Univariate and Multivariate Optimization of Spectrophotometric Determination of Europium (III) in Pure Form and Synthetic Sample

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Abstract

Two different approaches, univariate and multivariate (simplex method), have been used to obtain the optimum conditions for the quantitative Spectrophotometric determination of Eu^{3+} using Solochrome violet RS (3-Hydroxy-4-(2-hydroxy phenyl azo) naphthalene -1-sulfonic acid) (SVRS) as a chromogenic reagent. The investigation shows that Eu^{3+} ion forms a wine-red complex with SVRS in alkaline buffer solution having a maximum absorbance at 464 nm against reagent blank.

Calibration graphs obtained under univariate and simplex were found to be linear in the range of (0.30-8.0) µg/ml with detection limit 0.061µg/ml and molar absorptivity of 9877.66 L/mol.cm and (0.40-10.0)µg/ml with detection limit 0.055µg/ml and molar absorptivity of 10759.05 L/mol.cm respectively. The stoichiometric composition of the formed Eu-SVRS chelate complex is 1:4 (Metal:Ligand). Effect of the presence of some metal ions as interferences was studied and the method has been applied successfully to the determination of cited ion in synthetic sample.

Key words: Lanthanides, Simplex, Solochrome Violet(SVRS), spectrophotometric.

Introduction

Rare earth of elements have gained a great attention in the last few decades owing to their unique properties and wide range of applications that utilizes these elements in huge quantities, consequently, data on the total Lanthanide content often suffices in practical problems, particularly when all the Lanthanides beingchemically similar to one another, invariably occur together in the source mineral[1].

Europium is one of the rarest and most costly of the rare earth of elements accounting for only about 0.05 - 0.1 % of the rare earthelements present in the mineral monazite[2]Europium oxide is now widely used as a doping agent inred phosphors activatorandeuropium compounds are also used in color cathode-x-ray tube, liquid-crystal displays used in computer monitor, high-intensity mercury vapor lamps, neutron scintillations, charged-particle, detectors and optically red mercury systems[3]. Various methods such as mass spectrometry (MS), inductively coupled plasma atomic emission spectrometry (ICP-AEC)[4], inductively coupled plasma mass spectrometry (ICP-MS)[5-7], isotope dilution mass spectrometry, neutron activation analysis and x-ray fluorescence spectrometry are viable for low-level determination of rare earth ions in solution, these methods are either time-consuming, involving multiple sample manipulations, or too expensive for most analytical laboratories. On the contrary, UV-visible spectrophotometry is the most convenient techniques because of their inherent simplicity, adequate sensitivity, low cost and wide availability in all quality control laboratories.

Azo metal chelates have drawn the attention and can offer an inexpensive and convenient analysis method with metal ions in solution, provided that the acceptable sensitivity and selectivity are achieved[8,9]In experimental chemistry the optimization of technical system is the process of adjusting the control variables to find the levels that achieve the best optimization. Usually many conflicting response must be optimized simultaneously.

In lack of systematic approaches the optimization is done by trial and error, or by changing on control variable at a time while holding the rest constant, such methods require a lot of experiments to be carried out. Simplex system was first used to determine the optimal conditions for the variables in the testing process by the researcher Deming[10]and then applied in the field of analytical chemistry by Spendley[11]et al., and modified by Nelder and Mead[12]because it offers the capability of optimizing several factors simultaneously depending on a statistical design search to find the maxima or minima of response, by rejecting the point producing the worst response and a replacement of it by the new point which is obtained statistically.

[3-Hydroxy-4-(2-hydroxy phenyl azo) naphthalene -1-sulfonic acid] (SVRS) azo dye, used as metal indicator in the chelatometric determination of Al(III) in natural[13]. In addition, SVRS is a reactive azo dye belonging to the largest class of dyes commonly used in textile industry[14].

The present work describes the utility of Solochrome violet (SVRS) for spectrophotometric determination of Eu^{3+} and the optimization of chemical spectrophotometric variables of the proposed methods namely pH, reagent concentration and reaction time have been studied by using both classical univariate and modified simplex.

