



Research article

Development of differential pulse voltammetric method for determining samarium (III) through electroanalytical study of the metal ion in acetonitrile using Box–Behnken design

Santhy Wyantuti^{*}, Uji Pratomo, Latri A. Manullang, Diana Hendrati, Yeni Wahyuni Hartati, Husein H. Bahti*Department of Chemistry, Faculty of Mathematics and Natural Sciences, Universitas Padjadjaran, Jl. Raya Bandung-Sumedang Km. 21, Jatinangor, Sumedang, 45363 Indonesia*

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ABSTRACT

The development of methods for the efficient and reliable separation and routine analysis of rare-earth elements (REEs), including samarium (Sm), proceeds to draw in the interest of the many researchers, attributable to the similar physical and chemical properties of these elements. Note that although the voltammetric determination of Sm has been described in the literature, thus far, no chemometric and voltammetric methods for the quantification of the element in its mixtures with other lanthanides in an acetonitrile solution have been reported. This work was aimed toward the advancement of a method for the detection of Sm in acetonitrile, the intended function of which was to obtain a selective current response of Sm by Differential Pulse Voltammetry, utilizing the Box–Behnken experimental design, to identify the best conditions for the determination. In particular, the three selected factors for the experiment, namely the potential range, amplitude modulation, and the deposition time, were found to have optimal conditions of -1.5 to $+1.0$ V, 0.075 V, and 60 s, consecutively. The optimal conditions were observed to result in a selective current response for samarium with a detection limit of 2.25 mg/L and a limit of quantitation of 7.50 mg/L. Furthermore, the accuracy was 98.70% and the precision was found to be 1.91% in relative standard deviation (RSD), while the recovery was found to be 98.70% .

1. Introduction

A group of chemical components that features the lanthanides group, yttrium, and scandium is called Rare Earth Elements (REE) [1]. Lately, the research about the REE has gained enormous attention due to the high application interest of the REE. These elements can be applied in various fields such as metallurgy, medical, nuclear technology, ceramic industry, and electronics [2, 3]. Samarium (Sm) is one of the 17 REE, which is ordinarily discovered in monazite and in bastnaesite. This element is not found in nature in a free state but in the form of complex compounds, and hence, a chemical analysis method is needed to separate this REE from its complex compounds [4, 5, 6, 7, 8]. Sm is relatively stable at high temperatures and has a thermoelectric efficiency of up to 1100 °C. This element is widely used in industrial fields, such as the computer, telecommunications, nuclear, and magnet industries [9, 10, 11, 12]. Besides, it can be used in the production of special catalysts,

microwave and infrared equipment, lasers, and the nuclear energy industry [13, 14].

The sophisticated methods that are often used to determine the presence of Sm include HPLC offers a fast process, automatic and accurate analysis method, but in the process, this method is complicated and requires expensive equipment [15]. ICP–MS which has a high sensitivity for determining REEs, is simple, and only requires a small number of samples. However, spectral interference is the problem that must be solved in an ICP–MS analysis, because the molecular masses of REEs are adjacent [16]. Other methods such as ICP–OES, and XRF were used for analyzing many elements with sufficient sensitivity, but the performance of the tool is weak for REEs because of the complexity of the emission spectrum as well as the amount of interference from the major elements; therefore, the separation of the matrix by cation exchange is usually required [17]. These techniques must deal with complex and costly maintenance and

* Corresponding author.

E-mail address: santhy.wyantuti@unpad.ac.id (S. Wyantuti).

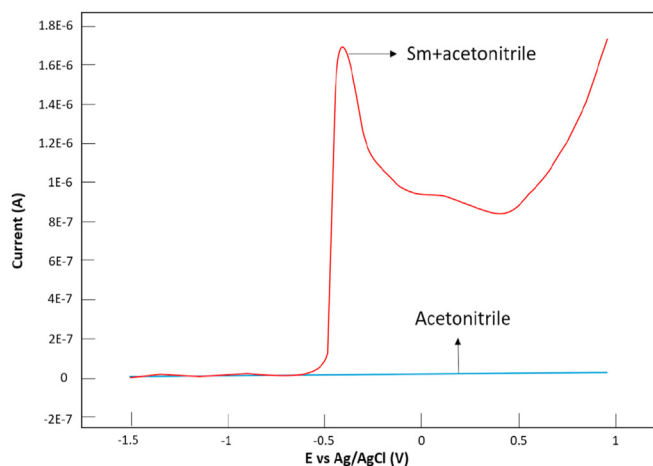


Figure 1. Current Response of acetonitrile and 10 mg/L Sm in acetonitrile.

operation although have advantages in high selectivity and sensitivity. Therefore, an alternative method of analysis that is fast, efficient, sensitive, relatively inexpensive, and simple, and has a low detection limit is needed.

Voltammetry is an alternative analytical method that has the criteria for obtaining information about analytes by measuring currents in electrochemical cells as a function of potential. The current measured in a voltammetry analysis results from a redox reaction on the electrode surface [18, 19, 20]. The data obtained can be used for qualitative and quantitative analysis. Qualitative information is obtained from the current peak that appears on the voltammogram, which is the fingerprint of a particular analyte, while quantitative information is obtained from the area ratio of the voltammogram, which shows the composition ratio of the identified analyte [21].

The use of organic solvents as the supporting electrolyte solutions for metal electrodeposition continues to attract interest because it provides an alternative pathway to the electrochemical process. Organic solvents can accelerate the solubilization of and the reaction for metal ions [22, 23, 24]. Organic solvents that can be used include dimethylformamide (DMF), dimethyl sulfoxide (DMSO), acetonitrile (AcN), tetrahydrofuran (THF), and dimethylacetamide (DMAc) [25]. Compare to the other organic solvent, acetonitrile is the most widely used organic solvent for electrochemical studies. It is considered to be an excellent medium for the electrooxidation process due to has a high permittivity value, $\epsilon = 36$, appropriate for a metal deposition because of a wide range of potential value, $-3.45 \text{ V} - 2.35 \text{ V}$, [26, 27] and a relatively high dielectric constant; therefore, it dissolves electrolyte salts and can be mixed with ionic liquids to achieve very high ionic conductivity in the electrodeposition of metal ions [28, 29, 30].

