Jurnal Kimia Valensi, Vol 8(1), May 2022, 69-78
Available online at Website: http://journal.uinjkt.ac.id/index.php/valensi

The Effect of Acetonitrile Solvent on the Quantitative Determination of Europium (III) by Voltammetry and its Optimization using the Box-Behnken Design

Uji Pratomo, Yenny Setyo Rahayu, Ari Hardianto, Yeni Wahyuni Hartati, Husein Hernandi Bahti, Santhy Wyantuti*

Department of Chemistry, Faculty of Mathematics and Natural Sciences, Universitas Padjadjaran.
Jl. Raya Bandung Sumedang Km. 21, Jatinangor, Sumedang 45363. Telp/Fax : 022-7794391.

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

Received: September 2021; Revision: September 2021; Accepted: April 2022; Available online: May 2022

Abstract

There is often a drawback during the determination of Eu in aqueous solvents using the voltammetric method. The current signal from water can reduce that of the element, which causes difficulty while separating the Eu signal from other rare earth elements (REE). Therefore, this study used acetonitrile as a solvent due to its high electrical conductivity and wide potential range. The optimum conditions for the determination of Eu in acetonitrile using the Box-Behnken design include 74.56 seconds deposition time, 0.125 V amplitude modulation, and -2.0 V potential deposition. The platinum electrode's performance showed a recovery value of 98.91% and accuracy and precision (in %RSD) of 96.67% and 1.11%, respectively. Furthermore, detection and quantitation limits of 0.6 mg/L and 5.1 mg/L were recorded from the analysis. It concluded that the differential pulse voltammetry method was applied to determine the presence of Eu in acetonitrile.

Keywords: Acetonitrile, Box-Behnken design, differential pulse voltammetry, europium.

***DOI:** 10.15408/jkv.v8i1.22508*

1. INTRODUCTION

Europium (Eu) is the 63rd rare earth element with an abundance of 47.80% in the earth's crust and 0.01% in monazite. Furthermore, it is widely used commercially in modern industrial fields to produce laser materials (Sharma et al., 2014). Analysis of its presence in samples is often carried out using spectrometric methods, such as visible light spectrophotometry, which involves the formation of a complex compound between the Eu^{3+} ion and methylene blue (Bhattacharya et al., 2000). Another method is the application of atomic absorption spectrometry to determine europium hydroxide by coprecipitation technique (Soylak & Gokhan, 2006). The Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES) can also detect Eu in mixed samples of rare earth elements (Ohnishi et al., 2010). The last two methods have high sensitivity and selectivity, but they are very expensive to maintain and operate (Chien et al., 2006; Rajendran et al., 2008).

Consequently, the voltammetric method is a common alternative because it is fast, efficient, sensitive, inexpensive, and easy to use (Wyantuti et al., 2019). Voltammetry is an electrochemical method based on measuring current as a potential function. The working principle is that the electrode is polarized at a specific potential range, and the current is measured due to a reduction and oxidation reaction occurring on their surface (Skoog et al., 2014; Scholz & Lange, 1992). Wyantuti et al., 2018 reported that voltammetric determination of Eu was carried out using water as a solvent. However, it cannot be determined from a rare earth element mixture because their peak often occurs at the same standard reduction potential, which does not correspond to that of rare earth metals.

An alternative to water solvent is acetonitrile, which has a vast range of potential and a high dielectric constant. Hence, it can dissolve metals. Furthermore, it is commonly used in electrochemical systems for the electrodeposition of nickel (Zhu et al., 2010) and silver using a mixed solvent of water, acetonitrile, and TBAP (Mele et al., 2013). In a previous study, the solvent was also used to determine some rare earth metals (Wyantuti et al., 2021a; Wyantuti et al., 2021b; Wyantuti et al., 2021c). The Eu content was also assessed with acetonitrile using the voltammetric method in this study.

The optimum conditions for Eu measurement were determined through a series of experiments with the Box-Behnken design, which can optimize a minimum of 3 factors using the response surface method. Furthermore, this method is an experimental condition optimization technique that involves changing factors simultaneously and it is best used when the observed response is influenced. It was chosen along with the Box-Behnken design to determine the minimum area, which can be used to obtain the maximum current response. The optimized experimental factors were deposition time, amplitude modulation, and deposition potential (Ferreira et al., 2007; Bezerra et al., 2008).

Therefore, this study aims to determine the effect of acetonitrile solvent on the measurement of Eu and its mixture using the DPV method. Optimization of the measurement conditions was carried out through the Box-Behnken design. The electrode performance parameters, such as accuracy, precision, recoverability, detection limit, and quantification limit, were also assessed.

