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Research Article

Comparative Study of Voltammetric Analysis with UV-Vis Spectrophotometry in Determining the Results of Liquid-Liquid Extraction of Samarium (III)

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Abstract

Rare earth elements (REEs) are garnering significant attention in diverse fields due to their important and fascinating properties. Among these REEs, samarium (Sm) has numerous advantages and benefits. Before using Sm, it must be separated from its natural sources due to the formation of complex compounds with other elements. To achieve this, liquid-liquid extraction emerges as one of the REE separation methods, presenting several advantages, including a streamlined process. Various methods can be used to analyze extraction results, such as ICP-MS and XRF. In comparison, UV-Vis spectrophotometry has significant advantages compared to other methods, it provides a simple approach to determining the level of a substance, and the results given are quite accurate, while differential pulse voltammetry (DPV) is one of the electrochemical analysis methods that is expected to provide faster and accurate analysis results. This study aims to determine the value of analytical parameters, Kd of Sm(III) liquid-liquid extraction results using DPV analysis and UV-Vis spectrophotometry methods. The DPV method yielded LoD 1.24 mg/L, accuracy 98.39%, and %recovery 106.69%. The extraction data obtained Kd Sm values ranging from 6.0019-7.3860. The UV-Vis spectrophotometry results provided an individual extraction efficiency of Sm(III) of 88.54%. This method obtained LoD 0.71 mg/L, accuracy 96.00%, and %recovery 104.00%.

Keywords: Differential pulse voltammetry, liquid-liquid extraction, samarium, UV-Vis spectrophotometry

1. INTRODUCTION

Rare earth elements (REEs) are garnering significant attention in diverse fields due to their important and fascinating properties. Indonesia, in particular, possesses numerous sources of REEs across several regions, specifically on the islands of Bangka, Belitung, and Singkep [1,2]. These REES sources mainly include monazite sand and xenotime, which are by-products of mining activities [3–5]. Monazite sand contains several REEs, including samarium (Sm), which is widely used in producing samarium-cobalt (SmCo) permanent magnets for light electronic equipment. In addition, it is also used for coatings and microwave frequency capacitors. The applications of Sm in various industrial fields contribute significantly to technological advancements and foster innovations [6–8].

Sm, as one of the REE, does not occur naturally in a free state but in the form of alloys forming complex compounds of phosphate and carbonate with other elements. Therefore, an appropriate chemical method is needed to separate it from its complex compounds. The individual REEs separation process can be carried out by several methods, including liquid-liquid extraction, one of the most successful and widely used separation methods to separate REEs, as it is considered more efficient and faster. Liquid-liquid extraction of REEs employs various extractants, and tributyl phosphate (TBP) stands out as a highly effective extractant in the extraction process [5,9–12].

REE extraction results can be analyzed using various methods, with UV-Vis spectrophotometry being a widely used approach [13,14]. However, this method has certain drawbacks, requiring multiple chemical reagents, including complex ligands, and time-consuming sample preparation times. Other analytical methods such as ICP-MS [15,16], ICP-OES [17], and XRF [18], have high sensitivity and selectivity, but maintenance and operation are complicated and expensive during the analysis process. Therefore, there is a need for an alternative analysis method. The voltammetric method offers a compelling alternative for analysis over traditional approaches [19]. This method proves to be significantly faster, more efficient, and cheaper, with a low detection limit, high sensitivity, and a wide linearity region, namely with a detection limit for lanthanide elements such as Gd, Sm, and Tb of 0.08 mg/L [20–22].

During investigations, the voltammetric analysis of REEs continues to evolve and flourish. Using voltammetric methods, recent studies successfully identified several REMs, including Gd, Sm, Dy, and Eu. For example, gadolinium was determined by DPV with Burman and Box-Behnken Placket designs [21]. In a separate investigation, the DPV Method was used to determine Dy(III) in acetonitrile solution, although it lacked selectivity when dealing with a mixture of Dy and Eu mixture [22,23]. Similarly, another study focused on developing a DPV method for determining Sm (III) through electroanalytical analysis of metal ions in acetonitrile, using the Box-Behnken design. This approach successfully allowed the determination of Sm in the mixture containing other elements [20].

