76.204	0.08560	4.0362
5	-1.5168	76.1311	0.08582	4.5063
6	-1.5165	76.0591	0.08603	4.3477
7	-1.5162	75.9871	0.08623	4.2352
8	-1.5159	75.9151	0.08644	4.1378
9	-1.5156	75.8431	0.08665	3.941
10	-1.5153	75.7711	0.08685	4.2377
11	-1.5150	75.6982	0.08706	3.9264

As shown in Figure 4, it is known that points 1 to point 5 have increased and the next point has decreased. From these 11 points, three points will be taken which will be re-optimized using the Box-Behnken method. To get the maximum current response, the midpoint with the highest current response is used. Then the three points chosen are points 4, 5, and 6.

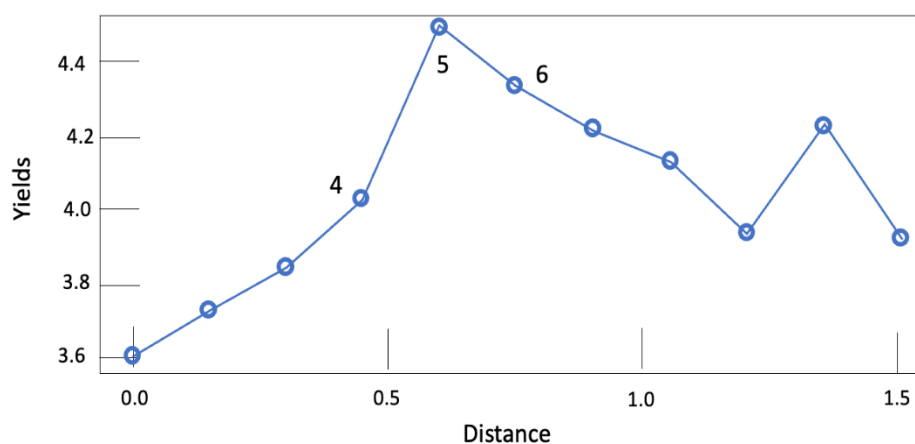


Figure 4. Plot diagram of Dy 20.0 mg/L measurement response using the steepest ascent method

3.4. Optimization of the analysis factors with Box-Behnken.

As shown in Table 3, the limit for each factor used in optimization with BBD and the results of the optimization. The limit of each factor used in this optimization utilizes the range of factors resulting from the steepest ascent optimization. In the Minitab 17 program, the Box-Behnken design uses 3 factors with 3 repetitions. The result of the measurement is the current response which will be processed and analyzed by the Minitab 17 program to obtain optimum conditions for Dy measurements and the regression equation. This equation will show the influence caused by each factor. This equation is shown in Equation 1.

$$Y = 4126946 + 4729610 X_1 + 6504 X_2 - 183252 X_3 + 1226052 X_1 * X_1 - 30.1 X_2 * X_2 - 8774782 X_3 * X_3 + 1379 X_1 * X_2 - 12975255 X_1 * X_3 + 2022 X_2 * X_3 \dots \dots \dots (1)$$

Note that Y is the current response, X₁ is the deposition potential factor, X₂ is the deposition time, and X₃ is the amplitude modulation.

From the regression equation, it is known that X₁ and X₂ have positive coefficients, which means that the deposition potential and deposition time factors have an influence on increasing the current response. While X₃ has a negative coefficient, which means that the amplitude modulation factor has influence to decreasing the current response.

Table 3. Experimental parameters of Box-Behnken Design and resulted in optimum conditions

