Journal of Radiation and Nuclear Applications
An International Journal

http://dx.doi.org/10.18576/jrna/050310

Optimization and Validation of the Spectrophotometric Method for Quantification of Europium in Aqueous Reprocessing Streams

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Received: 20 May .2020, Revised: 18 Jul .2020, Accepted: 14 Aug. 2020.

Abstract: Europium(III) ion reacts with 3, 6-bis[(2-Arsonophenyl)azo]-4,5dihydroxy-2,7-naphtalene di sulphonic acid (Arsenazo III) to form a raspberry-red colour complex. The complex formed instantaneously at pH 2.6-2.8, maintained by mono chloroacetic acid and sodium acetate buffer and stable for over 24 hrs. The 1:1 chelate complex exhibits maximum absorption at 654 nm, obeys Beer's law in the concentration range from 0.24 to 2.21 *µg* of Eu(III) per *mL*, has a molar absorptivity of $6.21\text{x}10^{4}$ $L.Mol^{-1}.cm^{-1}$ and a Sandell's sensitivity of $1.61\text{x}10^{-5}$ $\mu g/cm^{2}$. From ten repeated determinations correlation coefficient was found to be ±0.98%. The limit of detection (LOD) (3.3σ/S) and limit of quantitation (LOQ) (10σ/S) were found to be 0.082 *µg/mL* and 0.249 *µg/mL* respectively. Interference of other competing metal ions, pH, and the concentration of the complexing agent, the stability of the colour and volume of the buffer were examined systematically. The proposed method is directly applicable for the determination of europium in environmental, industrial, water and waste streams of the nuclear plant.

Keywords: Europium, Arsenazo III, Spectrophotometry, Molar Absorptivity, PUREX process.

1 Introduction

Europium is one of the troublesome fission products in terms of its behaviour towards the PUREX process.TBP extracts some of the fission products, even under the most favourable conditions. Some of the longer-lived and stable isotopes of europium have very high neutron cross-sections. They can cause serious neutron poisoning problems in the reactor [1] if they are allowed to build up or are incompletely removed in reprocessing. Europium isotopes such as ^{152}Eu, ^{154}Eu and ^{155}Eu are produced primarily as the fission products and have half-lives long enough ranging from 5 to 13 years to warrant potential concern. When a fissile nuclide such as an atom of ^{235}U and ^{239}Pu fissions, it generally splits asymmetrically into two large fragments, which can include the three europium isotopes and two or three neutrons. The fission yield of ^{155}Eu is about 0.03% while the output of the other two isotopes is much lower. During reprocessing, these isotopes of europium give intense beta and gamma exposure and also reduce the decontamination factor of reprocessed fuel.

Various analytical techniques such as inductively coupled plasma mass spectrometry [2-4], inductively coupled plasma mass and atomic emission spectrometry [5-6], neutron activation analysis [7], radiochemical [8], spectrofluorimetry [9], polarography [10], flow injection [11], voltammetry [12], potentiometry [13] and spectrophotometry [14-28] etc. are reported in the literature. However, the majority of these instruments is costly and needs high caring during the analysis. UV-Vis spectrophotometry is the most convenient method because of their simplicity, adequate sensitivity, low cost, easy availability and more suitable for process and plant control samples.

Azo metal chelates can offer an inexpensive and convenient analysis with various metal ions in solution, provided that the acceptable selectivity and sensitivity are achieved. Arsenazo III is commercially available and soluble in water and diluted acids. The reagent can form stable chelates and can work in a strongly acidic medium eliminating the chances of partial hydrolysis of metal ions to be determined. Its sensitivity due to the colour reaction is quite high (0.05–0.01 µg cm^{-3} of the element). The high sensitivity and stability are coupled with a sharp contrast in colour transition from pinkish (reagent) to blue-green or raspberry-red (complex with Arsenazo III) [28]. Therefore, there is a need for suitable laboratories equipped with inexpensive instrumentation, which allows the determination of europium to be carried out in a fast and cheap way without sacrificing precision. In the present

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work is to develop a method for direct, sensitive and accurate determination of traces of Eu(III) and the main focus to dispose of spectrophotometric waste directly. Chemical spectrophotometric variables, namely pH, reagent concentration, buffer and interference of other computed metal also studied and optimized. During the experiments, the generated spectrophotometric waste was collected and passing through activated carbon to remove the arsenazo III contain azo aromatic group and arsenic, which is a very toxic element. It is easy to adapt for on-site or at-line monitoring.