In light of the background above, this study aims to determine the value of analytical parameters, distribution coefficient (Kd), and extraction percent (%E) of Sm(III) using a TBP extractant and its DPV analysis under optimum conditions. Subsequently, this study will present and compare the results obtained with the previous findings achieved through UV-Vis spectrophotometry.

2. RESEARCH METHODS

Instrumentation

The tools used include general equipment commonly found in the laboratories such as glassware and Pyrex separatory funnel IWAKI made in Indonesia, Pt working electrode, Ag/AgCl comparison electrode, Pt auxiliary electrode, magnetic stirrer, digital analytical balance (Sartorius), analytical balance (Mettler Toledo: AL-204), Heidolph MR 3001 heater, pH meter MP 220 Mettler Toledo, Metrohm® μAutolab potentiostat connected to a computer using the NOVA 2 program. 1, 14 mL voltammetry cell, Genesys 10S UV-Vis spectrophotometer.

Procedure

Sm current measurement

A total of 10 mg/L Sm solution was pipetted in a volume of 10 mL and then transferred into the voltammetry cell. The three electrodes were connected to a potentiostat, and measurements were carried out using differential pulse voltammetry at a potential range of -1.5 V to +1.0 V, deposition potential of -1.5 V, deposition time of 60 seconds, amplitude modulation of 0.05 V, and a scan rate of 0.05 V sec-1. Therefore, a peak Sm current of 10 mg/L was obtained. The Sm current measurements were repeated at concentration variations of 5, 10, 15, 20, and 25 mg/L.

Preparation of Standard Curve by DPV

Samarium (III) solution with concentrations of 5, 10, 15, 20, and 25 mg/L in 100% acetonitrile solvent was pipetted and transferred into the voltammetry cell. The three electrodes were connected to a potentiostat device. Measurements were performed with differential pulse voltammetry with optimum conditions, which included a potential range of -1.5 V to +1.0 V, a deposition potential of -1.5 V, a deposition time of 60 seconds, a scan rate of 0.05 V sec-1 and amplitude modulation of 0.075 V. As a result, the peak of the Sm current was obtained, and this process was repeated with Sm solution with concentrations of 10, 15, 20, and 25 to establish the Sm calibration curve.

Sm(III) Extraction

A 1000 ppm Sm(III) solution was pipetted 2.5 mL into a 25 mL volumetric flask. The solution's pH was adjusted by adding sodium hydroxide until it reached a pH of 2.5 for Sm(III) plus buffer while stirring. Then distilled water was added until the mark was reached and homogenized. Furthermore, the solution was transferred into a separate funnel, and 25 mL of TBP in n-hexane was added with a metal-to-extractant ratio of 1:15 for samarium (III). The solution was put into a separate funnel shaken for 15 minutes, and allowed to stand for 30 minutes. Afterward, the extract phase and the raffinate phase were separated. The raffinate phase was taken, and the water phase was evaporated, followed by the addition of acetonitrile solvent. The resulting solution was then analyzed using voltammetry to determine the Kd and %E values for Sm(III) extraction in the raffinate phase.

Voltammetry Measurement of Sm(III) Extraction Results

The raffinate phase was separated and dried using a hotplate. Furthermore, HNO_3 was added to taste and dissolved using 100% acetonitrile. The solution was analyzed by DPV and transferred into a voltammetric cell. The three electrodes were connected to a potentiostat instrument, and DPV measurements were taken under optimum conditions, including a potential range of -1.5 V to +1.0 V, a deposition potential of -1.5 V, a deposition time of 60 seconds, a scan rate of 0.05 V second-1, and an amplitude modulation of 0.075 V. As a result, the peak current of Sm was obtained. The results of the Sm(III) extraction raffinate phase measurements will be determined based on the Kd and %E values.