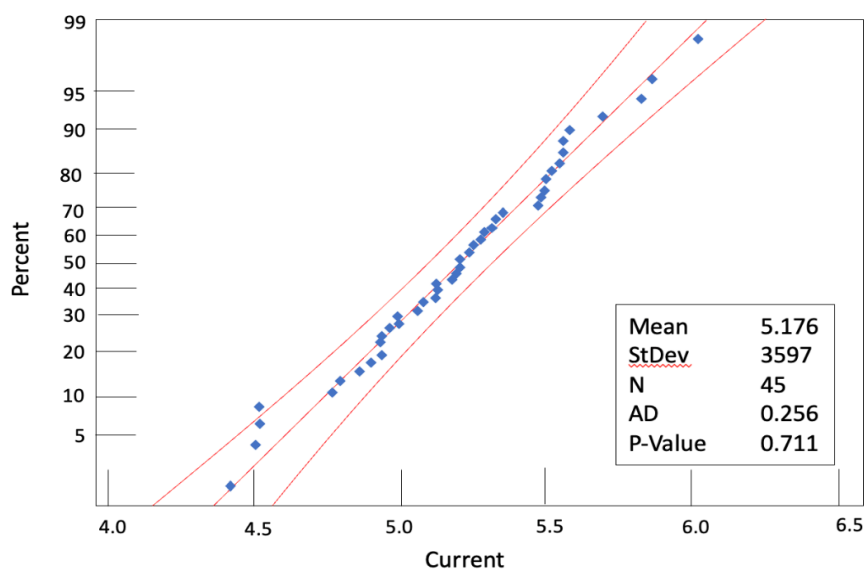
Factors	Level			Optimum conditions
	-1	0	+1	
Deposition potential (V)	-1.5171	-1.5168	-1.5165	-1.5171
Deposition time (s)	76.0591	76.1315	76.2040	76.0892
Amplitude modulation (V)	0.08582	0.08592	0.08603	0.08603

In addition to the regression equation, an ANOVA table is also shown in Table 4. As shown in Table 4, if the *p*-value of a factor is more than 0.05, then that factor has no significant effect on the current response. In contrast, if the value is less than 0.05, then this factor has a significant influence on the current response. Judging from the data in Table 4, it is known that the deposition potential has a *p*-value of 0.104, which means that the deposition potential factor has no significant effect on the resulting current response. The deposition time and amplitude modulation factors have *p*-values of 0.001 and 0.000 which are below 0.05, this means that these two factors have a significant influence on the current response.

To find out whether the model used is appropriate or not, a Lack-of-Fit test is carried out. Since the *p*-value is 0.024 indicates that there is a deviation or inaccuracy of the linear model. In addition to the lack of fit test, a residual analysis was carried out to show the adequacy of the model. Residual analysis is used to check whether the residuals from the model are equally distributed. This result is shown in Figure 5.

Table 4. ANOVA (Analysis of Variance) of optimization results of Box-Behnken design

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Model	9	4.09871	0.45541	9.99	0.000
Linear	3	1.71094	0.57031	12.51	0.000
Deposition Potential	1	0.12721	0.12721	2.79	0.104
Deposition Time	1	0.66281	0.66281	14.54	0.001
Amplitude modulation	1	0.92093	0.92093	20.20	0.000
Square	3	0.52208	0.17403	3.82	0.018
Deposition Potential*Deposition Potential	1	0.12440	0.12440	2.73	0.107
Deposition Time*Deposition Time	1	0.27711	0.27711	6.08	0.019
Amplitude Modulation*Amplitude modulation	1	0.09599	0.09599	2.11	0.156
2-Ways Interaction	3	1.86569	0.62190	13.64	0.000
Deposition Potential*Deposition Time	1	0.01035	0.01035	0.23	0.637
Deposition Potential*Amplitude modulation	1	1.85260	1.85260	40.64	0.000
Deposition Time*Amplitude modulation	1	0.00273	0.00273	0.06	0.808
Error	35	1.59554	0.04559		
Lack-of-Fit	3	0.40113	0.13371	3.58	0.024
Total	44	5.69425			

**Figure 5.** Box-Behnken Normality plot

As illustrated in Figure 5, the normal distribution curve of the hypothetical residuals accounts for the p-value of 0.711. According to the normality test hypothesis, if the null hypothesis (H_0) is accepted with a p-value ≥ 0.05 , it indicates that the result follows a normal distribution. Therefore, it can be concluded that H_0 is accepted, indicating a normal distributed.

This finding demonstrates that residuals are normally distributed and statistically significant. Consequently, the optimal conditions for Dy detection include a deposition potential, deposition time, and amplitude modulation of -1.5171 V, 76.0892 s, and 76.0892 V, respectively.

3.5. Determination of Dy in Mixtures of the Rare Earth Elements Sm, Eu, Gd, and Dy.

The rare earth elements are usually found in monazite forms. A monazite contains several different types of elements. According to BATAN, the Dy content in a monazite is 0.37%, while Gd is 0.58%, Eu is 0.01% and Sm is 4.21% [24]. Simulations were carried out to determine Dy in a mixture of Sm, Gd, Dy, and Eu according to the ratio of monazite.