2. MATERIALS AND METHODS

Tools and Materials

The tools used consist of a platinum working electrode (Antam), Ag/AgCl reference electrode (eDAQ), platinum wire counter electrode (Antam), digital analytical balance (Sartorius), pH meter (Jenway 3505), Micropipette (Eppendorf), Scanning Electron microscope (JEOL JSM-750), as well as potentiostat (Metrohm® Autolab) connected to a computer with the ANOVA 7.0.0 program and Minitab 17.1. Subsequently, the materials used in this study include 65% nitric acid (HNO_3, merck), acetonitrile (CH_3CN, merck), 99.9% europium oxide (Eu_2O_3, Sigma Aldrich), 99.9% samarium oxide (Sm_2O_3, Sigma Aldrich), 99.9% gadolinium oxide (Gd_2O_3, Sigma Aldrich), and 99.9% dysprosium oxide (Dy_2O_3, Sigma Aldrich).

Preparation of Europium Oxide Stock Solution 1000 mg/L

A total of 0.2895 g of Eu_2O_3 solid was placed in a 50 mL beaker, and 65% HNO_3 was added dropwise. Subsequently, the solution was stirred with a magnetic stirrer and heated on a hot plate until the solute was completely dissolved. It was then placed in a 250 mL volumetric flask, and distilled water was added to the mark. The prepared 1.000 mg/L Eu stock solution was diluted to various concentrations using acetonitrile as the solvent.

Acetonitrile Background Flow Measurement

A total of 10 mL of acetonitrile was placed in a voltammetric cell, after which it was measured for DPV at a potential range of -2.5 V to +1.0 V, -2.5 V deposition potential, 80 seconds deposition time, 0.1 V amplitude modulation, and 0.05V/s scan rate.

Europium Electrodeposition in 75% and 100% Acetonitrile on Pt Working Electrode by Cyclic Voltammetry (CV)

10 mL Eu solution in 75% acetonitrile was pipetted and placed in a voltammetric cell. Subsequently, electrodeposition was carried out by CV at a potential range of -2.0 to 1 V, and a scanning rate of 0.05 V/s. The same procedure was then repeated for the Eu solution in 100% acetonitrile.

Europium Current Measurement with 75% and 100% Acetonitrile by Differential Pulse Voltammetry (DPV)

A 10 mL Eu solution in 75% acetonitrile was pipetted and placed in a voltammetric cell. The DPV was then measured in the potential range of -2.5 V to +1.0 V, -2.5 V deposition potential, 80 seconds deposition time, 0.1 V amplitude modulation, and 0.05V/s scan rate. The procedure was then repeated for Eu solution in 100% acetonitrile.

Surface Analysis of Platinum Working Electrodes Before and After Electrodeposition

The surface of the Pt working electrode was observed under a Scanning Electrode Microscope (JEOL JSM-750). Furthermore, surface morphology analysis of the electrodes before and after Eu deposit at various concentrations of 75% and 100% acetonitrile and 100% was carried out at a voltage of 5 Kv with 4.300 x magnification.

Europium Current Response Measurement using Box-Behnken Design

The selected factors include deposition potential and time, as well as amplitude modulation, which had a positive effect on the response of the peak Eu current. Furthermore, they were optimized using the Box-Behnken design, and the measurement of the element by DPV was based on the results with 3 factors and 3 levels.

Current Response Measurement of Eu, Sm, Gd, and Dy

2.5 mL of 10 mg/L Eu solution was pipetted into a voltammetric cell. Subsequently, the three electrodes were connected to a potentiostat and then measured by DPV with a potential range of -2.0 V to +1.0 V, -2.0 V deposition potential, 74.56 seconds deposition time, 0.125 V amplitude modulation, and 0.05 V/s scan rate. The procedure was repeated for the Dy, Sm, and Gd solutions.

Measurement of Mixture (Eu, Sm, Gd, and Dy) at Optimum Condition Eu

A total of 10 mL Eu, Sm, Gd, and Dy solutions were pipetted into a voltammetric cell. The three electrodes were then connected to a potentiostat and measured by DPV with a potential range of -2.0 V to +1.0 V, -2.0 V deposition potential, 74.56 seconds deposition time, 0.125 amplitude modulation, and 0.05 V/s scan rate.

Calibration curve creation

A total of 10 mL Eu solution with concentrations of 2, 4, 6, 8, and 10 mg/L in 100% acetonitrile was pipetted and placed in a voltammetric cell alternately. The three electrodes were then connected to a potentiostat and then measured by DPV with a potential range of -2.0 V to +1.0 V, -2.0 V deposition potential, 74.56 seconds deposition time, 0.125 V amplitude modulation, and 0.05 V/s scan rate. Subsequently, the peak response of the Eu current obtained was plotted against the concentration.