Experimental

Apparatus

A Shimadzu (Model 1601 UV-visible spectrophotometer from Shimadzu, Kyoto, Japan) with 1cm quartz cells was used for the absorbance measurement and a pH-meter model BP 3001, (professional benchtop pH meter) was used for all pH measurements.

Material and Reagent

All chemicals used were of analytical reagent grade or chemically pure grade and double distilled water was used for all dilution of reagents and samples.

Preparation of Standard Solution

1. Standard Eu^{3+} (100 µg.mL^{-1}) was prepared by dissolving 0.0243 gm of Eu_2O_3 purity (99.5%) Fluka in 20 mL 5 M HNO_3 and then then diluted to 200 mL with distilled water.
2. Reagent Solochrome Violet (SVRS) purity (99.5%) Fluka, 1×10^{-3} M solution was prepared by dissolving 0.0367 gm in 100 mL distilled water by using a volumetric flask .

Preparation of Buffer Solution

Buffer solution (pH=10.4) was prepared by mixing 3.21 gm NH_4Cl with 2.24 gm KCl then 22.5 mL of concentrated NH_4OH solution was added and diluted to 100 mL with distilled water.

Preparation of Synthetic Europium Sample

1. 0.0243 gm of Eu_2O_3 purity in 20 mL 5 M HNO_3 and then then diluted to 200 mL with tap water (100 µg.mL^{-1} Eu^{3+}).
2. 10 mL of stock 100 µg.mL^{-1} Eu^{3+} was diluted to obtain 100 mL of 10 µg.mL^{-1} Eu^{3+} working solution.

General Procedure According to Univariate Optimization

An aliquot of the standard solution containing no more than (3 - 80 µg) was transferred into a series of 10 mL volumetric flasks, to each flask 1mL of 2.6×10^{-3} M of (SVRS) complexing agent followed by the addition of 1 mL of buffer solution (pH=10.4), then the resultant solutions was made up to 10 mL with distilled water. The absorbance was measured at 464 nm after 10 min against a reagent blank. All measurements were made at room temperature (25.0 ± 0.5). A calibration graph of the absorbance versus the concentration of Eu^{+3} was plotted.

General Procedure According to Simplex Optimization

Accurately measured aliquot of Eu^{3+} solution containing(4 – 100 µg) were transferred into 10 mL volumetric flask, 1mL of(3×10^{-3} M) of SVRS-reagent was added followed by(1.4 mL) of buffer solution (pH=10.4), then the mixture was completed to final volume and the resultant solution was measured at 464 nm after 15 min against a reagent blank treatedsimilarly.

Results and Discussion

The optimization of the method was carefully studied in order to achieve complete reaction formation, highest sensitivity and maximum absorbance.

Spectral Characteristics of Eu^{3+} –SVRS Complex

Under the conditions used, Eu^{+3} ions and RS reagent form a red-pink complex with an absorption maximum at 464 nm at pH = 9.42 against the reagent blank (Fig. 1).

The reaction between Eu^{3+} ion and the SVRS-reagent is rapid and instantaneously and the color obtained remained strictly stable for at least 2 hours.

Optimization of Experimental Variable

i. Univariable Method

The goal of this investigation was to find a simple, reliable and accurate method for the determination of the cited ion under study, so several parameters such as pH, reaction time reagent concentration, and order of mixing were optimized to achieve the best results. For this reason a variable was modified while maintaining the other variable at their constant value, then by maintaining that variable at its optimized value another was modified, all variable were optimized via this method.

Effect of Volume of Buffer

To study the effect of the volume of the pH on the absorbance of the complex formation, varying volumes of standard buffer (pH =10.4) in the range (0.2 - 1.2 mL) were added and measuring the absorbances of the solutions (Fig 2).

Maximum color intensity of the complex was achieved with 1mL of the buffer solution, which remained unaffected by further volume additions of buffer solution due to completeness of the reaction.