UV-Vis Spectrophotometry Measurement of Sm(III) Extraction Results

A 2.5 mL sample of Sm(III) 1000 ppm solution was transferred into a 25 mL volumetric flask. The solution's pH was adjusted using sodium hydroxide to achieve 2, 2.5, 3, 3.5, and 4 pH conditions. While stirring, the buffer was added according to the pH condition, and then distilled water was added to reach the flask's limit mark, followed by homogenization. The solution was transferred into a separating funnel, and TBP was added in n-hexane of about 25 mL with a ratio of mol metal: mol extractant = 1: 6, 1: 9, 1: 15, and 1: 20. Furthermore, the solution was put into a separatory funnel and shaken for 5, 10, 15, and 20 minutes and allowed to stand for 30 minutes. The extract phase and the raffinate phase were separated. The raffinate phase was taken and conditioned at pH 4.0. Then, 0.5 mL of ARS solution was added, and distilled water was also added until the limit mark. Sm-ARS solution was analyzed using a UV-Vis spectrophotometer at the maximum absorption wavelength of Sm-ARS.

3. RESULTS AND DISCUSSION

Sm Current Response

The measurement of Sm current response in acetonitrile was carried out by DPV using three electrodes: the Pt working electrode, the Ag/AgCl comparison electrode, and the Pt auxiliary electrode. The DPV parameters of optimum conditions were applied: potential range -1.5 V to +1.0 V, deposition potential -1.5 V, deposition time 60 seconds, and amplitude modulation 0.05 V. The voltammogram of Sm variation concentration analysis results is shown in **Figure 1**.

In **Figure 1**, it is evident that higher Sm concentration leads to an increased peak current response, attributed to a higher number of electroactive analyte ions (Sm^{3+}) being reduced or deposited on the working electrode, causing an increase in diffusion current. This is consistent with the Rendless-Sevcik equation, where the current is directly proportional to the analyte concentration. The reduction of Sm occurs at a potential of -0.3459 V, yielding a relatively good peak current, and there is a potential shift towards a more positive direction with a relatively good separation resolution.

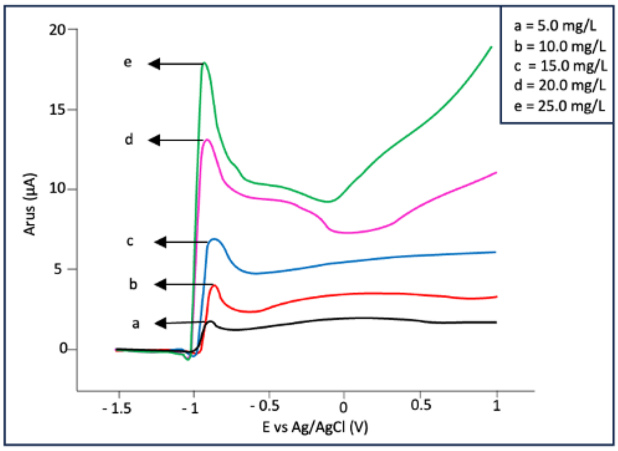

Figure 1. The voltammogram of Sm solution in acetonitrile (a) 5.0 mg/L, (b) 10.0 mg/L, (c) 15.0 mg/L, (d) 20.0 mg/L, (e) 25.0 mg/L, at potential range -1.5 V to +1.0 V, deposition potential -1.5 V, deposition time 60 second, amplitude modulation 0.05 V, and scan rate 0.05 V second^{-1}.

The diffusion current represents the electron transfer mechanism expected from voltammetric measurements. The negative potential applied to the Pt working electrode renders it negatively charged. The 3+ charged Sm ions on the surface of the working electrode will be reduced to Sm^{2+}. This leads to a decrease in the concentration of Sm ions on the working electrode's surface. As a result, Sm ions far from the working electrode (the concentration is greater than that on the electrode surface) will move toward the working electrode. This electron transfer mechanism, driven by the concentration difference, generates the diffusion current, directly proportional to the analyte concentration. The Sm reduction reaction occurs during the Sm deposition process with the measured analyte, expressed as follows:

$$Sm^{3+} + e \longrightarrow Sm^{2+} \qquad E^0 = -1{,}55 \text{ V}$$

During measurement, the analyte's Sm oxidation reaction occurs. This oxidation process is initiated from the lowest potential range and impacts the reduction peak due to the influence of solvent molecule oxidation.

