

Selective separation of cerium from lanthanides by extractive photometry using HDBE as novel reagent

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ABSTRACT

Striking similarities in properties of lanthanides make their separation a difficult task. Development of highly selective analytical reagent hexane-2,5-dione-bis(ethylenediamine) HDBE that forms brown coloured complex with Ce(IV) which is quantitatively extracted into xylene at pH 6.4. Transfer of extracted complex to organic phase is very fast (<1min.). Optimum concentration of reagent required for complexation and full colour development is very low (0.8 cm³ of 0.1 % HDBE). Absorption maximum exhibited at 518 nm. Beer's law is obeyed in the detectable range 0.3-4.0 ppm. The molar absorptivity and Sandell's sensitivity values are 0.421·10⁴ dm³·mol⁻¹·cm⁻¹ and 0.017 µg·cm⁻² respectively. The present method is time honoured, permits selective separation of cerium from associated lanthanones using HDBE as a novel complexing agent.

Keywords: lanthanides; HDBE; xylene; extracted complex; Beer's law; molar absorptivity; Sandell sensitivity.

1. INTRODUCTION

Quantitative separation has become much more time honored and selective with the application of Extractive photometric coupled technique. Liquid-liquid extraction processes continue to play an exciting and fruitful role in formulating strategic ways of dealing with delicate separation problems particularly separation at trace concentration level [1].

The essential feature of trace analysis is not the determination of minute quantity of substance but the determination of such quantity in presence of an overwhelming quantity of other substances. Although extensive work made on Extraction studies of rare earth metals [2-6] provided a fertile approach to the designing of chelating agents to enhance the selectivity of desired ion. It has been reported that quantitative extraction further coupled with spectrophotometric technique can be advantageously employed in determination of concentration of cerium at ppm level [7].

The limitation often faced by techniques in separation of cerium was its close association with other lanthanides [8]. Therefore designing such a reagent which could form

coloured complex with cerium and its subsequent extraction for photometric study to investigate the interference of other lanthanides was the primary task. As the present work makes an attempt to employ a method that involves use of very low concentrations and volumes of all reagents and solvents and imparting results with fairly high degree of precision and accuracy; it can claim to adhere to the criteria of Green Chemistry.

2. MATERIALS AND METHOD

2. 1. Apparatus and instruments

Calibrated sets of glasswares made up of Pyrex or corning were used throughout the analysis. An analytical balance of 0.001 g sensitivity was used for weighing the samples. An Elico Li 120 pH meter was used for pH measurements and all measurements of absorption spectra were recorded using Shimadzu UV2100 spectrophotometer.

2. 2. Preparation of stock solutions

Cerium solution: A stock solution of ceric sulphate was prepared by dissolving an appropriate quantity of ceric oxide in 1N sulphuric acid. Standardization of diluted solution was carried out by Gravimetry as ceric oxide after oxalate precipitation and ignition.

HDBE Reagent: A novel chelating ligand for cerium was prepared by combination of diketone and primary amine. A buff colored solid product was obtained after monitoring all reaction conditions which was purified by recrystallisation. Characterization was carried out using IR and NMR.

2. 3. Methodology for extraction and photometric studies

To 1.0 cm³ of an aqueous solution containing 0.1 mg of Ce(IV); 1.0 cm³ of 1 % solution of HDBE reagent was added. An appropriate pH was adjusted (6.4) keeping the total volume to 10.0 cm³. The solution was transferred to a separatory funnel and equilibrated with 10.0 cm³ of preselected solvent xylene. After shaking the two phases were allowed to separate. Organic layer was collected in 10.0 cm³ standard flask to record the absorbance at suitable wavelength for investigation of various parameters of spectrophotometric study [9] an aqueous phase collected was used to determine concentration of Ce(IV) by standard method.

3. RESULTS AND DISCUSSION

The novel reagent hexane-2,5-dione-bis(ethylenediamine) forms bright golden brown complex with Ce(IV) which was quantitatively extracted into xylene at pH 6.4 with absorption maximum at 518 nm. Transfer of complex into organic phase was very fast (<1.0 min). The results of the various photometric studies are discussed below:

3. 1. Optimum pH and reagent concentration

The extraction of complex has been investigated over the pH range 1-10. The maximum extraction was observed at pH 6.4, further the percentage extraction decreases with increase in pH (Fig. 1). With other factors constant, increasing volumes of 0.1 % reagent solution were added to an aliquot of sample solution containing 100 µg of cerium at

respective pH. The absorbance remained fairly constant above 0.8 cm³ indicating the optimum value of reagent concentration for full colour development as 0.8 cm³ (Table 1).