Effect of Reagent Concentration

The influence of the concentration of reagent on the development of color was investigated by treating varied concentrations (1×10^{-3} - 3.2×10^{-3}M) of reagent solution (Fig. 3). It was observed that the absorbance measured at 464 nm increased with the increase of concentration of reagent and became constant at 2.6×10^{-3} M due to the high stability of the complex, above this concentration no more increase in absorbance values was obtained, therefore, the cited concentration of reagent solution were used.

Effect of Time on the Stability of the Formed Complex

The reaction is instantaneous ,and the Eu^{+3}-reagent complex attained maximum and constant absorbance at 10min and remained constant up to 30min (Fig 4); therefore ,10 min of development time was selected as optimum through out the determination process.

Effect of Order of Addition

Different orders were used to mix the solutions of the reagent used in this investigation. It was found that the addition of the reagent solution followed by the buffer solution to the Eu^{3+} solution (order 1 in table 1) gave the best results.

ii. Simplex Method

Simplex method is used to confirm the optimum conditions, which were obtained by the univariate procedure. To set the simplex optimization of the three major studied variables (reagent concentration, volume of buffer and standing time). Four experimental conditions should be chosen and the values of these variables were selected within specified boundaries for each at which it affects the absorption signal of the colored product (Table 2).

The absorbances of these four initial experiments were measured and the results were fed to the computer program (Table 3). The program then started simplex by searching the worse absorption signal and reflected it in hyper-plane of the remaining points to produce a new set of experimental conditions, which were applied to carry out experiment and the measured absorption signal was fed again to the program. The process is repeated successively until optimum conditions were obtained (i.e. conditions yielding highest absorption signal). The procedure continued for further few experiments to ensure that the optimum conditions are reached similarly to those obtained by the univariate method.

Stoichiometry of the Complex

The stoichiometry of the complex was studied by the mole ratio method. A series of solutions were prepared by addition of varying amounts of reagent (SVRS) 6.026 - 60.26 µg to a constant amount of Eu^{3+} 50 µg. To each solution 1.4 mL of standard buffer solution was added and the resulted solutions were diluted up to the 10 mL with distilled water, then the absorbances were measured at 464 nm after 15 min against the reagent blank solution and plotted against the ratio of [Reagent SVRS] / [Eu^{3+}] (Figure 5).
Figure 5, shows that the mole ratio of Eu^{3+}: SVRS in the complex is **1:4**, therefore a structure of the complex could be proposed as shown in the following scheme.

Analytical Data and Calibration Graph

Employing the optimum experimental condition (under univariate and simplex conditions), two calibration graphs, Figures 6 and 7 respectively, for the determination of Eu^{3+} at 464 nm were obtained. Table (4) shows a brief comparison between the two recommended procedures. It is obvious, that the conditions obtained under multivariate simplex optimization gave better results; therefore these conditions were followed in subsequent work.

Accuracy and Precision

The accuracy of the proposed method was confirmed by performing five replicate analysis for three different amounts of Eu^{3+} (selected within Beer's Law) by calculating the relative error percentage (Table 5). The results indicated good accuracy of the method at each concentration level. The precision was determined in each case by calculating the percentage relative standard deviation (RSD %) for three determinations at each of the studied concentrations and level and were found to be in the range of 0.63-1.68.

Effect of Foreign Ions:

The effect of presence of some foreign ions on the trace level determination of Eu^{3+} has been studied. The results are depicted in table 6 which indicate that the studied ions have significant effect on the determination of the cited ion, so that prior separation would be essential. Otherwise, standard addition method must be followed for such purpose.