Determination of Precision and Accuracy

Determination of precision was carried out by measuring the level of Eu3+, which has been measured 3 times (triple). It (in %RSD) was then calculated using the formula described by Miller & Miller (2018):

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

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

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

Where SD = Standard Deviation
x = Concentration value of one measurement result
$\bar{x}$ = Mean concentration value of the measurement results
n = Total measurement
$\%CV$ = *Coefficient of variation*
$\%RSD$ = Precision

Meanwhile, the accuracy was calculated to determine the closeness of the measurement value to the actual amount of substance in the matrix. Its value can be obtained from equation 4 (Miller & Miller, 2018).

$$\text{Accuracy} = 100\% - \frac{\text{Mc - Rc}}{\text{Rc}} \qquad (4)$$

Where, Mc is measured concentration, and Rc is real concentration.

Determination of Recovery

Recovery is the difference between the average and the actual value that can be accepted, and it was calculated using equation 5 (Miller & Miller, 2018):

$$\%\,Recovery = \frac{\text{measured value}}{\text{real value}} \text{x } 100\% \qquad (5)$$

Detection Limit and Quantification Limit

Limit of detection (LoD) and limit of quantitation (LoQ) are terms used to describe the smallest detectable concentration of analyte that can be determined with acceptable accuracy and precision. The LoD and LoQ values were calculated using equations 6 and 7 below (Miller & Miller, 2018).

$$LoD = y_B + 3SD \qquad (6)$$

$$LoQ = y_B + 10SD \qquad (7)$$

Where *LoD* = *Limit of Detection*
LoQ = *Limit of Quantitation*
y_B = The analyte concentration giving a signal is equivalent to the blank value
SD = Standard Deviation intercept of linear regression on the calibration curve

3. RESULT AND DISCUSSION

Response of Acetonitrile Measurement

The main solvent used to determine the Eu content was acetonitrile. The measurement of its current response using DPV was carried out with a platinum working electrode, wire auxiliary, and Ag/AgCl reference electrodes. The measurement results show no peak in the acetonitrile current, which indicates that its response did not affect the measurement of Eu, as shown in Figure 1.

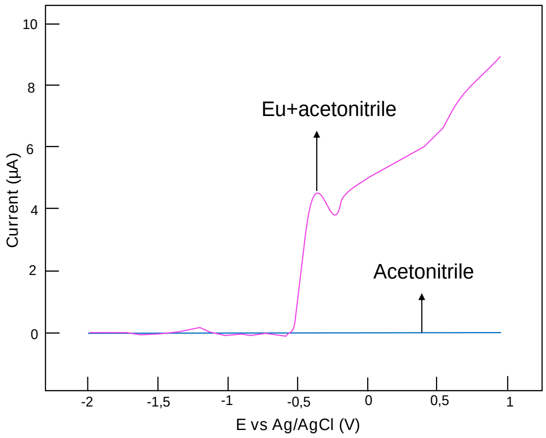

Figure 1. Voltammogram of (A) acetonitrile and (B) Eu 10 mg/L in acetonitrile by DPV in a potential range of -2.5 V to +1.0 V, deposition potential -2.5 V, deposition time 80 seconds, amplitude modulation 0.125 V, and a scan rate of 0.05 V.

Analysis of Europium Deposits with Variations in Acetonitrile Concentration on Platinum Electrodes Using SEM

The observation was carried out to determine the effect of acetonitrile solvent on Eu electrodeposition on a Pt electrode. A solution of the element in 100% and 75% acetonitrile was deposited on the electrode using CV. The measurement results of Eu electrodeposition in both solvents revealed a voltammogram peak, as shown in Figure 2. The observed peak reduction currents for 30 mg/L Eu were at a potential of -0.40 V and -0.1 V in 100% and 75% acetonitrile, respectively. The shift/difference in the reduction potential was caused by the difference in the ratio of the solvent used. Furthermore, the peaks were in the range for the reduction of acetonitrile, as reported by Krishnamurty & Gupta (2016). The reduction potential of Eu was in the potential range of -2.80 V to -0.35 V, which indicates that it can be deposited on platinum.

$$Eu^{3+} + 3e^{-} \rightarrow Eu \qquad (E° = -1.99\ V)$$
$$Eu^{3+} + e^{-} \rightarrow Eu^{2+} \qquad (E° = -0.35\ V)$$
$$Eu^{2+} + 2e^{-} \rightarrow Eu \qquad (E° = -2.80\ V)$$