2 Experimental

2.1 Reagents

All the chemical and reagents used were of analytical grade, and double-distilled water was used for all dilution of reagents and samples. A stock solution of europium (III) nitrate (1000 *µg/mL*) was prepared by dissolving europium (III) nitrate of 99.9% purity (obtained from M/s Alfa Aesar Chemicals) in 1*M* nitric acid. The solution was standardized by EDTA titration using xylenol orange as an indicator [29]. It was further diluted to get the required concentration of europium in solution. This solution was used as a working standard for further studies. The buffer solution of pH 2.6-2.8 was prepared by mixing of mono chloroacetic acid, and sodium acetate in 100 *mL* distilled water. 0.02% Arsenazo III of purity (99.5%) Fluka, was prepared by dissolving (obtained from Merck, India) in distilled water. Standard solutions of nitric acid (Merck) were prepared by appropriate diluting concentrated nitric acid. The stock solution of EDTA (0.01W/v) was prepared by dissolving 10 mg of ACS grade of disodium dihydrogen ethylenediamine tetraacetate dehydrate in 100 *mL* distilled water

2.2 Instrumentation

All absorbance was measured with an indigenously developed fiber optic aided spectrophotometer using dip type probe of 1 cm path length. pH adjustments were carried out using Chemlabs, digital pH-meter model Micro-07, Bangalore. All titration was performed on titration system model E526 manufactured by Metrohm, Switzerland.

2.3 Experimental Procedures

An aliquot of the europium standard containing 0.1-3.0 *µg* was taken into a series of 10 *mL* standard flasks and 0.5 *mL* of 0.02% Arsenazo III solution, 1.0 *mL* of the buffer solution with pH 2.8 was added to each flask and made volume up to mark with distilled water. The absorbance of the solutions was measured from 700-380 *nm* against a reagent blank prepared under identical conditions at room temperature (25±0.5)°C.

3 Results and Discussion

3.1 Spectral characteristics

Arsenazo III reacts with Eu(III) and forms a stable raspberry-red colour complex with maximum absorbance (λ_{max} = 654 *nm*) at pH 2.6-2.8 against a reagent blank and shown in Fig. 1. The complex is rapid, instantaneously and steady for 24 hours. In all instances, measurements were made at 654 *nm*. The characteristic of Arsenazo III–Eu(III) complex is represented in Table 1.

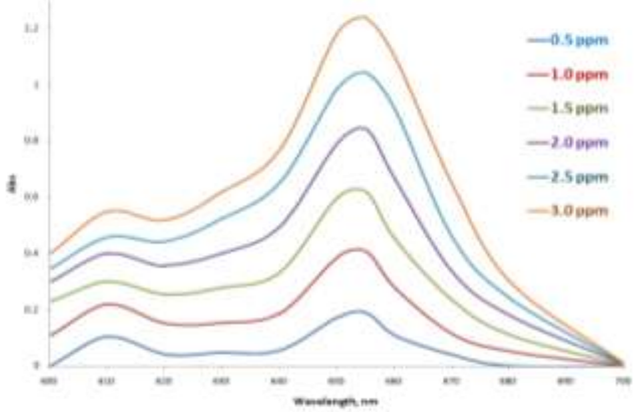

Fig.1: Typical absorption spectrum of Eu(III)-Arsenazo III complex at the pH 2.6-2.8 solutions; blank corrected. Buffer solution V = 1 *mL*, Arsenazo III solution V = 0.5 *mL*, [Eu(III)] = 0.2-3 *µg/mL*.

Table 1: Spectral characteristics of Eu-AR III complex.