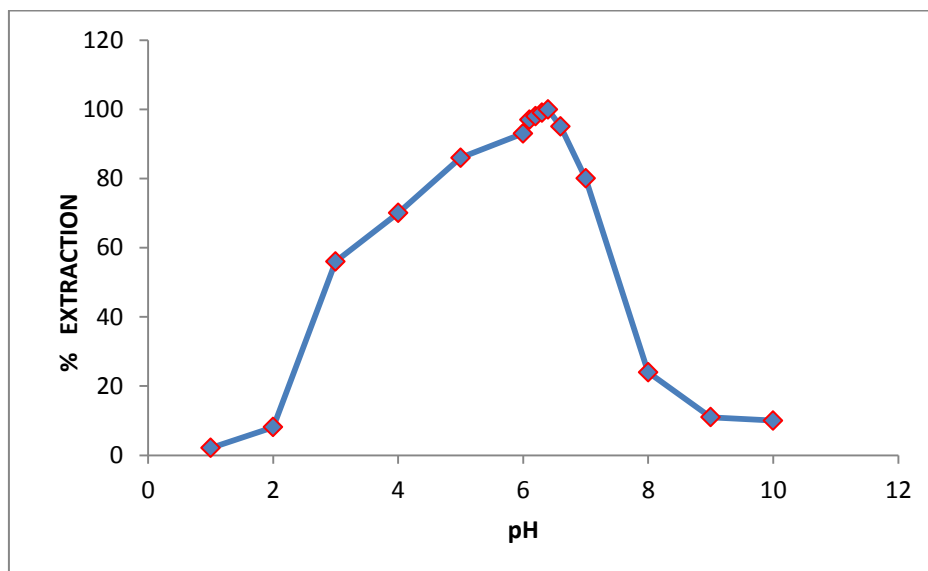


Figure1. Optimum pH determination for extraction of Ce(IV) - HDDE.
 Amount of Ce(IV) taken: 100µg; Organic phase : 10.0 cm³ (2x5) of xylene;
 Aqueous phase: 1.0cm³ of 100 µg Ce(IV) +1.0 cm³ of 0.1 % HDDE
 in methanol +8.0 cm³ of buffer (pH 1-10)

Table 1. Reagent concentration determination.

Amount of Ce(IV) taken: 100 µg; Aqueous phase: 1.0 cm³ of cerium +0.1% HDDE + buffer of pH 6.4 (Total vol.10.0cm³); Wavelength 518 nm.

Sr. No.	Vol. of HDDE in aqueous phase (cm ³)	Absorbance (nm)
1	0.1	0.073
2	0.2	0.174
3	0.3	0.220
4	0.4	0.294
5	0.5	0.367
6	0.6	0.441
7	0.7	0.514
8	0.8	0.688
9	0.9	0.688
10	1.0	0.687
11	1.1	0.688

3. 2. Selection of solvent

The value of percentage extraction of cerium enables to decide following order of organic solvents: xylene>toluene>n-heptane>chloroform>cyclohexane=cyclohexanone>nitrobenzene=ethyl acetate. Xylene selected as the most satisfactory solvent.

3. 3. Equilibration time

The study of change in absorbance with variation in equilibration time for the extraction of cerium shows that equilibration time of 30 seconds is sufficient for quantitative extraction.

3. 4. Colour Stability of extracted complex

The absorbance of colored extracted complex remained constant up to 28 hours at room temperature which is adequate for analytical applications. Throughout the experiment, for the reason of practical convenience, absorbance measurements had been carried out within one hour of extraction (Figure 2).