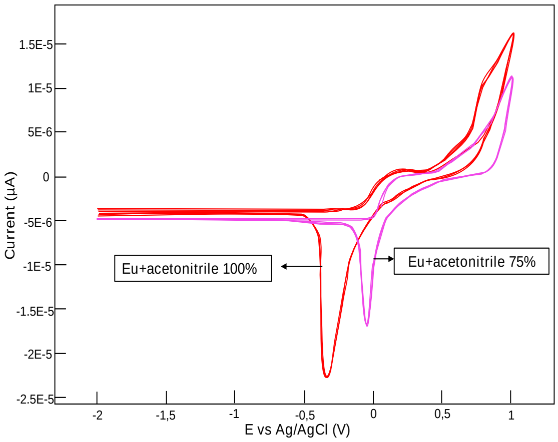

Figure 2. Cyclic voltammogram of Eu 30 mg/L in 75% acetonitrile and 100% acetonitrile over a potential range of -2 V to + 1.0 V, deposition time of 80 seconds, amplitude modulation 0.125 V, and a scan rate of 0.05 V/s.

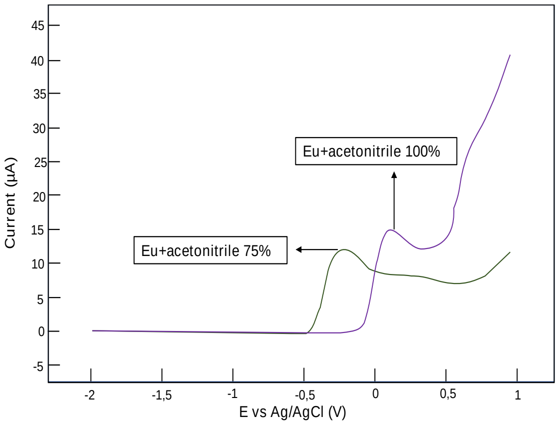

Figure 3. DPV Eu 30 mg/L voltammogram in 75% acetonitrile and 100% acetonitrile over a potential range of -2.0 V to +1.0 V, deposition time 80 seconds, amplitude modulation 0.125 V, and scan rate 0.05 V/s.

The response of current measurements for Eu in 100% and 75% acetonitrile using DPV showed that the higher the correlation between the solvent concentration and current, the more Eu is deposited, as shown in Figure 3.

Peak current values of 1.2 µA and 1.5 µA were obtained in 75% and 100% acetonitrile, respectively.

The electrode surfaces with Eu deposition and varying concentrations of 75% and 100% acetonitrile were then analyzed using SEM at 4300x magnification to determine the effect of the solvent on the electrodeposition. The analysis results showed the presence of a white layer on the surface of Pt in 100% acetonitrile, which indicates that more Eu was deposited than the electrode in 75% acetonitrile, as shown in Figure 4.

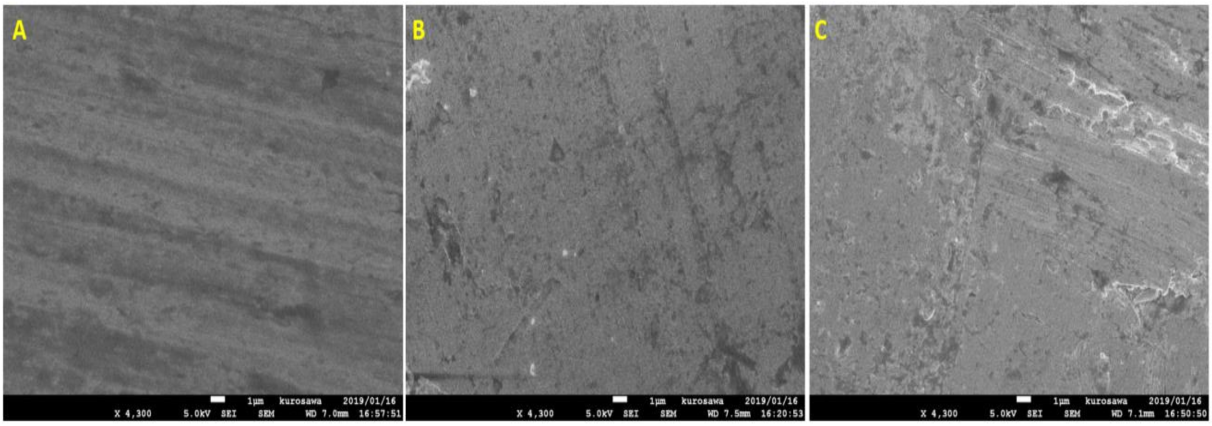

Figure 4. The results of the SEM analysis on the platinum electrode surface with a magnification of 4,300 (A) blank, (B) the results of the Eu electrodeposition in 75% acetonitrile, and (C) the results of the Eu electrodeposition in 100% acetonitrile.

