Fast and Simultaneous Detection of Sm, Eu, Gd, Tb and Dy using combination of Voltammetry Method and Multivariate Analysis

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Abstract

A series of rare earth elements (REE's) such as Sm, Eu, Gd, Tb and Dy, played an essential role in scientific and technological advancement. They are used in numerous daily applications, notably in electronic components, superconductors and medical devices. However, different REE's have similar physical and chemical properties, it is therefore difficult to determine the presence of elements. Consequently, the development of simple and less expensive analytical techniques for rapid detection of rare earth elements is desired; subsequently, we have employed a combination of voltammetry methods with multivariate analysis.

A graphite pencil electrode (GPE) with supporting electrolyte composed of 0.1 M ammonium chloride was used. We obtained the accuracy of simultaneous detection for Sm, Eu, Gd, Tb and Dy as above 99% with Principal Component Regression (PCR). Good agreement between the voltammetry method and multivariate analysis was confirmed by the coefficient of determination (r2) of each element being above 0.998. We believed these combination techniques can contribute to developing a powerful tool for the fast detection of REE without separation.

Keywords: Rare Earth Element, Graphite Pencil Electrode, Voltammetry, Multivariate Analysis, Principal Component Regression

Introduction

There is a huge and rising demand for rare earth elements which have varied applications in industries, especially in high-tech innovative products. A number of technologies use rare earth elements notably electronics, optoelectronics, superconductors, super-magnets, lasers, portable hybrid batteries, glass and ceramic materials[1-5]. Rare earth elements have unique chemical properties such as the same valence and close ion radii[6-8], which is attractive to sscientists aiming to prepare methods for fast detection using each rare earth material in small concentrations.

Due to the sample preparation, fast analysis time, low detection limits and good reproducibility, the voltammetric method is effective one. Simple sample preparation without separation from major elements is an advantage to reduce the source of error with a detection limit of up to 0.1 μg / L[9-11].

An additional advantage of this method is the multivariate analysis that it will provide such as good combination. A small number of responses of entire voltammetric profile can be transformed to the equation model to predict the optimal condition. Moreover, the optimization of multiple simultaneous responses thus becomes the optimization of a single function[12-15].

Herein, the rapid determination, without separation of samarium (Sm), europium (Eu), gadolinium (Gd), terbium (Tb), dysprosium (Dy) using the combination of linear sweep voltammetry method, multivariate analysis by principal component regression (PCR) and partial least square regression (PLSR) is reported. This result can contribute in analytical techniques for fast determination of medium group rare earth elements.

Material and Methods

Materials: The materials used in this study include the following: samarium oxide, europium oxide, gadolinium oxide, terbium oxide and dysprosium oxide, 0.1 M Ammonium chloride solution and 65% Nitric acid.

Instruments used: Digital analytical balance AL204 (Mettler Toledo) and voltammetry linier sweep Metrohm® µAutolab with NOVA 10.1 software and XLSTAT as data processing.

Preparation of rare earth metal stock solutions: Aqueous stock solutions of 3086.4400 ppm samarium, 1583.7500 ppm europium, 47512.5200 ppm gadolinium, 3877.0213 ppm terbium and 10614.2784 ppm dysprosium were prepared by dissolving the oxide solids of each element using 65% nitric acid until perfectly soluble before being diluted by double distilled water.

Preparation of training solution set: The training set solution is a mixture of solutions in which any concentration of rare earth element is known. The preparation of the training set solution was carried out by diluting the stock solution with enough double distilled water. Each concentration of rare earth metal elements is shown in table 1.

Analysis of stock solution: Linear sweep voltammetry was used to measure each stock solution of rare earth metals at a potential range of -1.5 to 1.0 V with a potential step of 0.02 V/s. The electrolyte solution used was 0.1 M ammonium chloride.

Analysis of training solution set: The training set solution was measured with linear sweep voltammetry in the potential range of -1.5 to 1.0 V with a potential step of 0.02 V s.

Data Processing with Multivariate Analysis Method (Factor analysis with principal component analysis (PCA)): A data matrix was produced from the result of linear sweep voltammetry (concentration variation at each potential). The distribution normality of each piece of data was tested using Jarque-Bera statistics. Furthermore, the normalization (data) on the data matrix was performed to get adequate data (complete, correct, consistent, integrated). The data matrix which had been pre-processed was then evaluated by PCA method with XLSTAT.

Modeling and determining prediction concentration with principal component regression (PCR) and partial least square regression (PLSR): Modeling and determination of predicted concentrations of rare-earth metals were conducted utilizing PCR and PLSR methods with XLSTAT software. The obtained mathematical model was then validated to verify that it was suitable for the determination of medium rare-earth elements.