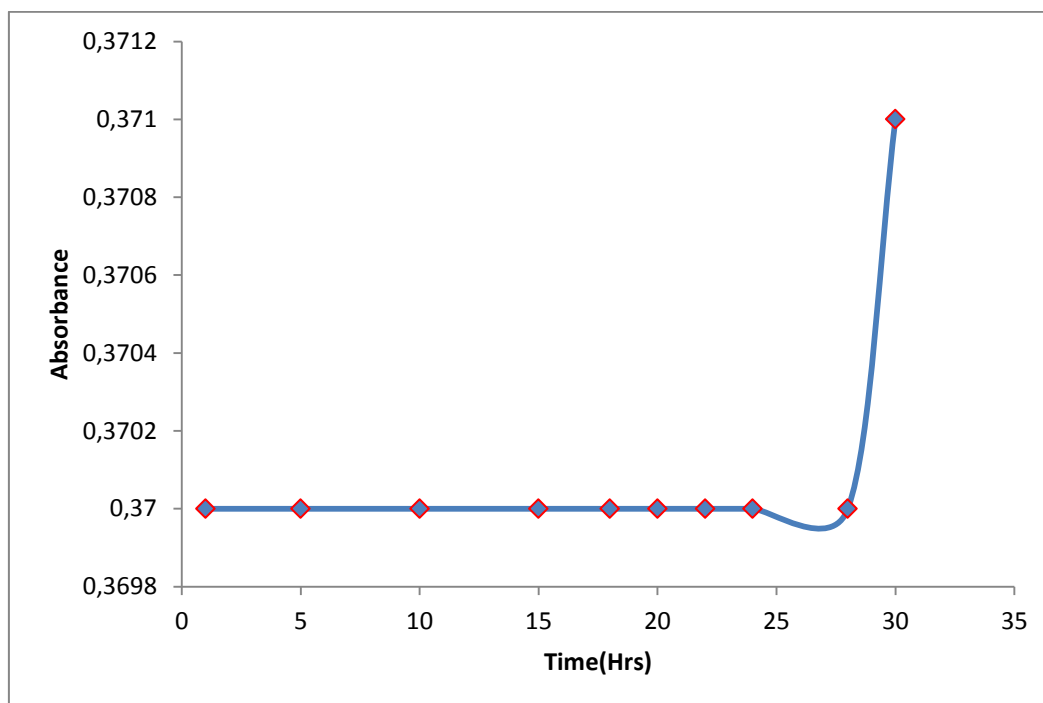


Figure 2. Colour stability of Ce-HDBE complex as a function of time.

3. 5. Calibration curve

The calibration plot of absorbance against concentration of Ce(IV) gives a linear reproducible graph in the concentration range 0.5 to 11.0 $\mu\text{g/mL}$ indicating that Beer's law is obeyed in this range. The molar absorptivity and Sandell sensitivity was calculated as $0.309 \cdot 10^4 \text{ Lmol}^{-1} \cdot \text{cm}^{-1}$ and $0.072 \mu\text{g} \cdot \text{cm}^{-2}$ respectively (Fig. 3).

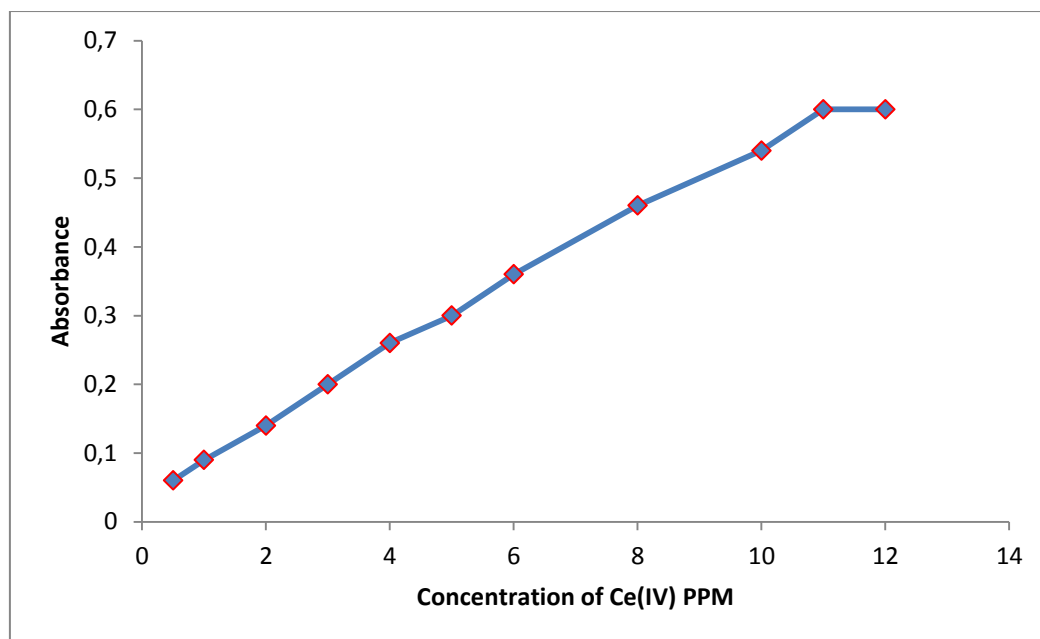


Figure 3. Calibration plot.

Aqueous phase: 1.0 cm^3 of Ce(IV) solution + 0.8 cm^3 of 0.1 % HDBE in methanol + 8.2 cm^3 of buffer of pH 6.4; Organic phase : 10.0 cm^3 of xylene; Wavelength: 518 nm

3. 6. Nature of extracted species

The composition of extracted species was determined by Job's continuous variation method (Fig. 4), supported by slope ratio and mole ratio method. It shows that the composition of Ce(IV): HDBE complex is 1:1.