Parameter	Eu(III)-ARIII complex	
λ max, (nm)	654	610
Beer's law limit ((µg/mL)	0.24-2.15	0.41-3.68
Molar absorptivity, (L.Mol^{-1}.cm^{-1})	6.35 x 10^4	3.72 x 10^4
Sandell's sensitivity (µg/cm^2)	1.57 x 10^{-5}	2.71 x 10^{-5}
Detection Limit# (µg/mL)	0.082	0.115
Quantitation Limit# (µg/mL)	0.249	0.351
Regression equation*	Y=63584x	Y=37186x
Correlation coefficient (r)	0.9993	0.999
Linear Range (µg/mL)	0.24-2.15	0.41-3.68
Stability formation region (pH)	2.6-2.8	2.6-2.8
Monochloro acetic acid & sodium acetate buffer (mL)	1	1
Arsenazo III (0.05%) (mL)	0.5	0.5

**Y is the absorbance and x is the concentration in µg/mL*
#calculated using ICH guidelines

3.2 Calibration Graph, Beer's Law and Sensitivity

A series of standard europium solutions were prepared, and the absorbance of each was measured and plotted against concentration. The well-known equation for spectrophotometric analysis in very dilute solution was derived from Beer's law. The calibration curve of Eu(III)-Arsenazo III complex was made with fixed concentrations of Arsenazo III (0.5 *mL*, 0.2%) and variable concentrations of Eu(III) (0.23-2.15 *µg/mL*) (in the presence of buffer pH = 2.8, 1 *mL*) at 654 and 610 *nm*. The results obtained are given in Fig.2. Plotting of the obtained data gives a linear regression equation at 654±0.5 *nm* obtained was: A = 63584 x C, Eu (*moles/L*), with a good correlation coefficient (R^2) equals 0.999. The slope of the relation verifies Beer's law in the equation mentioned above and gives the molar absorptivity (ε). It shows that molar absorptivity of 63584 $L.Mol^{-1}.cm^{-1}$ for 654 *nm* and 37186 $L.Mol^{-1}.cm^{-1}$ for 610 *nm*. Since the sensitivity of the spectrophotometric method is expressed in terms of the sensitivity index given by [30], the analytical sensitivities of Arsenazo III method for determining europium (atomic mass: 151.96 $g.mole^{-1}$, λ_{max} of 654±0.5 nm) in the aqueous medium. It was found that values of the sensitivity (concentration for 0.001 absorbance unit) are found to equal 1.57×10^{-5} for 654 nm and 2.71×10^{-5} $\mu g.cm^{-2}$ for 610 nm respectively.

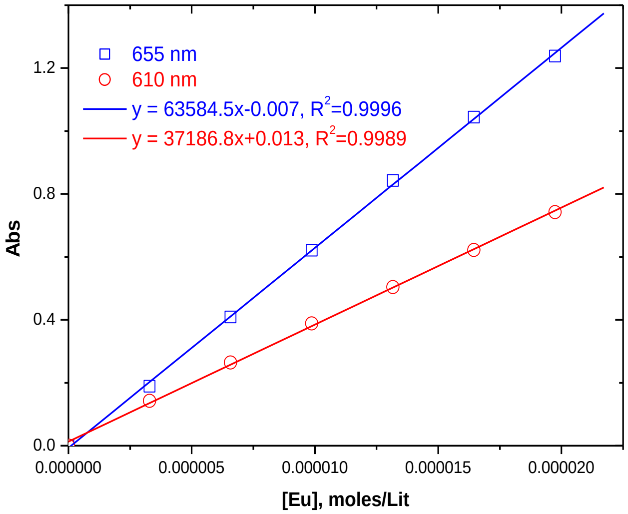

Fig. 2: Typical Calibration graph for determination of Eu (III) nitrate with Arsenazo III at 654 and 610 nm, blank corrected. Buffer solution V = 1 *mL*, Arsenazo III solution V = 0.5 *mL*, [Eu (III)] = 0-0.00002 *moles/L*.

