4, 4'-Diantipyrylmethane (DAM): A tool for spectrophotometric microdetermination of cerium (IV)

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Abstract

A simple and hasty method has been employed for the direct spectrophotometric determination of trace amount of Ce(IV) using a complexing agent 4,4'-diantipyryl methane (DAM) with absorption maximum at 445-455nm in acidic medium at 1.3 -1.5 pH. Molar absorptivity and Sandell's sensitivity were calculated to be 9.1×10^3 l mol^{-1} cm^{-1} and 0.015 µg Ce cm^{-2}. Beer's law was found to be defensible over the cerium concentration range of 0-5.5 µg ml^{-1}. Effect of large number of cations, anions and complexing agents was also studied and several analytically important ions do not cause interference in the procedure except thiourea and EDTA. The method has good reproducibility and has been satisfactorily applied in the determination of cerium in samples.

Keywords: Cerium, DAM, Spectrophotometric.

Introduction

Cerium, a rare earth metal belonging to lanthanide, is used in the metal industry, glass industry, in nuclear reactor, in microwave devices, agriculture, forestry, animal husbandry as well as for environmental pollution assessment and in studies of biochemical processes[1,2]. Cerium oxide is part of the catalyst of catalytic converters used to clean up exhaust of vehicles; it also catalyses the reduction of nitrogen oxides (NOx) to nitrogen gas. If a little cerium oxide is added to the fuel itself, it will catalyse the burning of the particulates and will eliminate them. Cerium is known to cause health problems due to the fact that damps and gasses can be inhaled with air. Cerium has an effect on human health, can enter the body through drinking water and food chain. Excessive amounts of Rare earth metals (REEs) are harmful to human health.

Therefore, development of a simple, sensitive and reliable method for the determination of cerium(IV) is essential. This necessitated the development of convenient and reliable analytical methods for the determination of cerium. These methods include spectrophotometric[3-12], spectrofluorimetric[13], chromatographic[14-19], electrophoresis[20], immunoassay[21,22], flow injection[23-25] and electrochemical methods[26-28].

However, these methods are expensive and operations are complex which limit their use. Spectrophotometric method has the characteristics of low price, simple operation with high practical value. Although spectrophotometric methods for the determination of cerium using methylorange[29], dibromocarboxyarsenazo[30], arsenazoIII[31] reagents have been proposed, the sensitivity and selectivity are still not ideal, so establishing a new spectrophotometric method for the determination of cerium is still needed.

Material and Methods

Reagents and solutions: A stock solution of cerium (IV) containing 1 mg ml^{-1} of the metal ion is prepared by dissolving an accurately weighed amount of $Ce(SO_4)_2.4H_2O$ in deionised water. Aliquots are suitably diluted giving solutions of cerium at µg ml^{-1} level.

Solutions of other elements are prepared by dissolving their commonly available chemically pure salt in distilled water or dilute hydrochloric/sulphuric acid to obtain ≤ 10 mg ml^{-1} of the metal ion. 4, 4'-diantipyrlmethane (DAM) is dissolved in acetone to get 0.5% (W/V) solution. H_2SO_4, 0.5M is used.

Samples: Synthetic samples are prepared by mixing solutions of cerium and other elements in suitable proportion.

Apparatus: UV-Visible (Shimadzu-140-02) spectrophotometer with 10nm matched cell is used for absorbance measurements and other spectral studies.

Procedure: To an aliquot of the solution containing 50 µg of Ce(IV) in a 50 ml beaker, add 1.4 ml 0.5M H_2SO_4 and 1ml 0.5% DAM reagent. Allow contents to stand undisturbed for 10-12 minutes and transfer to a 10 ml volumetric flask and make it up to the mark with distilled water. Mix it gently and measure the absorbance of the complex at 450 nm against the reagent blank prepared similarly using 10 mm matched cells on a UV-visible spectrophotometer.

In order to draw standard curve, different microgram amounts of the metal ion are taken in each set and their corresponding absorbance values are noted following the procedure and graph plotted between the two variables.

Results and Discussion

It has been observed that cerium (IV) reacts with DAM (Figure 1) forming a deep yellow colour complex in dilute sulphuric acid media whose absorption maximum lies at 450 nm. The effect of various parameters on the absorbance of cerium (IV)-DAM complex is investigated [Table 1]. The reaction of Ce(IV) with DAM is temperature dependent. At

20°C, the absorbance is 0.280 and increases to 0.320 at 25-40° C and declines thereafter. Hence 25-40°C is the suitable temperature range for the formation of the complex. The complex is found to have maximum absorbance in presence of 1.3-1.5ml of 0.5M H_2SO_4 considered as the suitable medium for working.