Results and Discussion

The stock solution was measured using linear sweep voltammetry within the potential range of 1.5 V to -1.5 V and a potential step of 0.02 V/s. As shown in fig. 1, the voltammogram of each rare earth element has a voltammogram pattern that eventually forms one. All of the solutions produced a peak at potential regions within -0.7 V to -1.3 V. Additionally, the voltammogram of ammonium chloride as the supporting electrolyte and aquabidest as the solvent gives a current value within the potential range of 1.0 V to -1.5 V.

This data indicates that the potential range of -1.5 to 1.0 V with a potential step of 0.02 V/s is suitable for pre-processing a data matrix. The following concentrations of true rare earth elements and average predicted concentration values with standard deviations of each rare-earth group metal element were obtained from PCR analysis as shown in tables 2 and 3. When compared to actual concentrations, the predicted concentrations of rare-earth elements by PCR analysis have relatively small values with the real concentrations of rare earth elements.

The prediction accuracy of each rare earth element (Sm, Eu, Gd, Tb and Dy) was determined from statistical parameters R^2 (coefficient of determination) and RMSE (Root Mean Square Error). The value of R^2 indicates the data quality between the real concentration and the predicted concentration and value ranges from 0 to 1. The value of R^2 which is close to 1 indicates that the real and predicted concentrations have very close values and a small error was made. The RSME value is an error generated from the calibration set. RMSE indicates the average value of errors obtained. A good regression model can be obtained with a small RMSE value.[16]

The result of analysis using PCR method resulted in less errors compared to PLSR method. This is indicated by the smaller RMSE and R^2 better than the PLSR method. Table 4 shows a comparison of R^2 and RMSE values of each rare earth metal element between the analysed results of PCR and PLSR. The mathematical model that had been obtained from the multivariate analysis method was then validated using multivariate PCR analysis method.

Based on table 4, it can be said that pre-processing to the data matrix can provide a better mathematical model where this can be seen from the value of R^2. The data in table 5 shows a comparison of RMSE and R^2 values between Partial Least Square and Principal Component Regression methods. A regression value from PCR indicated a small error compared to PLSR. The correlation indicated that residual standard deviation (RMSE) from PCR has a better fit to the regression line compared to the PLSR result.

Result of validation of mathematical model: To ensure a comparison of accuracy and precision values using PCR and PLS, a one tail t-test is performed. This t-test uses a 95% confidence level. For one tail t test, the hypothesis used is:

H0: $\mu1x<\mu2x$ (the average PCR accuracy or precision value is less than the PLSR average accuracy or precision value).

H1: $\mu1x>\mu2x$ (the average PCR accuracy or precision value is greater than the average PSLR accuracy or precision value).

The t_{count} value that is obtained for accuracy is 5.576 while the value of t_{table} obtained is 2.131. By this value, the result that we obtained is $t_{count}> t_{table}$ (5.576>2.131), then H0 is rejected. Based on these results, it can be said statistically that the average value of accuracy by PCR method is greater from the average value of accuracy by PLSR method for determination of Sm, Eu, Gd, Tb and Dy.

The value of t_{count} is obtained for precision of 0.413 while the value of t_{tables} obtained is 2.131. The result is $t_{count} <t_{table}$ (0.413< 2.131), then Ho is accepted. Based on these results, it can be argued that the average value of precision by PCR method is less than the average value of precision by PLSR method for determination of Sm, Eu, Gd, Tb and Dy.

Conclusion

1. The linear sweep voltammetry method combined with a multivariate analysis is an effective method to perform quick and simultaneous detection of Samarium, Europium, Gadolinium, Terbium and Dysprosium.

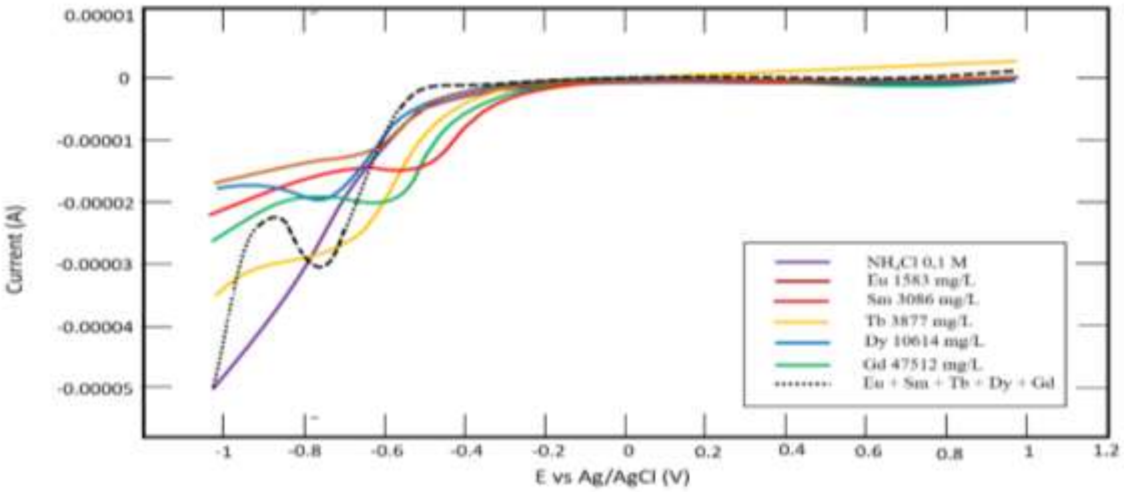

Figure 1: linear sweep voltammogram of Eu (brown), Sm (red), Tb (yellow), Dy (blue), Gd (green) and their mixture in NH_4Cl 0.1 M with potential range -1.5 to 1.0 V and step potential 0.02 V/s