Most of the analytical methods face the problem of time and high reagent consumption. An approach by the chemometric method can be

used to solve those problems. This method assessed the significant factor that will influence the response. Amongst the tools for the analysis of chemometric, the Box-Behnken is considered effective to assign the correlation between the results of the response and the relevant factors by employing a sequence of experiments to provide the best responses [31, 32, 33, 34, 35, 36]. The experimental design technique mutual combination with an electroanalytical method was very promising for the future development of the determination of Sm and other REEs in water [9, 20, 37, 38].

Based on this background, this research was intended to develop a differential pulse voltammetry method using acetonitrile as a solvent for determining Sm levels. The Box-Behnken design technique was utilized to evaluate the optimal conditions of the experiments. The acetonitrile solvent effect for determining the presence of Sm(III) and for electrodeposition of the metal ions was investigated as well.

2. Materials and methods

2.1. Materials

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

2.2. Apparatus

The tools and instruments utilized in this research included Ag/AgCl electrodes (eDAQ), Pt working electrodes (Antam), Pt wire for counter electrode (Antam), potentiostat (Metrohm® μ Autolab), the Minitab 17.1 program, the ANOVA 7.0.0 program, analytical balance (Sartorius), Scanning Electron Microscope (SEM) JEOL JSM-7500F, and Hitachi TM3030 SwiftED3000 for EDX measurement.

2.3. Preparation of stock solution Sm_2O_3 1000 mg/L

The 1000 mg/L Sm_2O_3 was prepared by dissolving 0.2898 g Sm_2O_3 in a portion of 65% HNO_3 followed by stirring and heating until homogeneous. Into the solution, a portion of 250 mL distilled water was added and followed by stirring. A Sm_2O_3 stock solution was diluted using acetonitrile to prepare various concentrations of Sm.

2.4. Background current measurement

The current response of acetonitrile was measured by differential pulse voltammetry under the specific conditions: a potential of deposition -1.5 V , time of deposition 60 s, range of potential -1.5 V to $+1.0 \text{ V}$, amplitude modulation of 0.05 V, and scanning rate of 0.05 V/s.

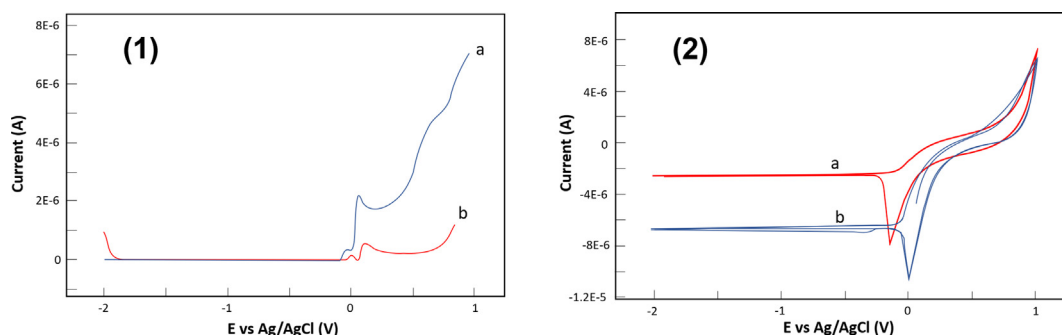


Figure 2. Differential pulse voltammogram (1) and cyclic voltammogram (2) profile of 30 mg/L Sm in (a) 100% acetonitrile and (b) 25% acetonitrile.

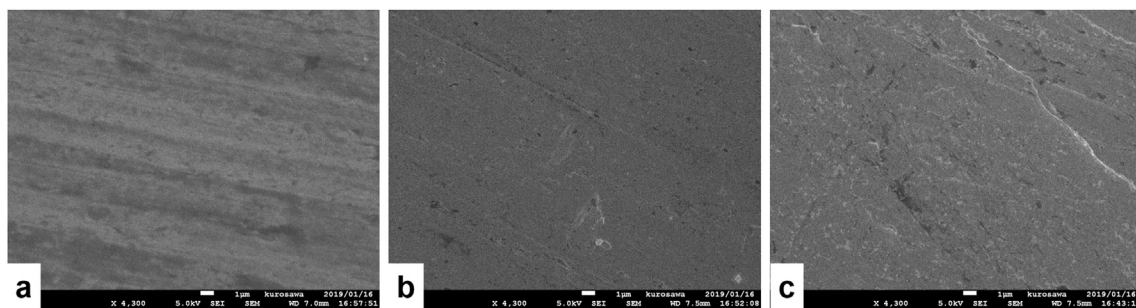


Figure 3. Pt electrode surface images (4300× magnification) before deposition(a), after deposition of Sm in 25% acetonitrile (b), and 100% acetonitrile (c).

2.5. Sm current measurement

The current response of a 10.0 mg/L Sm solution was examined by differential pulse voltammetry under the specific conditions: a potential of deposition -1.5 V, time of deposition 60 s, range of potential -1.5 V to $+1.0$ V, amplitude modulation of 0.05 V, and scanning rate of 0.05 V/s. The measurement was repeated for: 15.0, 20.0, 25.0, and 30.0 mg/L.

2.6. Electrodeposition of Sm in acetonitrile by cyclic voltammetry

The deposition of 30.0 mg/L Sm solutions, in 25% and 100% acetonitrile, onto the Pt electrode was conducted by cyclic voltammetry under the specific conditions: a potential of deposition -1.5 V, time of deposition 60 s, range of potential -1.5 V to $+1.0$ V, amplitude modulation of 0.05 V, and scanning rate of 0.05 V/s.

2.7. Sm current response in 25% and 100% acetonitrile by differential pulse voltammetry

The current response of 30.0 mg/L Sm solution in 25% and 100% acetonitrile were examined using differential pulse voltammetry under the following conditions: a potential of deposition -1.5 V, time of deposition 60 s, range of potential -1.5 V to $+1.0$ V, amplitude modulation of 0.05 V, and scanning rate of 0.05 V/s.