Standard Addition Method

The proposed method was applied to determine synthetic europium sample by standard addition technique according to following procedure:

Varying aliquots (0, 0.2, 0.4, 0.8, 1.0, 1.4, 2.0 mL) of standard 10 $\mu g.mL^{-1}$ Eu^{3+} solution were added to seven 10 mL volumetric flasks each of them contains 0.5 mL of the unknown (the synthetic europium sample solution), followed by addition of 1mL of 3×10^{-3} M of SVRS-reagent and 1.4 mL of buffer solution (pH=10.4). Each mixture was then diluted to final volume via distilled water and the absorbance was measured at the recommended wavelength after 15 min against its reagent blank (Fig. 8)-.

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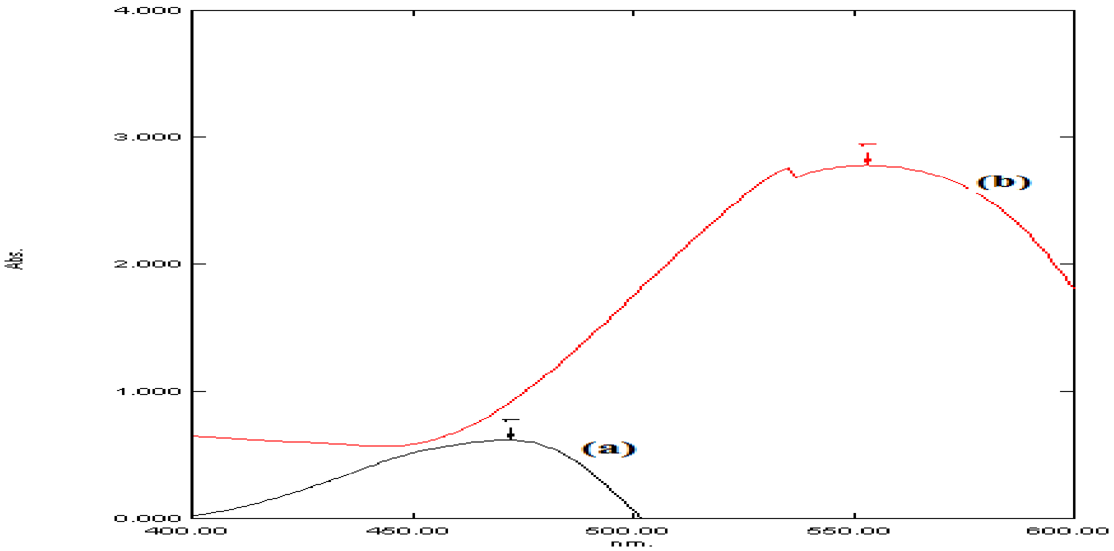
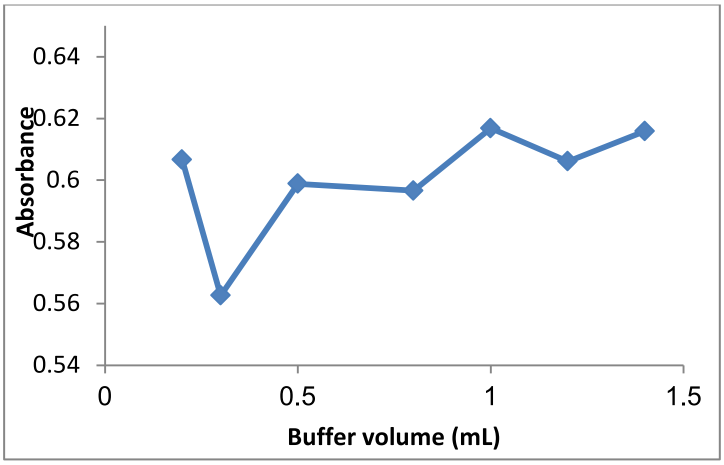
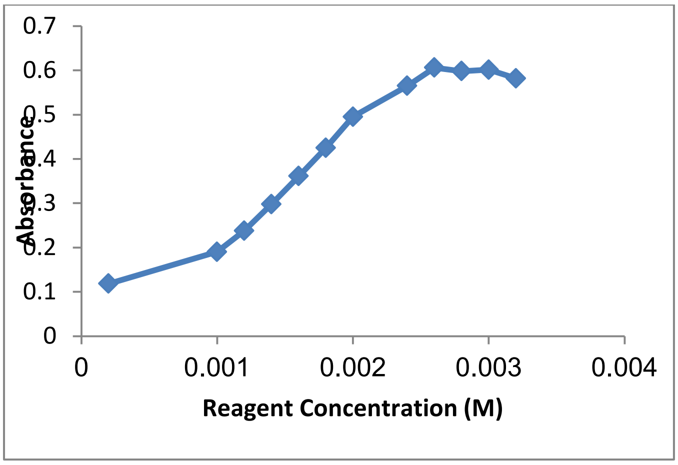