It has been observed that cerium in the tetravalent state reacts with 0.9-1.1ml of 0.5% DAM forming a deep yellow complex in dilute sulphuric acid medium. The formation of the complex between Ce(IV)-DAM is slow and takes 10-12 minutes to develop fully. The Ce(IV)-DAM complex was found to be non-extractable in different organic solvents and thus measured in aqueous phase. The absorption spectrum of the complex against a reagent blank exhibits a broad absorption band at 445-455nm (Figure 2). The spectrum of reagent blank against distilled water has shown zero absorbance value in this range.

Thus, all the measurements are carried out at 450nm against reagent blank. On the basis of the study of the above parameters, it is concluded that for ≤ 55 µg Ce: 1.3-1.5ml of 0.5M H_2SO_4, 0.9-1.1 ml 0f 0.5% DAM in distilled water in 10ml aqueous volume is the optimum conditions for the formation of the complex whose absorbance is measured at 450nm in order to estimate the amount of cerium.

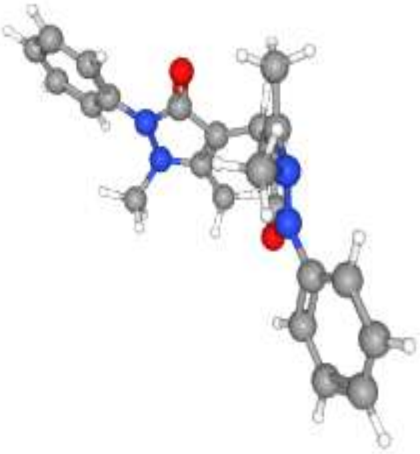

Figure 1: 3D structure of 4,4'- diantipyryl methane

Table 1
Effect of various parameters on the absorbance of cerium Complex.

1. Temperature (°C)^{a}	20	23	**25-40**	45	50			
Absorbance	0.280	0.310	**0.320**	0.310	0.300			
2. Acid (0.5M)^{b}	**H_2SO_4**	HNO_3	H_3PO_4	$HClO_4$	HCl	CH_3COOH		
Absorbance	**0.320**	0.100	turbidity	0.090	0.150	tubidity		
3. **H_2SO_4 (0.5M)^{c}, ml**	0	0.5	1.0	1.2	**1.3-1.5**	1.6	2.0	
Absorbance	0.090	0.230	0.300	0.310	**0.320**	0.310	0.270	
4. **DAM^{d} , ml** (0.5% in acetone)	0	0.5	0.7	**0.9- 1.1**	1.2	1.5	1.8	2.0
Absorbance	0.000	0.260	0.300	**0.320**	0.310	0.260	0.200	0.150
5. **Colour development Time (minutes)^{e}**	0	2	5	9	**10-12**	13	15	20
Absorbance	0.000	0.120	0.280	0.310	**0.320**	0.315	0.310	0.280

Experimental Conditions:
a) Ce(IV) = 50 µg, Acid (0.5M) = 1.4ml, DAM (0.5% in acetone) = 1ml, aqueous volume=10ml, colour development time = 10 min, λmax=450nm.
b) Ce(IV) = 50 µg, Acid (0.5M) = 1ml, DAM (0.5% in acetone) = 1ml, aqueous volume=10ml, colour development time = 10 min, λmax=450nm, at room temperature.
c) Ce(IV) = 50 µg, DAM (0.5% in acetone) = 1ml, aqueous volume=10ml, colour development time = 10 min, λmax=450nm, at room temperature.
d) Ce(IV) = 50 µg, Acid (0.5M) = 1ml, DAM (0.5% in acetone) = 1ml, aqueous volume=10ml, colour development time = 10 min, λmax=450nm, at room temperature.
e) Ce(IV) = 50 µg, H_2SO_4(0.5M) = 1.4ml, DAM (0.5% in acetone) = 1ml, aqueous volume=10ml, λmax=450nm, at room temperature