2.8. Surface morphology analysis of platinum by SEM and EDX

The surface morphology of Pt (around 1 cm), before and after deposition with Sm, was characterized using SEM (JEOL JSM-7500F) and EDX (Hitachi TM3030 SwiftED3000).

2.9. Box–Behnken experimental design

The current responses of 30.0 mg/L Sm solution for the selected factors: deposition potential, deposition time, and amplitude modulation by utilizing differential pulse voltammetry were recorded. The Box–Behnken experimental was used to optimized the selected factors. The design was set to three levels (-1 , 0 , $+1$) with up to 15 measurements conducted using the Minitab program 17.1 [38].

2.10. Sm, Eu, Gd, and Dy current responses under the optimum conditions

The current responses of a 40.0 mg/L Sm, 0.1 mg/L Eu, 5.0 mg/L Gd, and 3.0 mg/L Dy in acetonitrile were observed by utilizing differential pulse voltammetry under the optimum conditions: a potential of deposition -1.5 V, time of deposition 60 s, range of potential -1.5 V to $+1.0$ V, amplitude modulation of 0.075 V, and scanning rate of 0.05 V/s.

2.11. Calibration curve of Sm

The current response of 10.0, 15.0, 20.0, 25.0, and 30.0 mg/L Sm solution were measured by differential pulse voltammetry under the optimum conditions a potential of deposition -1.5 V, time of deposition 60 s, range of potential -1.5 V to $+1.0$ V, amplitude modulation of 0.075 V, and scanning rate of 0.05 V/s.

3. Results and discussion

3.1. The acetonitrile and samarium current response

The differential pulse voltammetry was used to investigate the current response of acetonitrile and Sm in acetonitrile. These experiments

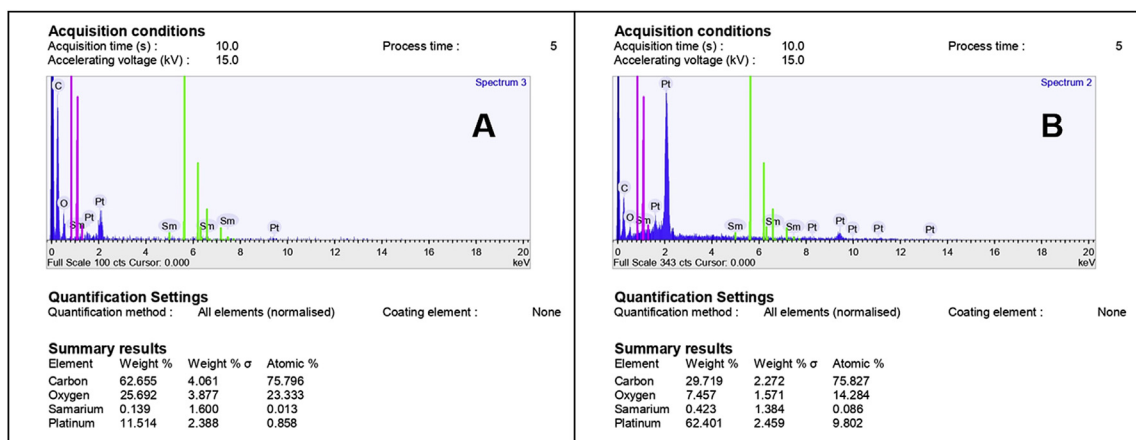


Figure 4. EDX spectrum of the Platinum Electrode Surface after deposition of (A) Sm in 25% acetonitrile and (B) Sm in 100% acetonitrile.

Table 1. The level of analysis and selected factors of Sm by differential pulse voltammetry.

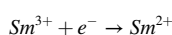
Symbol	Factor	Level		
		−1	0	+1
X1	Deposition Potential/V	−1.0	−1.5	−2.0
X2	Deposition Time/s	120	90	60
X3	Amplitude Modulation/V	0.075	0.05	0.025

The results of the current response were obtained and processed to obtain the coefficient of the response function in Eq. (1).

Table 2. ANOVA results.

Source	F-Value	P-Value
Model	2.79	0.135
Linear	6.18	0.039
Deposition Potential (X1)	0.46	0.526
Amplitude Modulation (X2)	11.97	0.018
Deposition Time (X3)	6.10	0.056
Square	0.43	0.738
Deposition Potential * Deposition Potential (X1 * X1)	0.03	0.878
Amplitude Modulation * Amplitude Modulation (X2 * X2)	0.15	0.711
Deposition Time * Deposition Time (X3 * X3)	1.06	0.349
Two-Way Interaction	1.76	0.271
Deposition Potential * Amplitude Modulation (X1 * X2)	0.10	0.761
Deposition Potential * Deposition Time (X1 * X3)	0.95	0.374
Amplitude Modulation * Deposition Time (X2 * X3)	4.22	0.095
Lack of Fit	0.24	0.865

were aimed to investigate whether the acetonitrile solvent shows a characteristic peak under the specific conditions. As shown in Figure 1, the acetonitrile solvent did not produce any current response, while the characteristic peak near -0.35 V is shown as the response of 10 mg/L Sm in acetonitrile. The reduction reaction of Sm could be expressed as follows:



The experiment was then conducted for investigated the current response of Sm in 25%, and 100% of acetonitrile solvent.

Table 3. The current response of Sm 30 mg/L in acetonitrile.