Figure(1): Absorption spectra of (a) 10 µg.mL^{-1} Eu^{3+}, 3 × 10^{-3} M reagent at pH 9.40 against blank reagent, (b) 3 × 10^{-3}M reagent at pH 9.40 against distilled water.



Figure(2): Effect of buffer volume.



Figure(3) : Effect of reagent Concentration

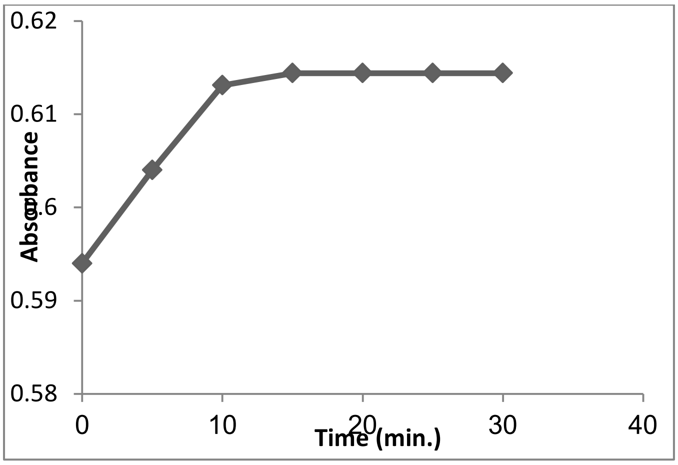
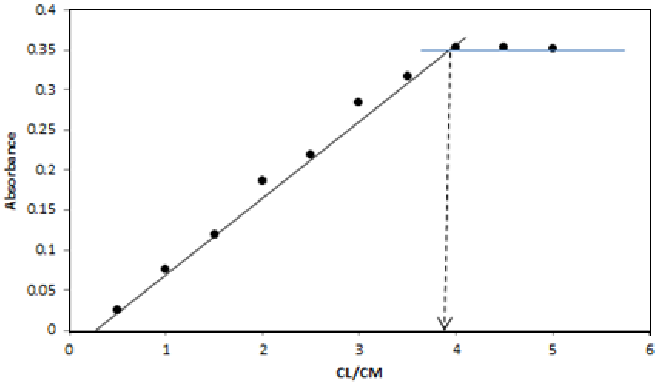


Figure (4): Effect of time on the stability of the formed complex.



Figure(5): Mole ratio method for 3.29 × 10^{-5} M Eu^{3+} with variable concentrations of reagent at pH = 9.4.