Acetonitrile as a solvent can provide a wide range of potential values and can be effectively combined with a relatively high dielectric constant. These characteristics contribute to its high solubility and ability to dissociate on the electrode surface, providing excellent solvation properties for various electrolytes. Additionally, acetonitrile is also known to be inert and will not react with the Pt working electrode or the Sm solution. When measurements are taken, it will not produce peaks that can interfere with the measurement process [20].

Verification of DPV Analysis Method

The determination of analytical parameters is carried out to ensure and confirm that the method used can produce valid data according to its purpose. Linearity, LoD, LoQ, accuracy, precision, and %recovery verify analytical methods.

Linearity

Linearity is shown by the curve of the relationship between current and Sm(III) concentration at optimum measurement conditions[20]. In this study, Sm(III) was measured at concentration variations of 5, 10, 15, 20, and 25 ppm, and the results showed that the higher the concentration of Sm, the higher the current generated. The current generated can be seen in **Figure 1**.

To further assess linearity, the Sm calibration curve was constructed based on the current response obtained from four measurements. This curve illustrates the relationship between the current response and the concentration of the standard solution over various concentration ranges. The calibration curve plots the measured current response value (y-axis) against the standard solution concentration (x-axis), as depicted in **Figure 2**. This calibration curve provides valuable insights into the linearity of the current response, allowing researchers to describe the method's behavior accurately at different concentration levels.

From the calibration curve, the linearity value can be evaluated. The linear regression equation obtained is $y = 0.6665x - 0.5753$ with an R^2 value of 0.9958. The analytical method is considered linear over a certain concentration range if the coefficient of determination (R^2) value obtained is > 0.99 [18]. The R^2 value obtained is close to one, indicating a linear response of the potential change of the Ag/AgCl electrode to changes in the concentration of the test solution. Based on the value of the Nernst factor and linearity, the Ag/AgCl comparison electrode that has been made can be used for further measurements. Therefore, it can be concluded that Sm analysis using DPV produces a good linearity of response in the range of 5 - 25 mg/L. The linearity measurement results can be seen in **Table 1**.

LoD & LoQ

The sensitivity of an analytical method is often expressed by its Limit of Detection (LoD), which represents the smallest analyte concentration in a sample that can still be reliably detected and distinguished from the blank or background noise. In this DPV study, the LoD was determined to be 1.61 mg/L. Meanwhile, LoQ shows the lowest concentration of analyte that can be accurately quantitated and shows the sensitivity of the analytical method used. The LoQ was determined to be 4.89 mg/L.

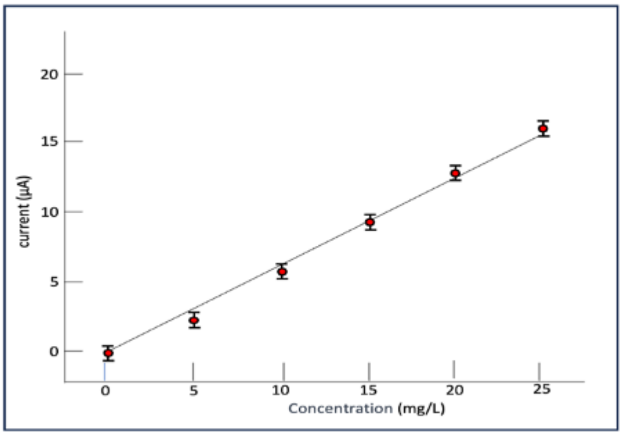

Figure 2. Calibration curves of Sm with concentrations of (a) 5.0 mg/L, (b) 10.0 mg/L, (c) 15.0 mg/L, (d) 20.0 mg/L, (d) 25.0 mg/L with optimum conditions at a deposition potential of -1.5 V, amplitude modulation of 0.075 V and deposition time of 60 seconds.