Run	Factor			Response/ μA
	Deposition Potential	Deposition Time	Amplitude Modulation	
1	−1.5 V	120 s	0.075 V	1.0646E−06
2	−1.5 V	90 s	0.050 V	4.4952E−07
3	−1.0 V	90 s	0.025 V	7.1832E−07
4	−1.0 V	60 s	0.050 V	1.4863E−06
5	−1.5 V	90 s	0.050 V	1.4640E−06
6	−1.5 V	90 s	0.050 V	1.1316E−06
7	−1.0 V	90 s	0.075 V	1.4838E−06
8	−2.0 V	60 s	0.050 V	1.7548E−06
9	−1.5 V	120 s	0.025 V	6.2622E−07
10	−1.0 V	120 s	0.050 V	1.1198E−06
11	−1.5 V	60 s	0.075 V	2.4401E−06
12	−2.0 V	120 s	0.050 V	6.4522E−07
13	−2.0 V	90 s	0.075 V	1.0978E−06
14	−1.5 V	60 s	0.025 V	4.3647E−07
15	−2.0 V	90 s	0.025 V	5.7724E−07

3.2. The current response of Sm in 25% and 100% acetonitrile and surface characterization of Pt electrodes

The electrochemical response investigation of Sm in 25% and in 100% acetonitrile was conducted by utilizing the differential pulse voltammetry and the cyclic voltammetry. The effect of the acetonitrile concentration on the deposition of Sm on the Pt electrode surface was evaluated in this experiment. The voltammograms of this experiment is presented in Figure 2.

As shown in Figure 2(1), the differential pulse voltammogram of 30 mg/L Sm showed that in 100% acetonitrile, the current response was higher than that in 25% acetonitrile, which was probably due to the more facile adsorption of the metal on the platinum surface in a pure organic solvent; therefore, the Sm could be easily deposited on the electrode surface. In contrast, the higher water concentrations make it more difficult to deposit Sm on Platinum Electrode Surface. The investigation using cyclic voltammetry during the deposition of Sm, as shown in Figure 2(2), showed that in the case of 100% acetonitrile, the potential standard reduction E_0 of Sm shifted toward a more cathodic potential. This indicates that the oxidation of Sm takes place more easily in 100% acetonitrile than in 25% acetonitrile.

The Pt surface was imaged before and after the deposition of Sm on the electrode surface by utilizing a Scanning Electron Microscope. These images are shown in Figure 3. As shown in Figure 3A, the image of bare Pt surface, whilst the morphology of the Pt surface after deposition of Sm in 25% and 100% acetonitrile are shown in Figures 3B and C. As shown in Figure 3B, there are a few 1 μm white aggregate particles on the Pt surface after deposition of Sm in 25% acetonitrile. Moreover, the white aggregate particles were found to be highly distributed on the platinum electrode surface after the deposition of Sm in 100% acetonitrile, as shown in Figure 3C. This result indicated that the concentration of acetonitrile solvent considerably influenced the deposition process of Sm ions on the platinum electrode.

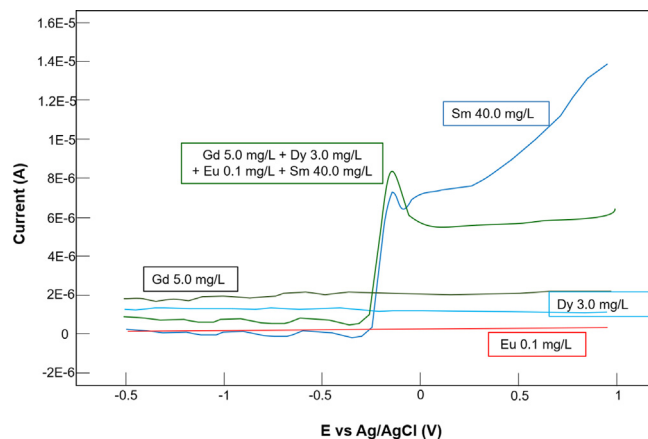


Figure 5. The individual current response of Sm 40.0 mg/L, Gd 5.0 mg/L, Dy 3.0 mg/L, and Eu 0.1 mg/L, and the mixture of Sm, Gd, Dy, and Eu under the optimum conditions by differential pulse voltammetry.

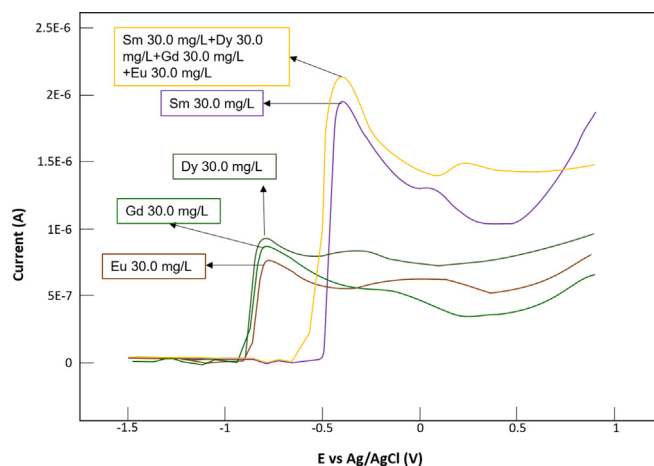


Figure 6. The individual current response of Sm 30.0 mg/L, Gd 30 mg/L, Dy 30 mg/L, Eu 30 mg/L, and the mixture of Sm, Gd, Dy, and Eu under the optimum conditions by differential pulse voltammetry.

Furthermore, the presence of Sm deposited on the Pt surface was supported by the EDX measurement result, as shown in Figure 4. The EDX spectrum presented in Figure 4A indicated the existence of Sm on the platinum surface with the %atomic of 0.013 after the deposition in 25% acetonitrile. The result of EDX spectra of the platinum surface after deposition of Sm in 100% acetonitrile shows the %atomic of 0.086, as shown in Figure 4B. This result confirmed that increasing the concentration of acetonitrile caused more Sm ions to deposit onto the platinum electrode.