Determination of the optimum condition for detection of Eu by *Box – Behnken* design

Table 1. Factors and levels of Eu analysis by DPV

Factor	Level		
	+1	**0**	**-1**
Deposition Potential (V)	-2	-2.5	-3
Amplitude Modulation (V)	0.125	0.1	0.075
Deposit time (seconds)	60	80	100

Table 2. The effect of the regression coefficient on the model

Source	F-Value	P-Value
Model	5.70	0.035
Linear	5.72	0.045
Deposition time	0.40	0.553
Amplitude modulation	9.22	0.029
Potential deposition	7.53	0.041
Square	2.24	0.202
Deposition time*Deposition time	2.21	0.197
Amplitude modulation*Amplitude modulation	0.97	0.370
Potential deposition*Potential deposition	3.05	0.141
2-Way Interaction	9.16	0.018
Deposition time*Amplitude modulation	0.09	0.778
Deposition time*Potential deposition	0.90	0.387
Amplitude modulation*Potential deposition	26.49	0.004
Error Lack-of-Fit	1.40	0.442

Assessment of the optimum conditions for the determination of Eu by voltammetry was carried out using the Box-Behnken design with 3 levels, namely low (-1), medium (0), and high levels (+1) of the 3 selected factors, including deposition potential, amplitude modulation and deposition time, as shown in Table 1. Based on the output of the analysis of variance, the factors that significantly influenced the measurement of the Eu current include amplitude modulation and potential deposition because the p-value was less than 5%, as shown in Table 2. Furthermore, the model adequacy of the resulting response surface method has been met, which was indicated by the little lack of fit with a p-value of 0.442. The optimum maximum current response was obtained at a deposition time of 74.56 seconds, amplitude modulation of 0.125 V and deposition potential of -2.0 V.

Determination of Eu in a Mixed Sm, Eu, Gd and Dy Simulation

Determination of the current response for Eu was carried out with DPV using the optimum conditions from the Box-Behnken design, while Sm, Gd, and Dy were determined using their conditions (Wyantuti et al., 2021a; Wyantuti et al., 2021b; Wyantuti et al., 2021c). Figure 5 shows the current response of each rare earth element, where Eu cannot be assessed from the mixture because its peak is in the same potential range as others.

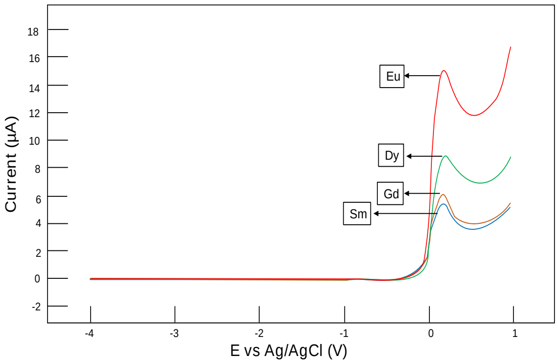

Figure 5. REE’s mixed voltammogram for peaks: (A) Eu with a deposition time of 74.56 seconds, amplitude modulation of 0.125 V, and a deposition potential of -2.0 V; (B) Dy with deposition time of 83.64 seconds, amplitude modulation of 0.0929 V, and deposition potential of -1.0 V: (C) Gd with deposition time of 64.65 seconds, amplitude modulation of 0.1 V, and deposition potential -1,328V; (D) Sm with 60 seconds deposition time, 0.05 V amplitude modulation, and -1.5 V deposition potential.

Therefore, to determine the Eu content in the mixture, one optimum condition was used due to the Box-Behnken design, namely a potential range of -2 V to +1.0 V, -2.0 V deposition potential, 74.56 seconds deposition time, 0.125 V, and 0.05 V/s scan rate. An investigation of the current response of each element, including Eu, Sm, Gd, and Dy, was carried out, and measurements were made for their mixture using the optimum condition of Eu. Figure 6 shows the voltammogram results of the process.