Table 1. Linearity measurement results using the DPV method.

Parameter	Value
Linear range	5.0-25 mg/L
Coefficient of determination (R^2)	0,9958
Slope	0.5753
Intercept	0.6665

Precision

Precision or accuracy is determined by the relative standard deviation (RSD) value. The smaller the %RSD, the more precise the method used. Precision was determined by measuring one standard concentration and six repetitions. The %RSD of Sm(III) was 3.29%, with a precision value of 96.70%. The RSD value for repeatability and precision in Sm analysis shows that the DPV method has good accuracy for Sm(III) measurement appropriate to the requirement that the acceptable %RSD is ≤ 5% and smaller than 2/3 CV Horwitz.

Accuracy

Accuracy is a parameter showing the closeness between the analysis results and the analyte levels, usually expressed as percent recovery. The accuracy value is acceptable because it meets the requirements in the average accuracy range of 90-107% [24], which can be seen in **Table 2** below.

Table 2. Accuracy and precision data of Sm 20 mg/L using DPV

Current (µA)	Measured Concentration (mg/L)	Sb	KV (%)	Accuracy (%)	Precision (%)
13.3057	20.11	0.43	3.29	98.39	96.70
13.0615					
13.0611					

The accuracy of an analytical method is considered satisfactory when the recovery percentage falls within the required range. In this study, the recovery from the analysis results is 106.69%. The measurement recovery value obtained is quite good because it meets the requirements. Namely, the value is in the range of 90%- 110%.

UV-Vis Spectrophotometry Analysis Method

To determine the maximum absorption wavelength of TBP and the formation of Sm-TBP complex compounds, measurements were performed using an ultraviolet (UV) spectrophotometer at 200-400 nm wavelength with a blank of n-hexane. **Figure 3** shows the results of the maximum absorption wavelength spectrum of TBP and Sm-TBP complexes.

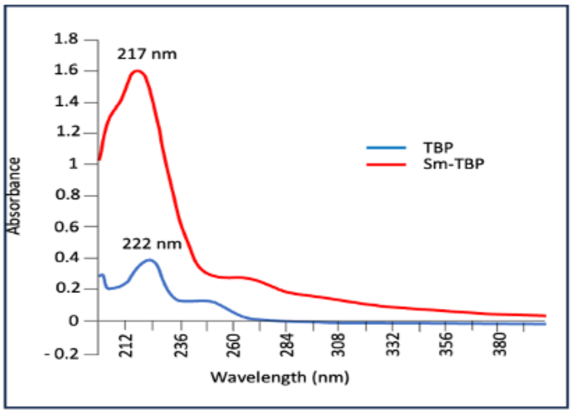

Figure 3. Maximum absorption wavelength curves of TBP and Sm-TBP complexes.

The UV-Vis spectrophotometry analysis yielded a linear regression equation of $y = 0.0465x + 0.1761$, representing the relationship between the concentration of the standard solution and the absorbance, with a correlation coefficient (R^2) value of 0.9934. The determination of LoD was obtained at 0.71 mg/L and LoQ at 2.16 mg/L. The accuracy obtained from the analysis results is 96.00%, and the precision value was 99.83%, with a relative standard deviation value or the coefficient of variation (%KV) <5%, indicating good precision parameters and repeatability well accepted[24]. The recovery obtained from the analysis results was 104.00%. The calibration curve of Sm can be seen in **Figure 4**. Meanwhile, the data from the analysis method using spectrophotometry can be seen in **Table 3**.