3.3. The determination of the optimum conditions

The optimum conditions for the measurement of Sm in acetonitrile were determined by the Box–Behnken method. The potential of deposition, amplitude modulation, and time of deposition was considered as the main factors that significantly influenced the determination of the optimum conditions of differential pulse voltammetry for the Sm analysis. The scanning potential was conducted from the negative potential (initial) to the positive potential (final). The given potential increased linearly, and the current was measured twice: before the pulse rose (given) and after the pulse fell (falls). Therefore, the deposition potential was chosen as a factor that might influence the Sm analysis. Furthermore, amplitude modulation affected the resolution (separation) and the sensitivity of the measurement. A large-amplitude modulation value would produce a large response. However, it would expand the peak and

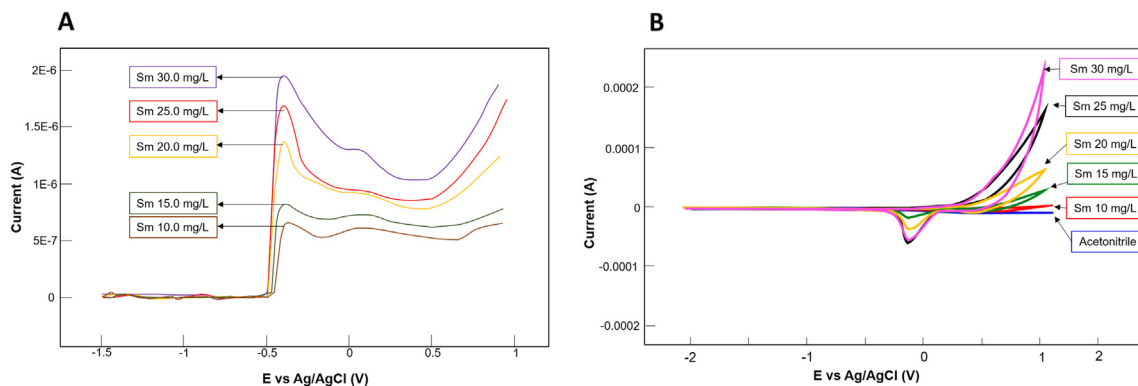


Figure 7. (A) Differential Pulse Voltammogram and (B) Cyclic Voltammogram of acetonitrile and variation concentration of Sm in acetonitrile from 10 to 30 mg/L (potential of deposition -1.5 V, range of potential -1.5 V to +1.0 V, amplitude modulation 0.075 V, time of deposition 60 s, and scanning rate of 0.05 V/s).

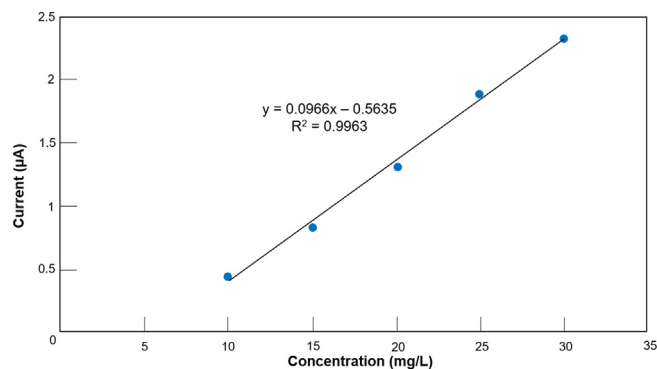


Figure 8. Calibration curve of Sm in acetonitrile from 10 to 30 mg/L.

decrease the potential resolution. The optimum deposition time was the time at which the maximum peak current reduction signal was observed. Therefore, amplitude modulation and deposition time were also chosen as factors that might affect the Sm analysis.

The Box–Behnken analysis of the optimum condition for Sm in acetonitrile by differential pulse voltammetry was performed after determining the factors that potentially influenced the Sm analysis. The three levels were chosen which are high level (+), low level (-), and middle level (0), where the values are shown for each level, as presented in Table 1. These levels were generated from the Sm analysis without optimization, which could affect the voltammetry measurement.

$$Y = -0.000002 - 0.000000X_1 + 0.000098X_2 + 0.000000X_3 + 0.000000X_1^2 - 0.000124X_2^2 + 0.000000X_3^2 + 0.000005X_1X_2 + 0.000001X_1X_3 - 0.000001X_2X_3 \quad (1)$$

As shown in Eq. (1), the X1 (deposition potential), X2 (amplitude modulation), and X3 (deposition time) were considered as the factors that had a positive or significant influence on the Sm analysis by the differential pulse voltammetry method. If the response coefficient was positive (+), the presence of these factors would increase the current response. A negative coefficient (-) indicated that the presence of these factors would decrease the current response. As shown in Eq. (1), the coefficient value of X1 (deposition potential) was negative, which implied a negative response in all three levels (-1, 0, +1). In contrast, the coefficient value of X2 and X3, i.e. amplitude modulation and deposition time, respectively, were positive, indicating the optimum current response that could be used in the Sm analysis will be increased due to the amplitude modulation and the time of deposition by utilizing differential pulse voltammetry.

Table 4. Current response of Sm for determination of LoQ and LoD.

	Sm/mg/L (x)	Current/ μ A (y)	\hat{y}	$y - \hat{y}$	$(y - \hat{y})^2$
	10	0.4495	0.4025	0.0470	0.0022
	15	0.8380	0.8855	-0.0475	0.0022
	20	1.3218	1.3685	-0.0467	0.0021
	25	1.8960	1.8515	0.0445	0.0019
	30	2.3350	2.3345	0.0005	0.0000
Σ	100	6.8404	6.8425	-0.0022	0.0086
Mean	20	1.3680			0

Table 5. Current response of Sm for determination of precision, accuracy, and recovery.