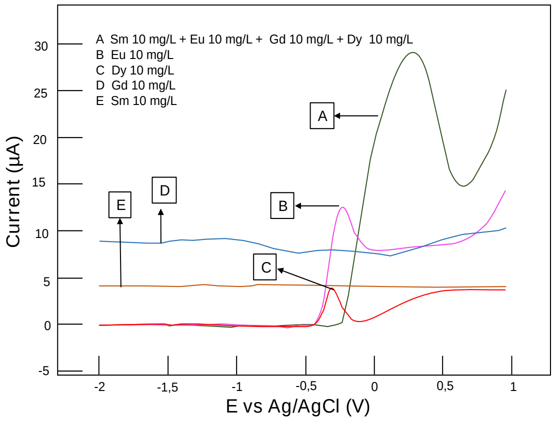

Figure 6. Voltammogram (A) mixed (Sm, Eu, Gd and Dy) 10 mg/L (B) Eu 10 mg/L (C) dysprosium 10 mg/L and (D) gadolinium 10 mg/L (E) samarium 10 mg/ L by DPV in the potential range of -2.0 V to +1.0 V, deposition potential of -2.0 V, deposition time of 74.56 seconds, amplitude modulation of 0.125 V, and scan rate of 0.05 V/s.

The voltammogram results for the mixture of Eu, Sm, Gd, and Dy with a concentration ratio of 1:1 showed a single peak, as shown in Figure 6A. Subsequently, in Figure 6B, Eu produced a single current response by DPV, distinguished from Sm and Gd because it did not respond to the measurement shown by a straight line in Figures 6D and 6E. However, Dy produced a response similar to a single Eu peak, as illustrated in Figure 6C. Sukhyat (2013) and Irawan (2013) reported that the total content of Eu, Gd, Sm, and Dy in monazite was 0.01%; 0.58%; 4.21%; and 0.37%, respectively. Therefore, for the next simulation, the Eu content of its mixture with Dy was determined using a concentration ratio of 1: 30, namely 1 mg/L Eu and 30 mg/L Dy with DPV under optimum conditions. Figure 7 shows the results of the current response for this mixed simulation.

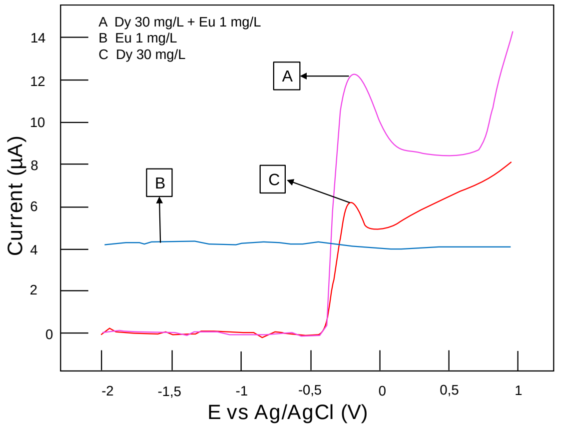

Figure 7. Voltammogram (A) of a mixture of dysprosium 30 mg/L and Eu 1 mg/L (B) Eu 1 mg/L (C) dysprosium 30 mg/L by DPV in a potential range of -2.0 V to +1.0 V , deposition potential of -2.0 V, deposition time of 74.56 seconds, amplitude modulation of 0.125 V, and scan rate of 0.05 V.

Based on the voltammogram in Figure 7, a single Eu peak cannot be determined due to low concentrations, but the current response for Dy showed a single peak.

Eu Calibration Curve

The calibration curve is an analytical parameter used to determine the ratio of the analyte concentration to the response given by the instrument in the form of linear regression. The curve used in this study was determined from the measurement results of Eu solution with 100% acetonitrile using DPV. The conditions were deposition time of 74.56 seconds, 0.125 amplitude modulation, and -2 to 0.1 V deposition potential at a concentration variations of 2.0; 4.0; 6.0; 8.0; and 10.0 mg/L. The measured values and the current response calibration curve for the Eu concentration are shown in Table 3 and Figure 8. Figure 8 reveals that the linear regression of the curve had an equation value of y = -0.061 + 0.23x.

Table 3. Calculation of deposition potential with variation of concentration

[Eu] (mg/L)	Current (µ)	$[Eu]_{measured}$ (mg/L)	SD	CV	Error (%)	Precision (%)	Accuracy (%)
	0.4399	1.9325					
2	0.4533	1.9913					
	0.4494	1.9742	0.030	0.015	0.017	98.46	98.30
Total	1.3426	5.8981					
Mean	0.4475	1.9660					
	0.8807	3.8690					
4	0.8265	3.6311					
	0.8075	3.5476	0.232	0.057	0.079	100	92.07
Total	2.5148	11.0478					
Mean	0.8382	3.6826					
	1.2697	5.5781					
6	1.2599	5.5352					
	1.2645	5.5551	0.021	0.004	0.074	99.61	92.60
Total	3.7942	16.668					
Mean	1.2647	5.5561					
	1.8497	8.0126					
8	1.8012	7.9129					
	1.8100	7.9515	0.113	0.014	0.0003	98.58	99.96
Total	5.4609	23.990					
Mean	1.8203	7.9968					
	2.2145	9.7286					
10	2.2998	10.1032					
	2.3022	10.1138	0.219	0.022	0.002	97.80	99.82
Total	6.8165	29.9457					
Mean	2.2721	9.9819					
			Total			494.45	483.38
			Mean			98.89	96.67