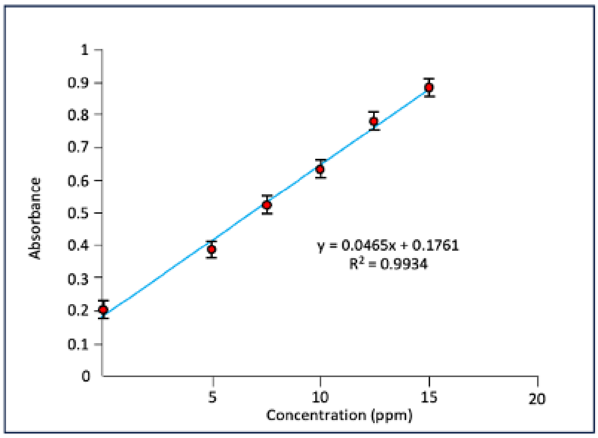

Figure 4. Sm-ARS standard curve at λmax 528 nm

Table 3. UV-Vis spectrophotometry analysis method data.

Parameter	Value
LoD	0.71
LoQ	2.16
Sb	0.01
KV	0.17%
Accuracy	96.00%
Precision	99.83%
Recovery	104.00%

Liquid-Liquid Extraction of Sm(III) using TBP Extractant

The extraction process of individual Sm(III) using TBP as the extractant was conducted under optimal pH conditions of 2.5. The pH level is a crucial factor that influences the formation of complexes. The extraction was carried out with pH 2.5, and in these pH conditions, there was a complex formation between Sm(III) and TBP. Subsequently, TBP was also used as an extractant, which is an electron donor, while the lanthanide ion (Ln^{3+}) or solute is an electron acceptor. TBP can extract Ln^{3+} from nitrate media according to the following reaction::

$$Ln^{3+}_{(aq)} + 3NO_3^-{}_{(aq)} + 3TBP_{(org)} \rightleftarrows Ln(NO_3)_3.3TBP_{(org)} + 3H^+$$

Based on the reaction above, Ln^{3+} requires 3 moles of TBP to form a neutral complex compound and release 3H+. The resulting Ln(TBP)3 complex is uncharged and can be attracted to the non-polar organic phase following the like-dissolve-like principle. Meanwhile, the remaining metal that does not react will be attracted to the raffinate phase. A mole ratio of metal to TBP extractant of 1:15 was used in this extraction process. The greater the extractant concentration, the more efficient the extraction of Ln from the feed solution is indicated by an increase in the distribution coefficient (Kd) value. The process involved shaking the solution for 15 minutes, allowing sufficient contact time between the aqueous and organic phases during extraction. After shaking, the solution was allowed to stand for 30 minutes, completely separating the organic and aqueous phases. Furthermore, the raffinate phase formed was used to determine the free Sm(III) concentration in the sample before and after extraction.

DPV Analysis on Evaluation of Sm(III) Liquid-Liquid Extraction Results using TBP Ligand

During the Sm(III) extraction process under the optimized conditions of pH 2.5, a mole ratio of metal to extractant of 1:15 and a shaking time of 15 minutes. This study used n-hexane as a solvent in the extraction process's organic phase to dissolve TBP. A current response was generated through analysis of the raffinate phase using DPV, enabling the determination of the Kd and %E values. The Kd and %E values are crucial indicators of the extraction's success, as they assess the efficiency of Sm(III) extraction at the optimized conditions using DPV analysis. The obtained Kd values ranged from 6.0019 to 7.3860, indicating that the extraction process effectively concentrated and separated Sm(III) from the sample. Similarly, the %E falls within the 85.71-88.07% range. These results show that voltammetry can be an alternative method for analyzing REM extraction results.

Comparison of Voltammetric Analysis with UV-Vis Spectrophotometry Analysis

To assess the DPV method's effectiveness, the DPV analysis results were compared with UV-Vis spectrophotometry analysis. The results are shown in **Table 4**.

In **Table 4**, the analytical parameters obtained using the DPV method show values that are comparable to the results obtained from UV-Vis spectrophotometry analysis. The LoD and LoQ values of the DPV method (1.61 mg/L and 4.89 mg/L, respectively) are not significantly different from the values obtained through UV-Vis spectrophotometry (0.71 mg/L and 2.16 mg/L, respectively). The determination of Sm by the DPV method has LoD and LoQ values that are not too different from the values in the analysis results using UV-Vis spectrophotometry.