Sm/mg/L (x)	Current/ μ A (y)	Sm _{experiment} /mg/L	$x - \bar{x}$	$(x - \bar{x})^2$	$\Sigma(x - \bar{x})^2$	Sb	KV	Precision/% RSD	Accuracy/%
10	0.4495	10.4865	-0.3723	0.1386	0.2565	0.3581	3.2979	3.30	91.41
	0.4884	10.8892	0.0304	0.0009					
	0.5185	11.2008	0.3420	0.1169					
Mean		10.8589							
15	0.8380	14.5083	0.0949	0.0090	0.0963	0.2194	1.5221	1.53	96.08
	0.8439	14.5694	0.1560	0.0243					
	08046	14.1625	-0.2509	0.0629					
Mean		14.4134							
20	1.3218	19.5166	-0.2460	0.0605	0.2057	0.3207	1.6226	1.63	98.81
	1.3343	19.6460	-0.1166	0.0136					
	1.3806	20.1253	0.3627	0.1315					
Mean		19.7626							
25	1.8960	25.4607	0.9907	0.9815	4.9645	1.5755	6.4386	6.44	97.87
	1.8801	25.2961	0.8261	0.6824					
	1.6248	22.6532	-1.8168	3.3007					
Mean		24.4700							
30	2.2343	28.9625	-0.6478	0.4197	0.6396	0.5655	1.9098	1.91	98.70
	2.3213	29.8634	0.2530	0.0640					
	2.3350	30.0052	0.3948	0.1559					
Mean		29.6014							
Mean								2.97	96.57

From the analysis of the current response obtained from the differential pulse voltammetry, we obtained the ANOVA results presented in Table 2, which explained the variability of the data. The p-value data of each factor was obtained from the ANOVA. A model that in accordance with the linear model is indicated by a p-value of less than 0.05, which implied that a single variable showed a linear effect. The interaction effect is showed from a combination of two variables, and to determine the significance of each variable, the p-value was used. The independent variable which had no significant effect is indicated by the p-value of more than 0.05.

The p-value of the deposition potential (X1) was more than 0.05, as shown in Table 2. This result indicated that although we obtained a negative response from Eq. (1), it would not significantly influence the measurement result. Therefore, we kept applying the deposition potential of -1.5 V. The p-value of the lack of fit test was obtained as 0.865, which was greater than 0.05; thus, it concluded that the resulting linear model was appropriate. This lack of fit signified a deviation or inaccuracy with the linear model, and tests were conducted to detect whether the linear model was appropriate.

Moreover, based on the Minitab 17.1 program, the number of the conducted experiment for the three levels and three parameters was 15. The corresponding results are presented in Table 3. As shown in Table 3, the condition of the deposition potential of -1.5 V, deposition time of 60 s, and amplitude modulation of 0.075 V showed the high current

response of 30 mg/L Sm in acetonitrile. This result was consistent with the result from the Box-Behnken method. Therefore, it concluded that the optimum conditions of the measurement were as follows: the potential of deposition -1.5 V, time of deposition 60 s, and amplitude modulation of 0.075 V.

3.4. Comparison of the responses of Sm, Eu, Gd, and Dy under the optimum conditions

The differential pulse voltammetry method was utilized to investigate the electrochemical responses of the Sm, Eu, Gd, and Dy under the optimum conditions. In nature, the monazite content of each REE (Sm, Eu, Gd, and Dy) is different from that of the others. The Sm content in the monazite of the Bangka and Belitung Islands is 4.21%, while the Eu content is 0.01%, the Gd content is 0.58%, and the Dy content is 0.37% [41, 42]. On the basis of this fact, we performed the measurement of different concentration ratios of Sm, Gd, Dy, and Eu. The Sm concentration used in this study was 40.0 mg/L, the Gd concentration was 5.0 mg/L, the Dy concentration was 3.0 mg/L, and the Eu concentration was 0.1 mg/L. The experiment result is shown in Figure 5.

As shown in Figure 5. The voltammogram shows a relatively no response to the lowest current response for individual Gd, Dy, and Eu in acetonitrile. In contrast, the presence of Sm shows a high current response. The voltammogram of the mixture of Sm, Eu, Dy, and Gd shows

Table 6. Comparison of the result with the previous work.

Method	Result
A study of electroanalysis and experimental design combination method for detection of Sm-DTPA complex (Solvent: NH ₄ Cl) [9]	LoD: 24.44 mg L ⁻¹ LoQ: 91.53 mg L ⁻¹ Not selective for Sm, Eu and Dy
An application of differential pulse voltammetry and experimental design method for determination of REE-DTPA complex (Solvent: NH ₄ Cl) [20]	LoD: 27.11 mg L ⁻¹ LoQ: 92.33 mg L ⁻¹ Not selective for Sm, Eu, and Dy
A differential pulse voltammetry study for detection of Dy (III) in acetonitrile (Solvent: CH ₃ CN) [38]	LoD: 0.64 mg L ⁻¹ LoQ: 2.14 mg L ⁻¹ Not selective for Eu and Dy
This work (Solvent: CH ₃ CN)	LoD: 2.25 mg L ⁻¹ LoQ: 7.50 mg L ⁻¹ Selective for Sm but not selective for Eu, Gd and Dy

the characteristic peak is similar for Sm. This result indicated that in the mixture with Eu, Dy, and Gd, the presence of Sm in acetonitrile can be identified.

Moreover, the observation of the electrochemical response of the individual Sm, Gd, Dy, and Eu and also its mixture under the same concentration (30 mg/L) was conducted by utilizing the differential pulse voltammetry. The voltammogram result is presented in Figure 6.

The responses of the mixture of Sm, Gd, Dy, and Eu (30 mg/L) is relatively similar to that of individual Sm, as shown in Figure 6. Therefore, this result confirmed that the presence of Sm can be identified in the mixture with Gd, Eu, and Dy.

3.5. Calibration curves, detection limits, and quantification limits

The current peak of Sm under various concentrations: 10.0, 15.0, 20.0, 25.0, and 30.0 mg/L in a 100% acetonitrile, were recorded and used to prepare the calibration curves for Sm. These calibration curves were utilized for a comparison of the analyte concentrations versus the responses given in the form of linear regression. The optimum conditions from the Box-Behnken were applied for the Sm current response measurement.

From the result, as shown in Figure 7, the increasing concentration is proportional to the current peak due to of the large number of electro-active analyte ions (Sm³⁺), which were reduced or deposited on the Pt electrode at -0.35 V. This was consistent to the Rendless-Sevcik equation, in which the current is correlated with the analyte concentration. The given negative potential promoted the Pt electrode to have a more negative charge. The Sm³⁺ ions on the surface of the electrode were reduced (capturing electrons) to Sm²⁺. As a consequence, this decreased the concentration of the Sm ions on Pt electrode surface, and the Sm ions far from the electrode (the concentration was greater than on Pt electrode surface) moved toward the Pt electrode. We assumed that the electron movement mechanism due to the different concentrations caused the current diffusion, which was equal to the analyte concentration.