The optimum concentration range for maximum precision was detected from Ringbom's plot [31]. The transmittance plotted against the logarithm of metal concentration. The linear portion of the curve indicates that the range was 0.1 to 0.5 ppm of Eu(III) (Fig.3) and slope of Ringbom's plot was 0.706.

3.3 Effect of pH Solution

The effect of pH on the colour development of europium complex formation was studied and found that the maximum absorbance and stability is for more than 24 hours at pH 2.6-2.8 with a fixed concentration of europium (2.8 *µg/mL* per 10 *mL* of solution) and 0.2 % arsenazo III. Hence pH 2.8 is optimum and mono chloroacetic acid /sodium acetate buffer solution was employed and found to be satisfactory. The volume of the buffer used found not to affect the absorbance. Same is maintained for all subsequent work.

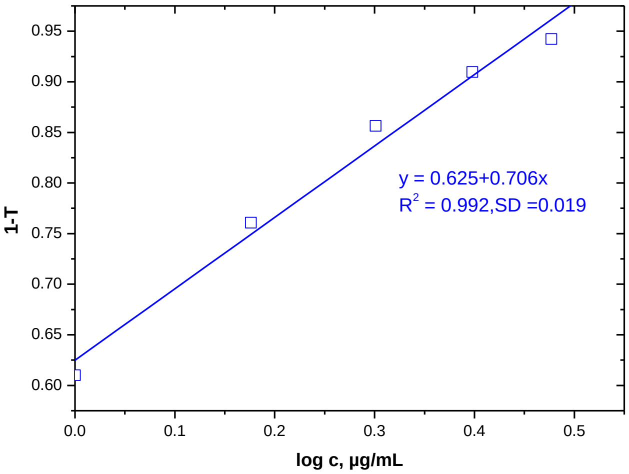

Fig. 3: Ringbom's plot for determination of Eu (III) nitrate with Arsenazo III at 654, blank corrected. Buffer solution V = 1 *mL*, Arsenazo III solution V = 0.5 *mL*, [Eu(III)] = 0.2-3 *µg/mL*.

3.4 Effect of Arsenazo III Dye Concentration

The influence of the concentration of Arsenazo III dye on the absorbance of europium complex at pH 2.8 was determined by measuring the absorbance on the solution kept constant Eu(III) concentration, fixed buffer solution and different volume of Arsenazo III from 0.1 to 1 *mL*. It was found that the maximum absorbance was the most obvious when adding 1 *mL* dye at 654 nm, once it exceeds this volume, absorbance would remain constant. So 1 *mL* of Arsenazo III is favourable and used in subsequent experiments.

3.5 Effect of Time and Temperature

The reaction is instantaneous constant and maximum absorbance was obtained just after diluting the solution and remained strictly unaltered for 2h hours. The Eu(III)-Ar(III) system obtained maximum and constant absorbance at room temperature (25±5)°C. Outside this range of temperature, the absorbance decreased.

3.6 The Composition of The Complex

The composition of Eu(III)-Arsenazo (III) was investigated by the Job's method of continuous variation [32] and the mole ratio methods [33] with a fixed concentration of Eu(III), and varying concentration of Arsenazo III. In the mole ratio method (Fig. 4) a break was observed when the Eu(III)-Arsenazo(III) ratio was 1:1, indicating an ML type complex formation. The plot of Job's method also confirms the formation of an ML type composition of the complex, which was represented in Fig. 5.

3.7 *Effect of Foreign Ions*

To investigate the influence of various metal ions on the determination of europium was studied under the experimental conditions. The most severe interferences like Nd(III), Sm(III), Gd(III), La(III), Nd(III), Y(III) and U(VI) are formed a complex with Arsenazo (III). The results are summarized in Table 2. Selectivity can be improved by prior separation or complexation must be followed. The interference ions are removed by using several masking agents such as 1% tartaric acid, 1% citric acid, 0.5% EDTA, 1% thiocyanate and thiourea or by a short single-step ion-exchange separation process using cation-exchange resin (ex) AG50 W-X8 [34]. If any precipitate formed during these studies, it was removed by centrifugation.