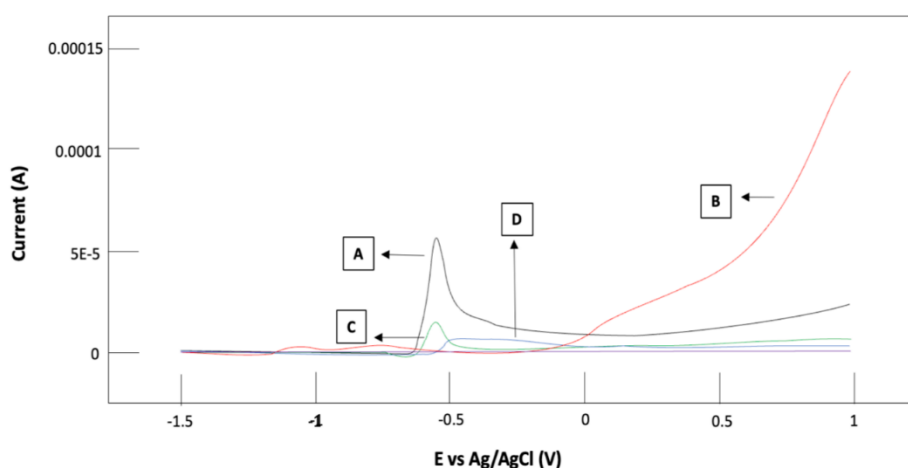


Figure 6. Voltamogram of (A) mixture of Sm (200.0 mg/L), Gd (25 mg/L), Dy (15 mg/L), Eu (0.5 mg/L); (B) Sm 400.0 mg/L; (C) Gd 50.0 mg/L; (D) Dy 30.0 mg/L; (E) Eu 1.0 mg/L by DPV under condition a potential range of -1.5 V to $+1.0$ V, deposition potential -1.5171 V, deposition time 76.0892 s, and amplitude modulation 76.0892 V, potential step 0.02 V, and scan rate 0.05 V/s

As shown in Figure 6A, the current response of the mixture was similar to the response of single Gd elements and Dy elements. While the current response for Sm and Eu elements was not observed. This result indicates that Dy cannot be determined in the mixture with monazite ratio. To simplify the analysis, a comparison is made between the two elements.

The simulation was carried out with a comparison of the concentrations of Dy (30 mg/L) and Gd (50 mg/L) under the optimum conditions. The comparison of the concentrations of Dy and Gd used was magnified by 10 times, because the limit for measuring the current Dy was predicted at a concentration of 20.0 mg/L. As shown in Figure 7, it is observed that a single Dy current peak and a single Gd current peak appear. Therefore, it can be concluded that Dy cannot be determined in a mixture of Gd.

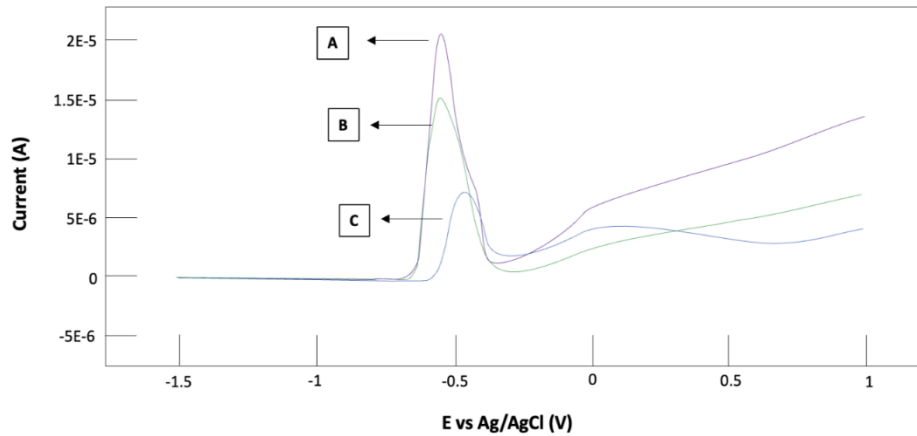


Figure 7. Voltammograms of (A) a mixture of Dy (30 mg/L) and Gd (50 mg/L); (B) Gd 50.0 mg/L; (C) Dy 30.0 mg/L by DPV under condition a potential range of -1, 5 V to +1.0V, deposition potential -1.51712 V, deposition time 76.0892 s, and amplitude modulation 0.086032 V, potential step 0.02 V, and scan rate 0.05 V/s.