Table 4. Comparison of spectrophotometry and voltammetry analytical methods for the measurement of Sm(III) extracted samples.

Analytical Parameters	UV-Vis Spectrophotometry	DPV
Sb	0.01	0.43
KV	0.17	3.29
LoD (mg/L)	0.71	1.61
LoQ(mg/L)	2.16	4.89
Accuracy	96.00%	98.39%
Precision	99.84%	96.70%
Recovery	104.00%	106.69%

The standard deviation (SD), coefficient of variation (KV), or relative standard deviation (RSD) of each analysis result can be calculated and compared to assess accuracy. In UV-Vis spectrophotometry analysis, the average KV value was 0.17%, while the average KV value in the DPV method was 3.29%. Both methods are considered to have good accuracy as their KV or RSD values are within the acceptable range of ≤ 5%, indicating high precision. Smaller RSD values suggest a more precise and reliable method. The data above shows that the test methods used by UV-Vis spectrophotometry and DPV have good accuracy because they meet the requirements of the acceptance range, where the KV results of both do not exceed 5%. Therefore, both methods are deemed thorough and suitable for Sm(III) analysis, providing valuable insights for further analytical studies.

The measurement of the precision of an analytical procedure reflects the closeness of the concentration determination results to the actual concentration. This parameter is described by the recovery value. The recovery result obtained in UV-Vis spectrophotometry is 104.00%, while in DPV, the recovery value is 106.69%, and a good recovery value is not less than 90.0% and not more than 110%. The recovery value describes this parameter. The recovery result obtained in UV-Vis spectrophotometry is 104.00%, while in DPV, the recovery value is 106.69%, and a good recovery value is not less than 90.0% and not more than 110%. The UV-Vis spectrophotometry and DPV methods have good accuracy and can be used for an alternative analysis of Sm(III) liquid-liquid extraction results.

The liquid-liquid extraction analysis of Sm(III) using DPV yielded Kd values in the 6.0019-7.3860, along with %E, within the 85.71-88.07% range. UV-Vis spectrophotometry analysis results obtained a Kd value of 7.7229 and %E of 88.53%. These results show that the Kd and %E values from the DPV analysis are not much different from those obtained from the UV-Vis spectrophotometry analysis. The Kd and %E values in UV-Vis spectrophotometry and DPV analysis are shown in **Table 5.**

Table 5. Comparison of Kd and %E of UV-Vis spectrophotometry and DPV methods in the measurement of Sm(III) extracted samples

Method	Kd	%E
UV-Vis spectrophotometry	7.7229	88.53%
DPV	6.0019 -7.3860	85.71-88.07%

From the results obtained, it is evident that the DPV method analysis parameters fall within the acceptable range, as required by AOAC standards. Furthermore, the Kd and %E values derived from the DPV analysis are comparable to those obtained from UV-Vis spectrophotometry. It can be concluded that the DPV can be used as an alternative analytical method that can overcome the problems that arise in the analysis using UV-Vis spectrophotometry methods, methods, such as the need for various chemical reagents, complex sample preparation procedures, and the need to consider complex stability. DPV alleviates these challenges, making the method more practical, efficient, and cost-effective. The DPV method's ability to accurately determine Sm(III) concentration in the liquid-liquid extraction process without the complexities of UV-Vis spectrophotometry enhances its potential as a viable alternative for future analytical studies.

4. CONCLUSIONS

In conclusion, DPV and UV-Vis spectrophotometry can be used as alternative analysis methods for Sm(III) liquid-liquid extraction results based on this study. The DPV method provided LoD 1.24 mg/L, LoQ 4.89 mg/L, precision 96.70%, accuracy 98.39%, and % recovery 106.69%. Furthermore, UV-Vis spectrophotometry obtained LoD 0.71 mg/L, LoQ 2.16 mg/L, precision 99.83%, accuracy 96.00%, and %recovery 104.00%.

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