As shown in Figure 8, the linear regression of calibration curve was calculated to be $y = 0.0966x - 0.5635$ with R² equal to 0.9963. This value suggested that Sm had a strong variable relationship between the response and the concentration.

We performed the experiments under the optimal condition and calculated the values of the limit of quantification (LoQ) and the limit of detection (LoD) [39, 40]. As shown in Table 4, the LoD value obtained was 2.25 mg/L, and the LoQ was 7.50 mg/L. The experiment for the determination of accuracy, precision, and recovery was also investigated. The results are presented in Table 5. The accuracy (for 30 mg/L Sm) was 98.70% while the precision values was 1.91% in RSD. The recovery of 30 mg/L Sm was 98.70% (see Table 6).

4. Conclusion

The results of this study indicated that Sm in acetonitrile could be deposited on platinum electrodes. Based on the Box-Behnken experimental design result, the optimum conditions for determining Sm by differential pulse voltammetry were as follows: potential of deposition -1.5 V, amplitude modulation 0.075 V, and time of deposition 60 s. The LoD obtained was 2.25 mg/L, and the LoQ was 7.50 mg/L. The accuracy was 96.70%, and the precision was 1.91% in RSD, while the recovery was 98.70%. This study suggested that the differential pulse voltammetry method could determine the presence of Sm in acetonitrile.

Declarations

Author contribution statement

Santhy Wyantuti: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

Uji Pratomo: Performed the experiments; Analyzed and interpreted the data; Wrote the paper.

Lastris A. Manullang, Diana Hendrati: Performed the experiments; Analyzed and interpreted the data.

Yeni Wahyuni Hartati: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Wrote the paper.

Husein H. Bahti: Conceived and designed the experiments; Contributed reagents, materials, analysis tools or data; Wrote the paper.

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Data availability statement

Data associated with this study has been deposited at Penerapan Desain Box-Behnken pada Penentuan Kadar Sm (III) Tunggal dan Dalam Campuran Sm, Eu, Gd, Dy Menggunakan Pelarut Asetonitril Secara Voltametri under the accession number <http://repository.unpad.ac.id/frontdoor/index/index/docId/12088>.

Declaration of interests statement

The authors declare no conflict of interest.

Additional information

No additional information is available for this paper.

References

- [1] R.D. Abre, C. Morais, Purification of rare earth elements from monazite sulphuric acid leach liquor and the production of high-purity ceric oxide, *Miner. Eng.* 23 (2010) 536–540.
- [2] M.E. de Vasconcellos, C.A.S. Queiroz, A. Abrao, Sequential separation of the yttrium heavy rare earths by fractional hydroxide precipitation, *J. Alloys Compd.* (2004) 405–407.
- [3] P. Davodi-Nasab, A. Rahbar-Kelishami, J. Safdari, A. Hossein, Evaluation of the emulsion liquid membrane performance on the removal of gadolinium from acidic solutions, *J. Mol. Liquid. Iran* 262 (2018) 97–103.
- [4] C. Hurst, China's Rare Earth Elements Industry: what Can the West Learn, IAGS, USA, 2010.
- [5] I. Rodliyah, R. Siti, W. Tatang, Extraction of rare earth metals from monazite mineral using acid method, *Indonesian Mining J.* 18 (1) (2014) 39.
- [6] I. Taam, C.S. Jesus, J.L. Mantovano, V. Gante, Quantitative analysis of rare earths by x-ray fluorescence spectrometry, *Int. Nuclear Atlantic Conf.* (2013) 24–29.