Table 4. Comparison of the results of this study with previous studies

Method	Result
Wyantuti *et al.*, 2021a	LoD: 0.64 mg L^{-1} LoQ: 2.14 mg L^{-1} Solvent: CH_3CN Can determine Dy but not selective for mixtures of Dy and Eu
Wyantuti *et al.*, 2021b	LoD: 2.25 mg L^{-1} LoQ: 7.50 mg L^{-1} Solvent: CH_3CN Selective for Sm but cannot distinguish Eu, Gd, and Dy signals
This study	LoD: 2.72 mg L^{-1} LoQ: 5.12 mg L^{-1} Solvent: CH_3CN Can determine Eu but cannot distinguish mixture of Eu and Dy

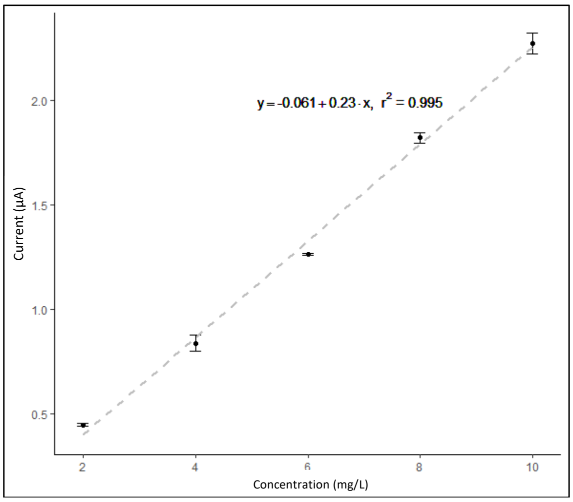

Figure 8. Eu calibration curve ranges from 2 mg/L to 10 mg/L by DPV with optimization conditions in the potential range of -2.0 V to +1.0 V, deposition potential of -2.5 V, deposition time of 74.56 seconds, 0.125 V amplitude modulation, and 0.05 V/s scan rate.

As shown in Table 3, the Eu measurement's precision value (%RSD) was 1.11 ± 0.12 %, with an accuracy of 96.67 ± 0.12 %. Based on equations 6 and 7, the calculated value for the detection limit value and quantification limit was 2.72 mg/L and 5.12 mg/L, respectively. Furthermore, the yield of Eu recovery was 98.91 ± 0.11%, with a confidence concentration range of 7.1 mg/L to 8.1 mg/L. A comparison of the results of this study with previous studies using acetonitrile as a solvent and the determination of rare earth metals mixtures content are shown in table 4. The assessment of the Eu content in the solvent was carried out using the DPV method. However, in mixed conditions with Dy, the observed current signal cannot be distinguished from that of Dy.

4. CONCLUSION

The result showed that more Eu was deposited on the Pt electrode in the 100% acetonitrile than the other. The optimum conditions for the determination of the metal using DPV include -2.5 V deposition potential, 74.56 seconds deposition time, 0.125 V amplitude modulation, and 0.05 V/s scan rate. Assessment of platinum electrode performance for the determination of Eu and its mixture with a concentration range of 2 to 10 mg/L obtained precision results (%RSD) of 1.11 ± 0.12 %, 98.91 ± 0.11% recovery, 2.72 mg/L detection limit, and 5.12 g/L quantitation limit. Based on the results, the DPV method can detect the content of Eu in acetonitrile solvent.

ACKNOWLEDGMENTS

The authors are grateful to the Padjadjaran University Bandung for the Academic Leadership Grant. The authors are also grateful to the Directorate of Research and Community Service through Unpad Lecturer Competency Research (DRPM-RKDU) with contract no: 1959/UN6.3.1/PT.00/2021.

REFERENCES

Bezerra, M.A., Santelli, R.E., Oliveiraa, E.P., Villar, L.S., & Escaleira, L.A. 2008. Response surface methodology (RSM) as a tool for optimization in analytical chemistry. *Talanta*, **76**:965–977.

Bhattacharya, S., Samuel, J.L., & Reza, M. 2000. Spektrophotometric Determination Of Europium in Lanthanide and Other Mixtures By Use Of Methylene Blue. *Talanta*. **27**:59-60.

Chien, N.X., Khai, P.N., Hien, T.D., Nguyen, D., Bot, D.C., Van Trung, T., Cuc, N.T., Minh, L.H., Thuc, N.V., Ngan, B.T., & Van Thuan, D. 2006. The determination of rare earth elements in geological and environmental samples by inductively coupled plasma mass spectrometry. *VAEC*. **6**:217–225.