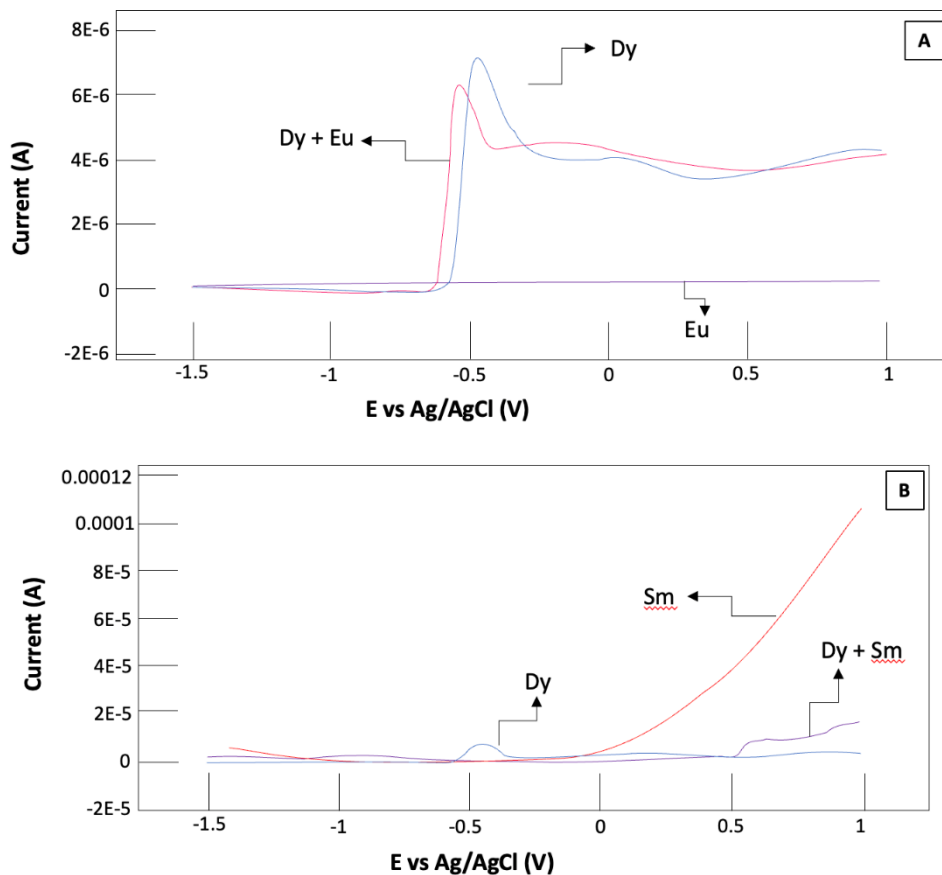


Figure 8. Voltammogram of (A) a mixture of Dy 30 mg/L and Eu 1 mg/L; (B) a mixture of Dy 30 mg/L and Sm 400 mg/L by DPV under condition a potential range of -1.5 V to +1.0V, deposition potential -1.5171 V, deposition time 76.0892 s, and amplitude modulation 0.08603 V, potential step 0.02 V, and scan rate 0.05 V/s

For the mixture of the elements Dy and Eu, a ratio of 30:1 was used with a concentration of Dy of 30 mg/L while Eu was 1 mg/L under the optimum conditions. As shown in Figure 8(A), it is observed that the visible current peak is only a single current Dy peak. It can be interpreted that a single Dy can be determined from Eu. It was also observed that the mixed current peaks Dy and Eu were below the current peak Dy and above the Eu current response. Probably this is due to dilution during the preparation of the Dy and Eu mixture.

As shown in Figure 8(B) it is observed that the visible current response peak is only from a single current Dy peak. The Sm peak cannot be observed because the current response does not produce a peak. The mixture of Dy and Sm does not show a clear current response peak. It can be interpreted that the presence of Dy can not detected in a mixture with Sm.

3.6. Dy calibration curve

A calibration curve was prepared using various concentrations of 20, 30, 40, 50, and 60 mg/L under the optimum condition of Dy using the DPV method, as shown in Figure 9(A). It can be observed that the higher the concentration of the analyte being analyzed, the higher the peak current obtained. This is because Dy(III) are reduced or deposited on the surface of the Pt working electrode as the diffusion current increases. This current response follows the Rendless-Sevcik equation where the current generated is directly proportional to the concentration of the analyte being tested. Then a linear regression calculation is performed and the resulting equation is $y = 0.4268x - 5.725$ with $R^2 = 0.9950$. The correlation coefficient (R) obtained is 0.9950 which concludes that the linear regression equation can be used to determine analytical parameters. The accuracy and precision values obtained are 97.0589% and 95.1919%, respectively. The detection limits and quantitation limits are 2.1223 mg/L and 7.0744 mg/L, respectively, meanwhile, the recovery (%R) of Dy is 99.470%.