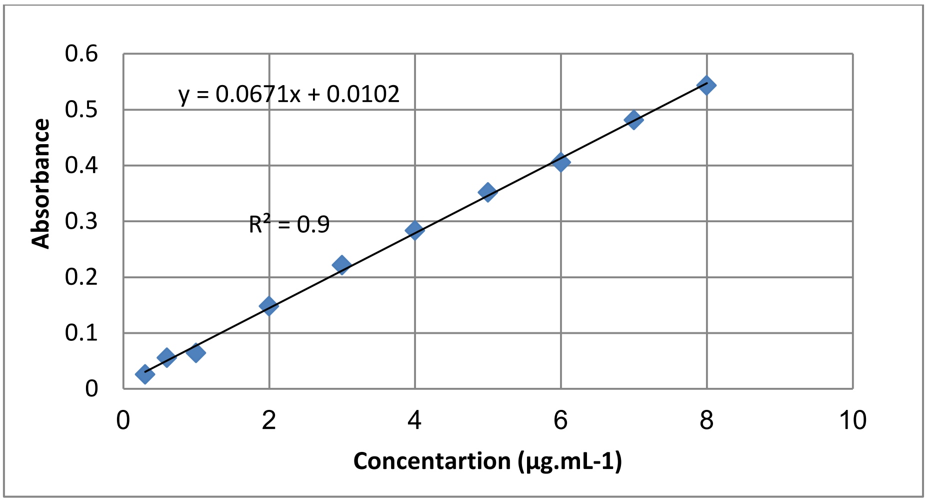


Figure (6): Calibration curve for the determination of Eu $^{3+}$ under optimum conditions obtained via univariate optimization.

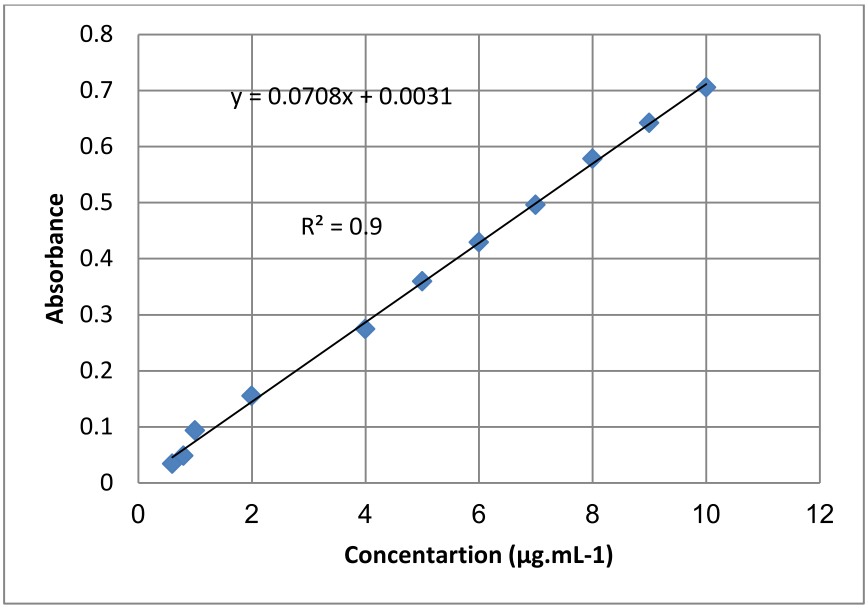


Figure (7): Calibration curve for the determination of Eu $^{3+}$ under optimum conditions obtained via multivariate simplex optimization.

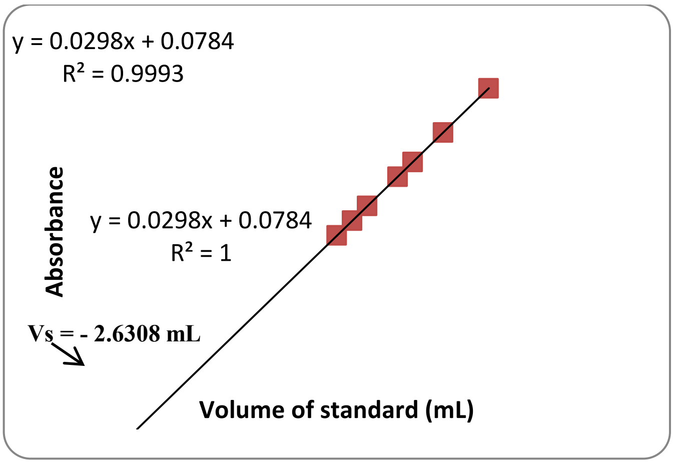


Figure (8): Standard addition plot for the determination of Eu^{3+} in synthetic sample.

Table (1): Effect of sequence of addition on the absorbances of 10μg.mL^{-1} (Eu^{+3}), 2.6x10^{-3}M at pH=9.4.