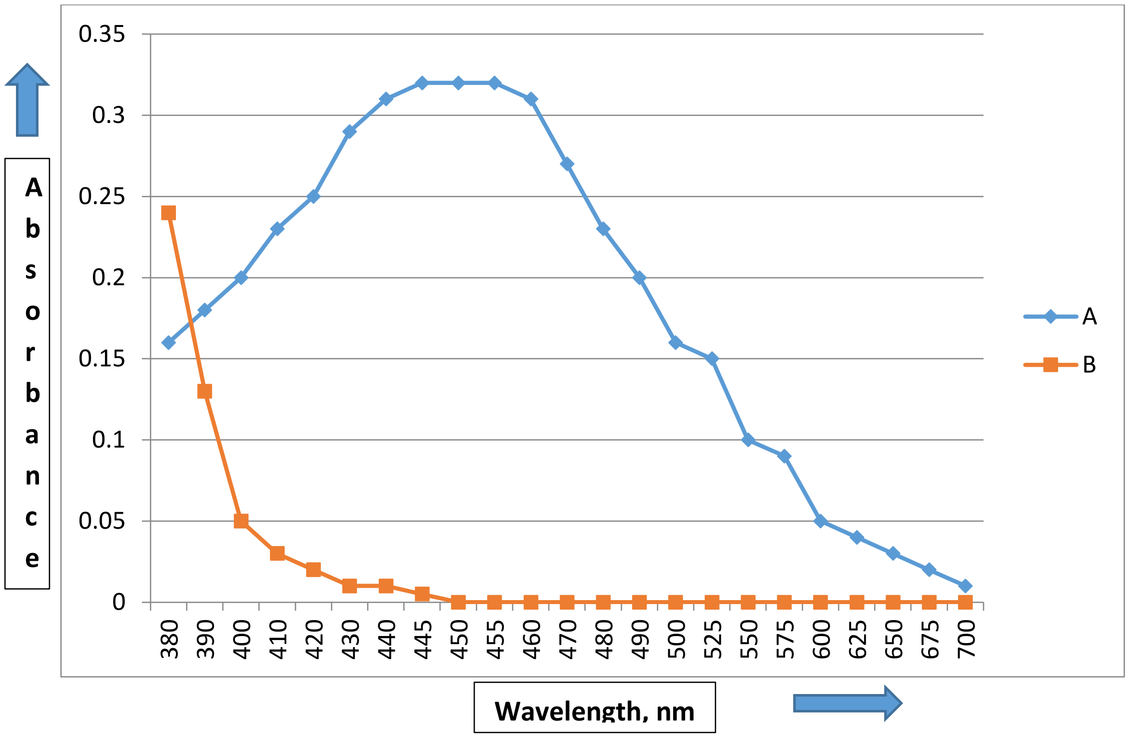

Figure 2: Absorption spectrum of Ce(IV)-DAM complex
Curve A- Ce(IV) complex measured against reagent Blank
Curve B- Reagent blank measured against distilled water

Table 2
Analysis of different samples by the proposed method

S.N.	Composition of the samples Matrix^{a}	Ce(IV) added (µg)	Ce (IV) found (µg)
1.	La(0.05), Pr(0.4)	20	20
2.	Nd(0.05), Gd(0.05)	25	24
3.	Eu(0.05), Sm(0.02)	30	31
4	Tb(0.05), Dy(0.05)	40	41
5	Ho(0.05), Eu(0.05)	30	31
6	Y(0.05), Pr(0.05), Eu(0.05)	25	24
7	La(0.05), Pr(0.05), Eu(0.05)	20	20
8	Nd(0.2), Gd(0.5),Os(0.4)	30	31
9	Cu(0.1), Os(0.1), Re(0.1),Eu(0.1)	25	24
10	Sm(0.02), Tb(0.05),Nd(0.05),Gd(0.05)	20	20

*Figure in bracket indicates the amount of metal ion in mg.

Effect of diverse ions: The influence of different anions and complexing agents on the absorbance of the complex is given in table 2. Under the optimum conditions of the procedure, the ions and/or complexing agents are added as their sodium or potassium salts in the aqueous phase (mg/10ml amounts, in parentheses) such as sulphate, chloride, bromide, iodide, thiocyanate, nitrate, tartrate, oxalate (10mg each); acetate, nitrite, sulphosalicylic acid, citrate (5mg each); fluoride, EDTA, thiourea, phosphate (1mg each) added initially to the aqueous phase do not affect the absorbance of Ce(IV)-DAM complex.

Under the optimum conditions of the procedure, the effect of different metal ions on the absorbance is shown in table 2. It is studied by measuring absorbance of these ions added to the aqueous phase (10ml) before the addition of DAM. Among the cations (mg/10ml amounts, in parentheses), Rh(VII), Os(VIII), Cu(II), Eu(III), Ps(III) (0.5mg each); Co(II), Ni(II), Mn(II), Ti(III), V(V), W(VI), Cd(II),HG(I),Zr(IV), NB(V), Mo(VI), Fe(II), Tl(III), La(III), Nd(III), Gd(III0, Sm(III0, Tb(III), Dy(III), Yt(III), Ho(III), (0.1mg each); As(III), U(VI), Pt(IV), Sn(II), (0.05mg each); Cr(VI), Pd(II), Th(IV), Ru(III), 0.01mg each) are added without effect.