- [7] R. Schramm, Use of x-ray fluorescence analysis for the determination of rare earth elements, *Phys. Sci. Rev.* (2016) 1–17.
- [8] A. Smoli, M. Stempin, N. Howaniec, Determination of rare earth elements in combustion ashes from selected Polish coal mines by wavelength dispersive x-ray fluorescence spectrometry, *Spectrochim. Acta, Part B* 116 (2016) 63–74.
- [9] S. Wyantuti, U. Pratomo, Y.W. Hartati, D. Hendrati, H.H. Bahti, A study of green electro-analysis conducted by experimental design method for detection of samarium as complex with diethylenetriaminepentaacetic acid (DTPA), *AIP Conf. Proc.* (2018), 030010.
- [10] H. Elsner, *Heavy Minerals of Economic Importance: Assessment Manual*, Federal Institute of Geosciences and Natural Resource (BGR), Hannover, 2010.
- [11] D. Fontana, F. Loris, Separation of middle rare earths by solvent extraction using 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester, *J. Rare Earths* 27 (3) (2009) 117–135.
- [12] B.L. Liu, M. Lu, Z.I. Wang, A study of nanostructured gold modified glassy carbon electrode for the determination of trace Cr (IV). *Indian Academy of Sciences, J. Chem. Sci.* 120 (2008) 493–498.
- [13] R. Torkaman, M.A. Moosavian, M. Torab-Mostaedi, J. Safdari, Solvent extraction of samarium from aqueous nitrate solution by Cyanex 301 and D2EHPA, *Hydrometallurgy* 137 (2013) 101–107.
- [14] I.G. Finlay, M.D. Mason, M. Shelley, Radioisotopes for the palliation of metastatic bone cancer: a systematic review, *Lancet Oncol.* 6 (6) (2005) 392–400.
- [15] M. Sakr, R. Hanafi, M. Fouad, H. Al-Easa, S. El-Moghazy, Design and optimization of a luminescent Samarium complex of isoprenaline: a chemometric approach based on Factorial design and Box-Behnken response surface methodology, *Spectrochim. Acta Mol. Biomol. Spectrosc.* 208 (2019) 114–123.
- [16] B. Zawisza, K. Pytlakowska, B. Feist, M. Polowniak, A. Kita, R. Sitko, Determination of rare earth elements by spectroscopic techniques: a review, *J. Anal. Atomic Spectrom.* 26 (12) (2011) 2373–2390.
- [17] F. Ardini, F. Soggia, F. Rugi, R. Udisti, M. Grotti, Comparison of inductively coupled plasma spectrometry techniques for the direct determination of rare earth elements in digests from geological samples, *Anal. Chim. Acta* 678 (1) (2010) 18–25.
- [18] M.R. Ganjali, R. Zare-Dorabei, P. Norouzi, Design and construction of a novel optical sensor for determination of trace amounts of dysprosium ion, *Sensor. Actuator. B Chem.* 143 (1) (2009) 233–238.
- [19] D.A. Skoog, D.M. West, F.J. Holler, *Fundamentals of Analytical Chemistry*, Cengage Learning, Boston, 2014.
- [20] S. Wyantuti, U. Pratomo, Y.W. Hartati, D. Hendrati, H.H. Bahti, Application of experimental design by differential pulse voltammetry for determination of rare earth elements as complexes with diethylenetriaminepentaacetic acid (DTPA), *Int. J. Recent Technol. Eng.* 8 (2019) 33–37.
- [21] F. Scholz, B. Lange, Abrasive stripping voltammetry — an electrochemical solid state spectroscopy of wide applicability, *Trac. Trends Anal. Chem.* 11 (10) (1992) 359–367.
- [22] K. Neuróhr, L. Pogány, B.G. Tóth, Á. Révész, I. Bakonyi, I. Péter, Electrodeposition of Ni from various non-aqueous media: the case of alcoholic solutions, *J. Electrochem. Soc.* 162 (7) (2015) D256–D264.
- [23] E. Bourbos, A. Karantonis, L. Sygellou, I. Paspaliaris, D. Panyas, Study of Nd electrodeposition from the aprotic organic solvent dimethyl sulfoxide, *Metals* 8 (2018) 803.
- [24] S.H. Mirzamohammadi, H. Khorsand, M. Aliofkhaezrai, Effect of different organic solvents on electrodeposition and wear behavior of Ni-alumina nanocomposite coatings, *Surf. Coating. Technol.* 313 (2017) 202–213.
- [25] Y. Jung, S. Kim, B.-S. Kim, D.-H. Han, S.-M. Park, J. Kwak, Effect of organic solvents and electrode materials on electrochemical reduction of sulfur, *Int. J. Electrochem. Sci.* 3 (2008) 566–577.
- [26] L. Kiss, Electrooxidation of low-permittivity solvents in acetonitrile and solubility of trihexylamine in acetonitrile, *J. Iran. Chem. Soc.* 17 (2020) 67–71.
- [27] N. Elgrishi, K.J. Rountree, B.D. McCarthy, E.S. Rountree, T.T. Eisenhart, J.L. Dempsey, A practical beginner's guide to cyclic voltammetry, *J. Chem. Educ.* 95 (2018) 197–206.
- [28] V.O. Koverga, A new potential model for acetonitrile: insight into the local structure organization, *J. Mol. Liq.* 233 (2017) 251–261.
- [29] B. Suchacz, M. Wesolowski, F. Yu, X.X. Wang, N. Yang, R.G. Compton, M. Yu, S. Dai, G. Liu, A.O. Shakil, W.M. Lee, Voltammetric quantitation of acetaminophen in tablets using solid graphite electrodes, *Anal. Methods* 8 (16) (2016) 3307–3315.
- [30] I. Yanez, Hydrogen oxidation and hydrogen evolution on a platinum electrode in acetonitrile, *ChemElectroChem* (2015) 1612–1622.
- [31] C.R.T. Tarley, G. Silveira, W.N.L. dos Santos, G.D. Matos, E.G.P. da Silva, M.A. Bezerra, M. Miro, S.L.C. Ferreira, Chemometric tools in electroanalytical chemistry: methods for optimization based on factorial design and response surface methodology, *Microchem. J.* 92 (2009) 58–67.
- [32] H.E. Wiik, *Methods for Analyzing the 12 Run Plackett–Burman Design*, Norwegian University of Science and Technology, Norway, 2014.
- [33] D.C. Montgomery, *Design and Analysis of Experiments*, John Wiley & Sons, Singapore, 2001.
- [34] R. Bezerra, Response surface methodology (RSM) as a tool for optimization in analytical chemistry, *Talanta* (2008) 965–977.
- [35] M.S. Elazazy, M. El-Hamshary, M. Sakr, H.S. Al-Easa, Plackett-Burman and Box-Behnken designs as chemometric tools for micro-determination of LOrnithine, *Spectrochim. Acta Mol. Biomol. Spectrosc.* 193 (2018) 397–406.
- [36] E. Morgan, *Chemometrics: Experimental Design*, Published on behalf of ACOL by John Wiley & Sons, Chichester, 1997.
- [37] S. Wyantuti, U. Pratomo, Y.W. Hartati, A. Anggraeni, H.H. Bahti, Fast and simultaneous detection of Sm, Eu, Gd, Tb and Dy using combination of voltammetry method and multivariate analysis, *Res. J. Chem. Environ.* 22 (2018) 302–306.
- [38] S. Wyantuti, U. Pratomo, S. Shauvina, Y.W. Hartati, H.H. Bahti, Differential pulse voltammetry study for quantitative determination of dysprosium (III) in acetonitrile solution, *Int. J. Renew. Energy Dev.* 10 (2021) 191–199.
- [39] J.N. Miller, J.C. Miller, R.D. Miller, *Statistics and Chemometrics for Analytical Chemistry*, seventh ed., Pearson Education Limited, Harlow, 2018.
- [40] J.A. Bard, L.R. Faulkner, *Electrochemical Methods: Fundamentals and Applications*, second ed., John Wiley & Sons, 2001.
- [41] S. Irawan, *Rare Earth Element Mineral Processing in PT Timah Tbk: Workshop on Rare Earth Element Mineral Processing and Refining in Indonesia*, Bandung, 2013.
- [42] R. Suhkyat, Potential and distribution of Indonesia mineral resources and deposits. Seminar on Acceleration Attempts to Increase Domestic Minerals Added Value, 2013. Indonesia.