Table 1
Training set solution

S.N.	Concentration (ppm)				
	Sm	Eu	Gd	Tb	Dy
1	170	25	200	30	215
2	263	25	560	44	323
3	356	25	920	58	431
4	449	25	1280	72	539
5	542	25	1640	86	647
6	635	25	2000	100	755
7	263	25	200	30	323
8	356	47	560	44	431
9	449	47	920	58	539
10	542	47	1280	72	647
11	635	47	1640	86	755
12	170	47	2000	100	215
13	356	47	200	30	431
14	449	47	560	44	539
15	542	69	920	58	647
16	635	69	1280	72	755
17	170	69	1640	86	215
18	263	69	2000	100	323
19	449	69	200	30	539
20	542	69	560	44	647
21	635	69	920	58	755
22	170	91	1280	72	215
23	263	91	1640	86	323
24	356	91	2000	100	431
25	542	91	200	30	647
26	635	91	560	44	755
27	356	113	1640	86	431
28	449	113	2000	100	539
29	635	113	200	30	755
30	170	113	560	44	215
31	263	113	920	58	323
32	542	135	2000	100	647
33	170	135	200	30	215

Table 2
Real concentration of each rare earth elements

C_{Sm} /ppm	C_{Eu} /ppm	C_{Gd} /ppm	C_{Tb} /ppm	C_{Dy} /ppm
170	25	200	30	215
263	47	560	44	323
356	69	920	58	431
449	91	1280	72	539
542	113	1640	86	647
635	135	2000	100	755

Table 3
Prediction concentration of each rare earth elements by PCR from data matrix at potential range from -1.5 to 1.0 V and step potential 0.02 V/s

C_{Sm}/ppm	C_{Eu}/ppm	C_{Gd}/ppm	C_{Tb}/ppm	C_{Dy}/ppm
167.571±2.466	25.194±2.875	231.814±5.241	29.889±1.359	212.180±2.264
271.068±3.363	47.062±0.506	562.880±0.514	44.112±0.254	332.370±3.181
353.312±0.954	68.906±0.382	920.244±1.169	58.009±0.721	427.879±0.915
445.594 ±1.111	90.474±1.497	1301.809±1.851	72.848±1.279	535.044±1.075
542.756±0.543	113.077±0.568	1621.907±2.147	85.296±1.592	647.878±0.528
635.027±0.148	135.553±0.410	2000.695±0.354	100.032±0.276	755.032±0.144

Table 4
Comparison of RMSE and R2 values between PCR and PLSR analysis results on potential data matrix of -1.5 to 1.0 V with potential step 0.02 V / s.

REE's	R^2		RMSE	
	PCR	PLSR	PCR	PLSR
Sm	0.998	0.049	41.674	143.833
Eu	1	0.133	6.0911	30.767
Gd	1	0.137	141.769	603.311
Tb	1	0.133	5.513	23.462
Dy	0.998	0.173	48.396	167.032

Table 5
Value of accuracy and precision of RMSE and R^2 obtained by Partial Least Square Regression (PLSR) and Principal Component Regression (PCR)

	Accuracy (%)		Precision (%)					
	PCR	PLS	PCR			PLS		
Eu	99.65	65.783	84.25	±	0.891	7.004	±	11.71
Gd	99.96	69.333	28.66	±	20.34	4.093	±	220.8
Sm	98.974	66.452	8.338	±	6.128	93.91	±	70.34
Tb	99.574	69.343	86.02	±	0.791	51.82	±	8.589
Dy	99.032	66.778	25.81	±	7.117	44.09	±	81.69

2. The accuracy of simultaneous detection for Samarium, Europium, Gadolinium, Terbium and Dysprosium is above 99% with Principal Component Regression (PCR) and R^2 is above 0.998. In contrast, the result accuracy analyzed by Partial Least Square Regression (PLSR) is about 66% and R^2 is about 0.1.

Acknowledgement

Authors would like to acknowledge the financial support from Academic Leadership Grant Program, Universitas Padjadjaran and the Directorate of Research and Community Service through Superior Research of Higher Education (DRPM-PUPT), Universitas for providing the research fund under contract number 1129/UN6.D/LT/2018 and Yuni Sulistiawati who contributed to this research.

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