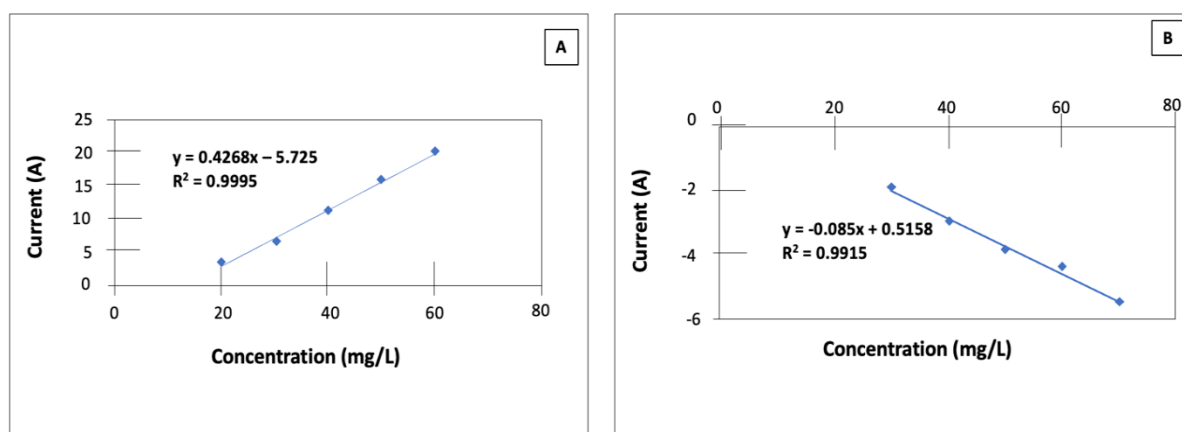


Figure 9. Dy calibration curve by (A) DPV and (B) CV with various concentrations

As shown in Figure 9(B), a calibration curve of Dy by cyclic voltammetry under optimum conditions was carried out. The utilization of cyclic voltammetry is applied to detect the presence of an electrochemical reaction of an electroactive compound on the electrode surface. The current response obtained was carried out by calculating the linear regression measurement results with cyclic voltammetry and the resulting equation $y = -0.085x + 0.5158$ with $R^2 = 0.9915$. The accuracy and precision values obtained are 96.950% and 94.0710%, respectively. The detection limit (LoD) was 5.6942 mg/L and the quantitation limit (LoQ) was 18.9807 mg/L, while the recovery (% R) Dy was 98.050%.

4. CONCLUSION

The optimal conditions found by utilizing the Steepest Ascent and Box-behnken designs for measuring Dy using DPV are deposition potential of -1.5171 V, deposition time of 76.0892 s, and amplitude modulation of 0.0860 V. Employing the Steepest Ascent and Box-behnken designs for DPV analysis within a concentration range of 20.0 to 60.0 mg/L on a mixture containing Dy along Gd, Sm, and Eu, yielded promising outcomes. The recovery rate attained was 99.47%, with average accuracy and precision of 97.06% and 95.19%, respectively. Additionally, the detection and quantitation limits were determined as 2.1223 mg/L and 7.0744 mg/L, respectively. It was also possible to specifically identify Dy in the presence of Eu within the mixture.

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Declarations of interest

The authors declare no conflict of interest in this reported work.

REFERENCES

- [1] Y. Lu, X. Liang, C. Niyungeko, J. Zhou, J. Xu, and G. Tian, *Talanta*, 178 (2018) 324.
- [2] S. Sawan, R. Maalouf, A. Errachid, and N. Jaffrezic-Renault, *TrAC Trends in Anal. Chem.* 131 (2020) 116014.
- [3] B. J. Venton, and D.J. DiScenza, *Electrochemistry for Bioanalysis*, Elsevier (2020).
- [4] F. Scholz, *Chem. Texts* 1 (2015)17.
- [5] Scholz F, *Electroanalytical methods. Guide to experiments and applications*, Springer (2010).