Types of mixing				Absorbance
Order 1	Metal	Reagent	Buffer	0.613
Order 2	Metal	Buffer	Reagent	0.569
Order 3	Reagent	Buffer	Metal	0.609

Table (2):Boundary conditions for the studied variables.

Variable	Range
Reagent concentration M ×10^{-3}	1.2 - 3.0
Buffer volume (mL)	0.1 - 1.4
Standing time (min)	0.0 – 30

Table (3):Absorbance of each of the simplexes in the optimization of color development for determination of Eu^{3+}.

Exp. No.	Reagent Conc. ×10^{-3} M	Vol. of buffer (mL)	Time (min)	Absorbance
1	1.2	0.5	5	0.2888
2	2.0	1.4	0	0.5142
3	2.6	0.8	30	0.6330
4	3.0	1.0	10	0.6524
5	3.0	1.4	20	0.6607
6	3.0	1.0	30	0.6802
7	3.0	1.4	15	0.7127
8	3.0	1.4	30	0.6743
9	3.0	1.2	25	0.6925
10	3.0	1.2	10	0.6848
11	3.0	1.4	5	0.6610
12	3.0	1.4	30	0.7002
13	3.0	1.2	20	0.6607

Table (4): comparison between the two recommended procedures.

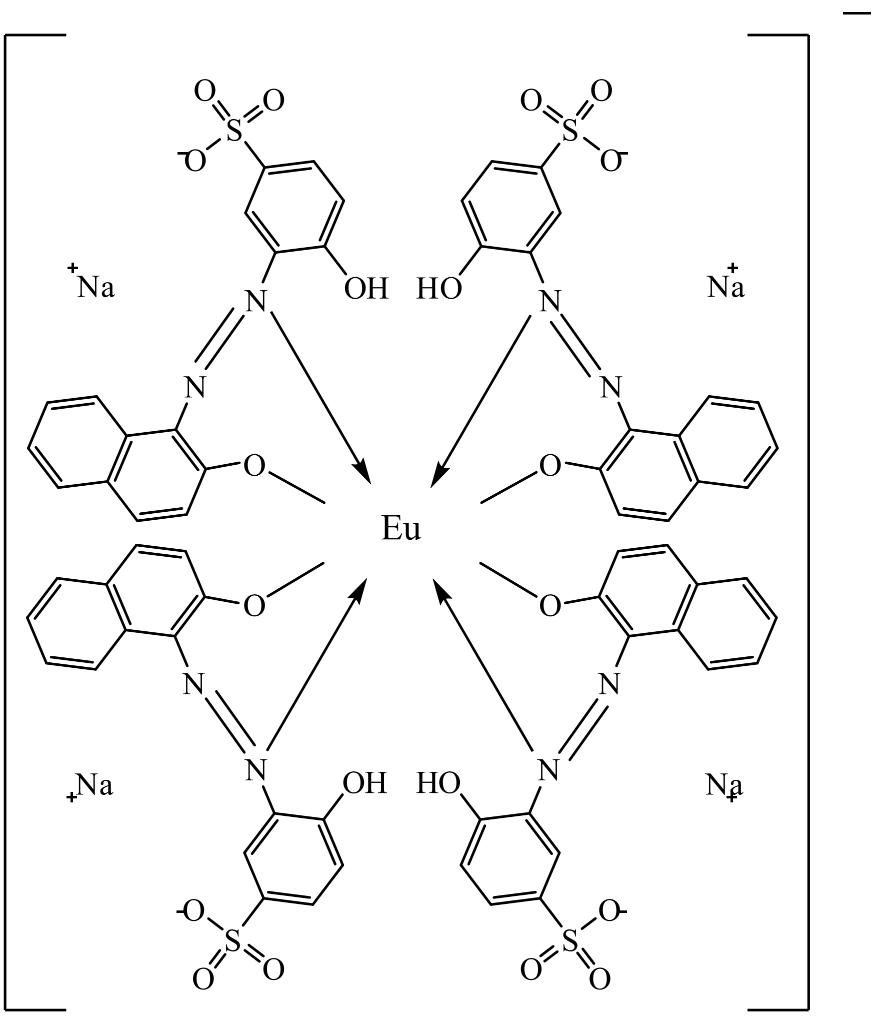
Condition	Univariate optimization	Simplex optimization
Conc. of reagent(mol.L^{-1})	2.6x10^{-3}	3.0x10^{-3}
Volume of buffer (mL)	1.0	1.4
Stability of complex(min)	10	15
regression equation	A=0.065[Eu3+]μg.mL^{-1} +0.013	A=0.0708[Eu^{3+}]μg.mL^{-1}+0.0031
Detection limit (μg.mL^{-1})	0.3013	0.055
ε (L.mole^{-1}cm^{-1})	9877.66	10759.051
Calibration range (μg.mL^{-1})	0.3-8.0	0.4-10