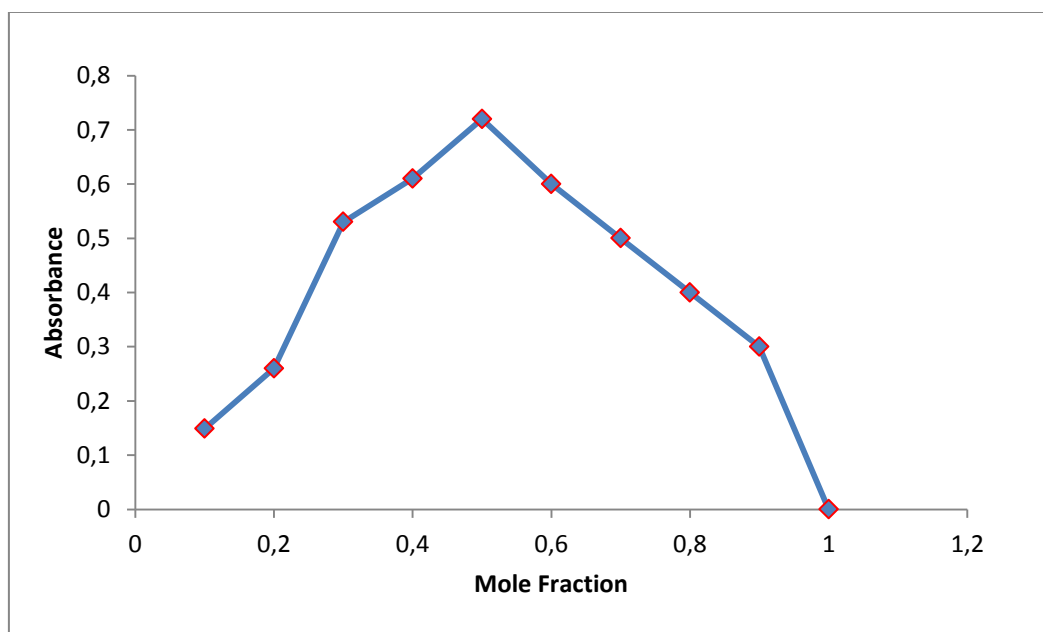


Figure 4. Composition of Ce(IV) by Job's continuous variation method. Concentration of Ce(IV): $1 \times 10^{-3} \text{ M}$, Concentration of HDBE; $1 \times 10^{-3} \text{ M}$.

3. 7. Interference of diverse ions

The effect of foreign ions added in manifold amount to 50 μg of Ce(IV) indicates no interference at pH 6.4. The ions which show interference were masked by using appropriate masking agents (Table 2).

Table 2. Interference study of foreign ions.

Sr. No.	Foreign ions	Amount added (mg)	Absorbance (± 0.03)
1	-----	-----	0.366
2	Gd ³⁺	18.5	0.367
3	Y ³⁺	10.0	0.367
4	W ⁶⁺	12.5	0.365
5	V ⁵⁺	10.0	0.364
6	Nd ³⁺	11.0	0.366
7	Cl ⁻	22.0	0.364
8	NO ²⁻	17.0	0.365
9	NO ³⁻	11.0	0.365
10	CN ⁻	9.5	0.365
11	Tartaret	18.0	0.124*
12	CNS ⁻	18.0	0.356

*indicate serious interference which is masked by sodium molybdate

Applications:

Close association of Ce(IV) with other lanthanides and similarities in properties make its separation a difficult task. Attempt to prepare highly selective chelating ligand [10] forming colored complex at appropriate pH can facilitate the separation. A novel chelating ligand HDBE with high selectivity for Ce(IV) overcomes the difficulty. Varying amount of lanthanide solutions were spiked with trace concentration of Ce(IV) solution and the concentration of cerium in synthetic mixture of lanthanides was determined using the present method (Table 3).

Table 3. Application of present method in synthetic mixtures.

Sr. No.	Mixture (ppm)	Cerium added (ppm)	Cerium found (ppm)#	Relative Error %
1	La(60), Nd(40), Pr(15)	2.0	2.08	+3.5
2	Sm(20), Zr(4), Y(2)	0.5	0.52	+4.0
3	U(10), La(30), Gd(60)	4.0	3.97	-0.75

indicate average of three determinations.

4. CONCLUSION

Hexane-2,5-dione-bis(ethylenediamine) HDBE proposed as a novel reagent is effectively used for selective quantitative extraction and photometric determination of precious Cerium. A highly stable brown complex requires very less amount of solvent. The equilibration time is very less that facilitates complete extraction. The method has been used over a wide detectable range and successfully applied for the separation of Ce(IV) from associated lanthanides.

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