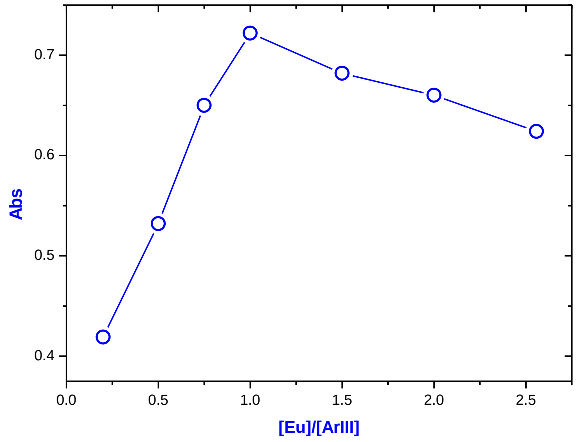

Fig. 4: Mole ratio method.

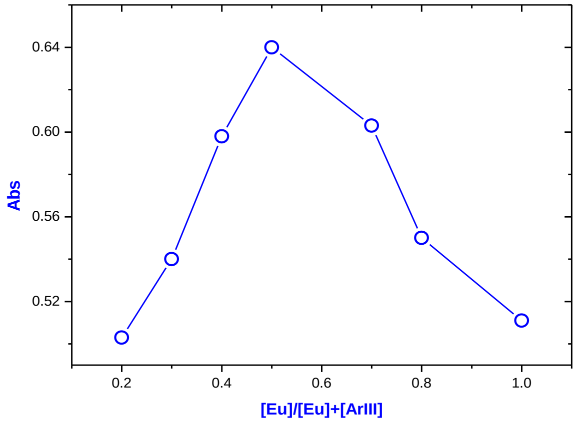

Fig. 5: Job's continuous variation method.

Masked with 1 mL 1% aqueous thiocyanate solution, Anions are effectively masked by the addition of 0.3 mL 0.5% EDTA, ii. Sm(III), La(III), U(VI) interfering ions are effectively separated by convenient type cation -exchange resin (ex) AG50 W-X8.

Table 2: Interference of metal ions during the determination of europium

Interference of metal ions		Concentration of Europium (μg/mL)		% error
Metal	Conc. Taken (μg/mL)	Taken	Obtained	
$Sm(NO_3)_3$	10	1.35	1.792	+32.71
$Zr(NO_3)_4$	10	1.35	1.687	+24.96
$UO_2(NO_3)_2$	10	1.35	1.544	+14.37
$Gd(NO_3)_3$	10	1.35	1.528	+13.18
$Nd(NO_3)_3$	10	1.35	1.492	+10.48
Ru(III)	10	1.35	Peak Shifted	
$Y(NO_3)_3$	10	1.35	1.379	+2.13

4 Validation of the Proposed Method

The proposed method was validated according to the international conference for Harmonization (ICH) guidelines [35] under the optimized experimental conditions: linearity, accuracy, precision and specificity.

4.1 *Precision and Accuracy*

The accuracy and precision of the present method were evaluated by determining different concentration levels of europium (each analysis replicate at least five times). The relative standard deviation ($n = 5$) was 1.32% for 0.5 to 500 µg of europium in 10 mL, indicating that this method is highly precise and reproducible. Five sample solutions of each concentration were analyzed under the same experimental conditions within one day (intra-day precision) and in five consecutive days (inter-day precision). The % RSD and data are summarized in Table.3. Hence, the precision and accuracy of the method were found to be excellent.

Table 3: Accuracy and precision of proposed method.