Table (5): Evaluation of accuracy and precision of the proposed method.

Concentration (μg/mL)		R.E. %	R.S.D %
Taken	Found		
1	0.96	-3.78	1.68
5	5.11	2.17	0.93
8	8.22	2.78	0.63

Table (6):Determination of (6.0μg/ml) of Eu^{3+} in the presence of foreign ions.

Interfering ion	Eu^{+3} (6 μg.mL^{-1})		
	Taken (μg.mL^{-1})	Ratio	RE%
Cr^{3+}	6	1:1	-20.44
	60	10:1	-86.94
Fe^{3+}	6	1:1	-82.71
	60	10:1	-77.95
Co^{2+}	6	1:1	-64.46
	60	10:1	-70.38
Cu^{2+}	6	01:1	-64.46
	60	10:1	-70.38
Mg^{2+}	6	1:1	-13.60
	60	10:1	-75.09
Na^{+}	6	1:1	-5.02
	60	10:1	0.52
	300	50:1	-3.26
	600	100:1	-1.58



Scheme (1): The proposed structure of Eu^{3+} –SVRS complex.

الظروف الفضليات الاحادية والمتعددة للتقدير الطيفي لايون اليوربيوم الثلاثي في حالته النقية وفي أنموذج مصنع

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استلم البحث في : 29 كانون الأول 2013 ، قبل البحث في : 2 شباط 2014

الخلاصة

أُتبع اسلوبان للوصول الى الظروف الفضليات للتقدير الطيفي الكمي لايون اليوربيوم الثلاثي باستخدام الكاشف الكروموجيني Solochrome Violet(SVRS). اظهرت الدراسة ان ايون اليوربيوم يكون معقداً احمراً شرابياً مع الكاشف في وسط قلوي ويظهر محلوله امتصاص اعظم عند الطول الموجي 464 نانوميتر مقابل المحلول الخلب.امكن الحصول على منحنيي معايرة باتباع الظروف الفضليات التي تم الحصول عليها باسلوبين هما المتغير الواحد والسمبلكس وبمجال خطي مقداره (8.0-0.3) مايكروغرام/مل وحد كشفي مقدارة 0.3مايكروغرام/مل ،وامتصاصية مولارية مقدارها 9877.66لتر/مول.سم بالنسبة الى الاسلوب الاول وبمدى خطية مقداره (10.0-0.40) مايكروغرام/مل وحد كشفي مقداره 0.055 مايكروغرام/مل وامتصاصية مولارية مقدارها 10759.05لتر/مول.سم باسلوب السمبلكس.

اظهرت دراسة تكافؤية المعقد الكليتي المتكون ،ان نسبة الكاشف الى العنصر كانت 1:4، ثم درس تاثير وجود ايونات مختلفة في تقدير العنصر وطبقت الطريقة المقترحة لتقدير كميته في أنموذج مصنع.

الكلمات المفتاحية: اللانثانات، السمبلكس، سولوكروم فايوليت، المطيافية.