Beer's Law and Sensitivity: The absorbance of the metal complex in distilled water shows linear response upto 5.5 µg Ce ml^{-1} [Figure 3]. However, the optimum range for the determination of cerium as evaluated from a Ringbom plot[32] is calculated to be 2.3-5.4 ppm. The molar absorptivity and Sandell's sensitivity of the system are 9.1 x 10^3 l mol^{-1} cm^{-1} and 0.015 µg Ce cm^{-2} respectively; at 450 nm, Sandell's sensitivity (S) represents the number of microgram of the determined per ml of a solution having an absorbance (A) of 0.001 for a path length (l) of 1cm.Thus,

$S = 10^{-3} / a = \mu g\ cm^{-2}$

where a is the specific absorptivity and its value (in ml g^{-1} cm^{-1}) corresponds to the absorbance of 1 µg ml^{-1} solution of the determinand in a cuvette with an optical path length of 1cm. Also

$a = € / at. Wt. \times 1000$
$€ = \text{molar absorptivity} = A / c.l$

where c is the molar concentration of the determined and l = 1 cm. Eight replicate determinations containing each time 50µg cerium give mean absorbance value of 0.319 with a standard deviation of ± 0.001.

Stoichiometry of the complex: Equimolar solutions (0.0005 M) of Ce(IV) and DAM are utilized to determine the metal to ligand ratio by Job's method of continuous variation[33,34] (Figure 4). The absorbance values are measured at two different wavelength 450 nm and 470 nm. The obtained curves are indicative of 1 : 2 stoichiometry in the aqueous species. This is further confirmed by mole ratio method[35] (Figure 5) by using equimolar solutions of Ce (IV) and DAM (0.0005 M) and that of the reagent varied from 0.1-3-0 ml. The graph is plotted between the mole ratio of the reagent and the corresponding values at 450 and 470 nm.

The proposed method handles satisfactorily the analysis of a wide variety of samples with corresponding composition and the results obtained are reproducible (Table 2).

The procedure is simple, rapid and free from the interference of a large number of metal ions of great analytical importance. Besides as far as the determination of cerium is concerned, it compares well with some of the existing method[36-39] (Table 3) in respect of its sensitivity and selectivity.

Conclusion

A simple, rapid and sensitive system of spectrophotometric determination of cerium is developed with DAM i.e. 4,4'-diantipyryl methane in sulphuric acid medium. The method is free from the interference of a large number of metal ions of analytical interest. The method obeys Beer's law in the range 0-55 µg Ce/10ml and has a Sandell's sensitivity of 0.015 µg Ce cm^{-2}. The method is highly reproducible with a standard deviation of ± 0.001. Stoichiometry of the complex is 1:2 (metal to ligand) is also established.

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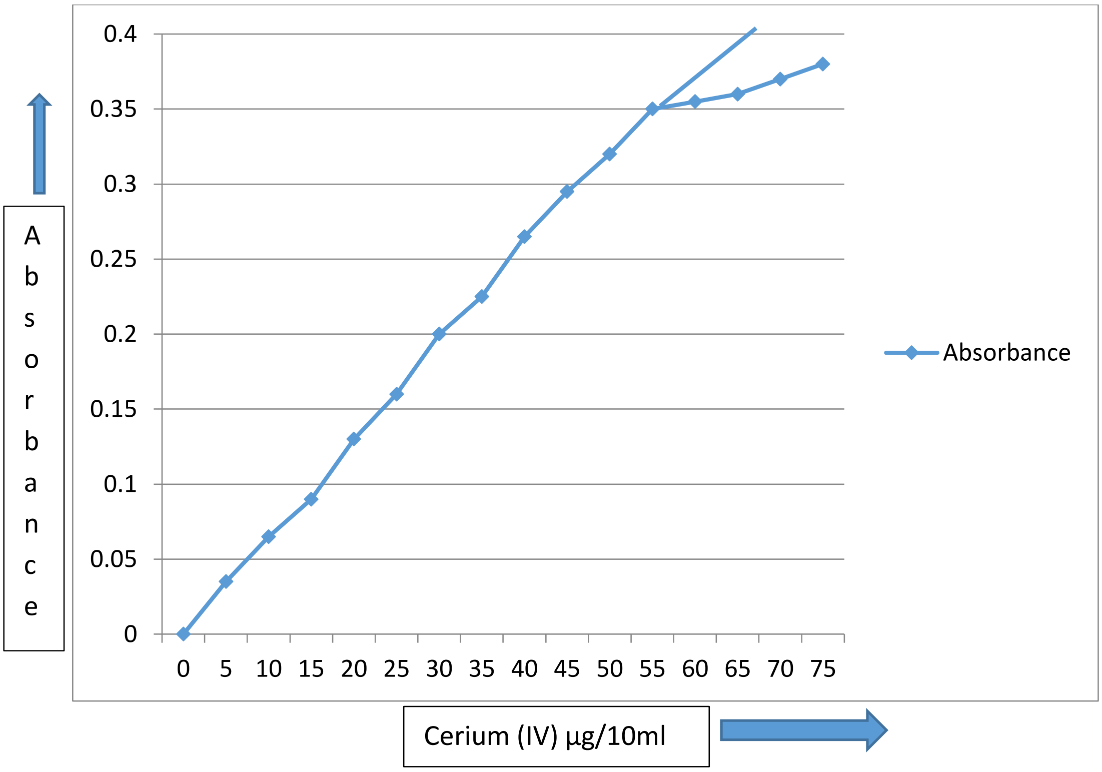