	[Eu] taken, ppm	[Eu] found, ppm	RSD (%)
Intra-day	0.12	0.114	1.68
	0.5	0.487	0.81
	1.35	1.342	2.28
Inter-day	0.12	0.129	1.57
	0.5	0.512	0.54
	1.35	1.362	1.91

**Mean for five independent determinations*

4.2 *Detection Limit and Quantitation Limit*

The limit of detection has been calculated as (3.3σ/S), where σ denotes the standard deviation for blank (n=10) and S stands for the slope of the analytical curve from the calibration graph. The limit of detection (LOD) was found to be 0.082 *µg/mL*, whereas the limit of quantitation (LOQ)

$(10\sigma/S)$ was 0.249 *μg/mL* with precision (was evaluated by determination of the different concentration of europium) expressed as relative standard deviation (RSD) of 1.32%. The obtained results indicate that this method is highly precise and reproducible. Calculations were made the recommendations by IUPAC (1978). The best agreement between theoretically computed and practically verified values of LOD and LOQ was approached namely at significance level $\alpha = 0.05$.

4.3 Robustness and Ruggedness

Robustness was examined by evaluating the influence of a small variation of the method variables including the concentration of analytical reagent and the pH of the solution. It was found that small variations in these variables did not affect the method significantly. This was an indication of the reliability of the proposed method during its routine application. The ruggedness was tested by applying the proposed method of analysis of europium under the same experimental conditions by two different analysts. Results obtained from inter-day RSD and within-day RSD were found to be reproducible and between 0.81 and 0% (Table.4).

Table 4: Reproducibility of the method by two different analysts.

	[Eu], ppm		% RSD
	Taken	Obtained	
Analyst 1	1.35	1.36	0.81
Analyst 2	1.35	1.37	
Analyst 1	0.54	0.57	0.54
Analyst 2	0.54	0.53	

4.4 Range and Linearity

The precision and accuracy of the method were tested by taking known two different trace amounts of europium. As shown in table 5, mean values were obtained with Student's t-values at 95% confidence level and the variance ratio F-values calculated (p=0.05) for 5 degree of freedom. The results showed comparable accuracy (t-test) and precision (F-test) and did not exceed the theoretical values, indicating that there was no significant difference in accuracy and precision. The performance of the proposed method was verified with of other existing UV-Vis spectrophotometric method using Chrome azurol S as chromogenic reagent reported in the literature [19]. It is clear from the table 5, that the calculated t value is less than the tabulated t value at the 95% confidence level for four degrees of freedom is 2.776. Therefore, $t_{cal} < t_{table}$, and there is no significant difference between the two methods at this confidence level. The proposed method is simple and requires less time to complete the analysis. The method is simple, fast, versatile, accurate and useful due to high tolerance limits from cations and anions.

5 Applications

The proposed method was examined for the determination of europium concentration during the solvent extraction behavior of it with the TBP-HNO_3 system at conditions prevalent in FBR fuel reprocessing.

Table 5: Evaluation data of accuracy and precision calculation for Eu-Arsenazo III complex.

	Variable 1		Variable 2	
	Present Method	Reference Method*	Present Method	Reference Method*
Mean	1.7202	1.7132	0.9576	0.966
Standard Deviation	0.02	0.0283	0.0265	0.02
Variance	0.0004	0.0008	0.0007	0.0004
RSD	1.163	1.652	2.767	2.0704
Degree of freedom	4	4	4	4
f-Test cal	1.416		0.615	
f-Test table	3.051			
p (Probability)	0.05		0.05	
$f_{cal} < f_{table}$	No significant different		No significant different	
Confidence level	95%		95%	
t-Test cal	0.4518		0.5652	
t-Test table	2.306		2.306	
$t_{cal} < t_{table}$	No significant different		No significant different	

* [19]

6 Conclusions

In this paper, a simple, accurate, sensitive and inexpensive fast method for the determination of Eu^{3+} ions in nitric acid medium relevant to the PUREX process used for spent nuclear fuel reprocessing and nuclear industry. The generated spectrophotometric waste solution was treated with activated carbon to remove the toxic material like arsenic and easy to dispose of the waste. The proposed method is easy to adapt for continuous monitoring of Eu(III) using flow injection mode. This method does not require the use of expensive, toxic and carcinogenic organic solvents, less complicated when compared to other techniques. The accuracy and selectivity in terms of the relative standard deviation of the present method are reliable for the determination of europium in real samples to microgram levels in the aqueous medium at room temperature $(25 \pm 5)^{o}$C.

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