Ferreira, S. L. C., Bruns, R. E., Ferreira, H. S., Matos, G. D., David, J. M., Brandao, G.C., Silva, E. G. P., Portugal, L.A., Reis, P. S., Souza, A. S., & Santos, W.N.L. 2007. Box-Behnken design: An alternative for the optimization of analytical methods. *Analytica Chimica Acta*. **597**:179–186.

Irawan, S. 2013. *Rare Earth Element Mineral Processing in PT Timah Tbk*: Workshop on Rare Earth Element Mineral Processing and Refining in Indonesia, Bandung.

Krishnamurthy, N. & Gupta, C.K. 2016. *Extractive Metallurgy of Rare Earth*. 2nd ed. New York: Taylor & Francis Group, LLC.

Mele, C., Sandra, R., & Lucia, D. 2013. Silver Electrodeposition From Water-Acetonitrile Mixed Solvents and Electrolytes in the Presence of Tetrabutylammonium Perchlorate. Part 1-Electrochemical nucleation on glassy carbon electrode. *J. Solid State Electrochem*. **13**:1577-1584.

Miller, J., & Miller, J.C. Statistics and chemometrics for analytical chemistry (7th ed.). 2018. Harlow: Pearson Education Limited.

Ohnishi, K., Kan, K., Hiroyasu, S., Eri, T., Shinichi, S., & Koichi, K. 2010. *Inductively Coupled Plasma Atomic Emission Spectroscopy Method For Precise Determination Of Trace Europium in Biological Fluid* : A Technical Note.

Rajendran, J., Balasubramanian, G., & Thampi, P. 2008. Determination of rare earth elements in Indian coastal monazite by ICP-AES and ICP-MS analysis and their geochemical significance. *Current Science*. **94**:1–7.

Scholz, F., & Lange, B. 1992. Abrasive stripping voltammetry-an electrochemical solid state spectroscopy of wide applicability, *TrAc. Trends Anal. Chem*. **11** (10):359–367.

Sharma, P., Bais,R., Singhvi,S & Bhandari,H. 2014. Voltammetri Trace Determination of Europium. *International Jurnal of Chemical Studies*. **2**:1-4.

Skoog, D.A., West, D.M., & Holler, F.J. 2014. *Fundamentals of Analytical Chemistry*. Cengage Learning, Boston.

Soylak, M., & Gokhan, O. 2006. Determination of trace metals by atomic absorption spectrometry After coprecipitation with europium hydroxide. *Journal of Hazardous*.1130-1134.

Suhkyat, R. 2013. *Potential and distribution of Indonesia mineral resources and deposits.* Seminar on Acceleration Attempts to Increase Domestic Minerals Added Value. Indonesia.

Wyantuti, S., Pratomo, U., Hartati, Y.W., Anggraeni, A., & Bahti, H.H. 2018. Fast and Simultaneous Detection of Sm, Eu, Gd, Tb and Dy using combination of Voltammetry Method and Multivariate Analysis. *Research Journal of Chemistry and Environment.* **22**:302-306.

Wyantuti, S., Pratomo, U., Hartati, Y.W., Hendrati, D., & Bahti, H.H. 2019. Aplication of Experimental Design by Differential Pulse Voltammetry for Determination of Rare Earth Elements as Complexes with diethylenetriaminepentaacetic acid (DTPA). *International Journal of Recent Technology and Engineering*. **8**:33-37.

Wyantuti, S., Pratomo, U., Shauvina, S., Hartati, Y.W., & Bahti, H.H. 2021a. Differential pulse voltammetry study for quantitative determination of dysprosium (III) in acetonitrile solution. *Int. J. Renew. Energy Dev*. **10**:191–199.

Wyantuti, S., Pratomo, U., Manullang, L.A., Hendrati, D., Hartati, Y.W., & Bahti, H.H. 2021b. Development of differential pulse voltammetric method for determining samarium (III) through electroanalytical study of the metal ion in acetonitrile using Box–Behnken design. *Heliyon.* **7:**e06602.

Wyantuti, S., Oktaviani, W.R.,, Hendrati D., Hartati, Y.W., & Rahmidar, L. 2021c. Determination of Gd (III) Concentration by Voltammetry and Its Usage as a Learning Module for Chemistry Student *Proceeding of ICETeP 2020*: 434-437.

Zhu, Y., Yasushi, K., & Takashi, M. 2010. Effects of acetonitrile on electrodeposition of Ni from a hydrophobic ionic liquid. *Electrochimica Acta*. **55**:9019-9023.