- [6] A. B. Monnappa, J. G. Manjunatha, and A. S. Bhatt, *ACS Omega* 5 (2020) 23481.
- [7] S. Baluta, F. Meloni, K. Halicka, A. Szyszka, A. Zucca, M. I. Pilo, and J. Cabaj. *RSC Adv.* 12 (2022) 25342.
- [8] M. Grabarczyk, M. Fialek, and E. Wlazlowska, *Molecules* 28 (2023) 7755.
- [9] M. Makombe, C. v. d. Horst, B. Silwana, E. Iwuoha, and V. Somerset, *Environ.* 5 (2018) 112.
- [10] J. Li, S. Liu, X. Mao, P. Gao, and Z. Yan, *J. Electroanal. Chem.* 561 (2004) 137.
- [11] H. T. Mnculwane, *Analytica* 3 (2022) 135.
- [12] N. Bahramifar, and Y. Yamini, *Anal. Chim. Acta* 540 (2005) 325.
- [13] S. Sun, X. Wu, J. Yang, L. Li, and Y. Wang, *Spectrochim. Acta A* 60 (2004) 261.
- [14] Y. Sun, *J. Chromatogr. A* 1048 (2004) 245.
- [15] P. Tack, E. D. Pauw, B. Tkalcec , M. Lindner, B. Bazi, and B. Vekeman, *Earth Planets and Space*, 74 (2022) 146.
- [16] B. Zawisza, K. Pytlakowska, B. Feist, M. Polowniak, A. Kita, and R. Sitko, *J. Anal. At. Spectro.* 26 (2011) 2373.
- [17] M. R Ganjali, R. Zare-Dorabei, and P. Norouzi, *Sens. Actuators B Chem.* 143 (2009) 233.
- [18] F. S. Santana, M. Perfetti, M. Briganti, F. Sacco, G. Poneti, E. Ravera, J. F. Soares, and R. Sessol, *Chem. Sci.* 13 (2022) 5860.
- [19] V. D. Risovany, A.V. Zakharov, E.M. Muraleva, V.M. Kosenkov, and R.N. Latypov. *J. Nucl. Mater.* 355 (2006) 163.
- [20] D. Mara, F. Artizzu, J. Goura, M. Jayendran, B. Bokić, B. Kolaric, T. Verbiest, and R. V. Deun, *J. Lumin.* 243 (2022) 118646.
- [21] K. Nava Andrade, G.G. Carbajal Arízaga, E. Bautista, and V. Rodríguez-González, *J. Taiwan Inst. Chem. Eng.* 113 (2020) 293.
- [22] M. Monisha, V. Hegde, S.K. Melanthota, N. Mazumder, M.I. Sayyed, H.A. Ghamdi, A.H. Almuqrin, and S.D. Kamath, *Mater. Chem. Phys.* 274 (2021) 125157.
- [23] P. Evans, D. Reta, G.F.S. Whitehead, N.F. Chilton, and D.P. Mills, *J. Am. Chem. Soc.* 141 (2019) 19935.
- [24] S. Wyantuti, U. Pratomo, S.A. Asyifadewi, Y.W. Hartati, and H.H. Bahti, *Int. J. Renew. Energy Dev.* 10 (2021) 191.
- [25] S. Wyantuti, J. Iskandar, R. P. Fauzia, and H.H. Bahti, *NHC* 40 (2023) 13.
- [26] K. Gong, Q. Fang, Gu. S. Huang, S. F. Y. Li, and Y. Yan, *Energy Environ. Sci.* 8 (2015) 3515.
- [27] U. Pratomo, Y. S. Rahayu, A. Hardianto, Y. W. Hartati, H. H. Bahti, and S. Wyantuty, *J. Kim. Valensi* 8 (2022) 69.
- [28] S. Wyantuti, U. Pratomo, L.A. Manullang, D. Hendrati, Y.W. Hartati, and H.H. Bahti, *Heliyon* 7 (2021) e06602.

- [29] R. G. Brereton, *Steepest Ascent, Steepest Descent, and Gradient Methods*, Elsevier, Oxford (2009).
- [30] X.L. Yu, and Y. He. And Y. He, *Sci. Rep.* 7 (2017) 2789.
- [31] A. R. Zanganeh, *Anal. Methods* 14 (2022) 1623.
- [32] S. L. C. Ferreira, R. E. Bruns, H. S. Ferreira, G. D. Maltos, J. M. David, G. C. Brandao, E. G. P. da Silva, L. A. Portugal, P. S. dos Reis, A. S. Souza, and W. N. L. dos Santos, *Anal. Chim. Acta* 597 (2007) 179.