Figure 3: Beer's Law obedience of Ce(IV)-DAM complex

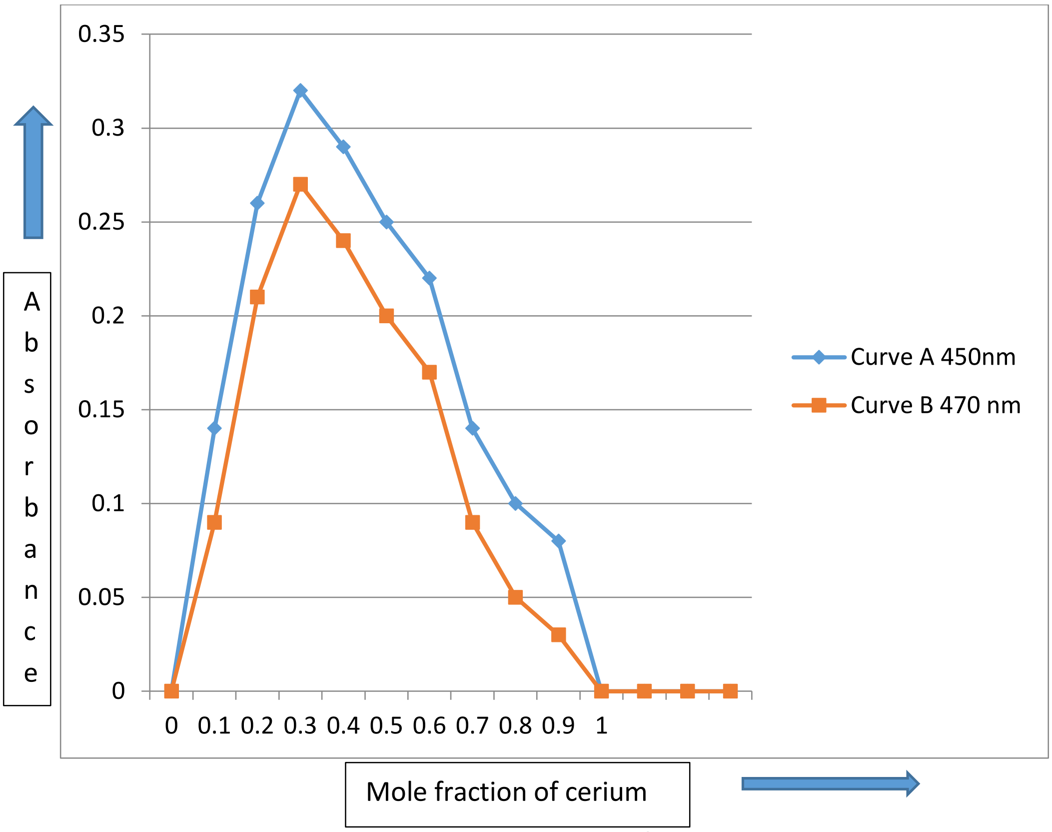

Figure 4: Continuous variation of Ce(IV) and DAM
*Cerium= 0.0005M; DAM= 0.0005M; Curve A- 450 nm; Curve B = 470nm

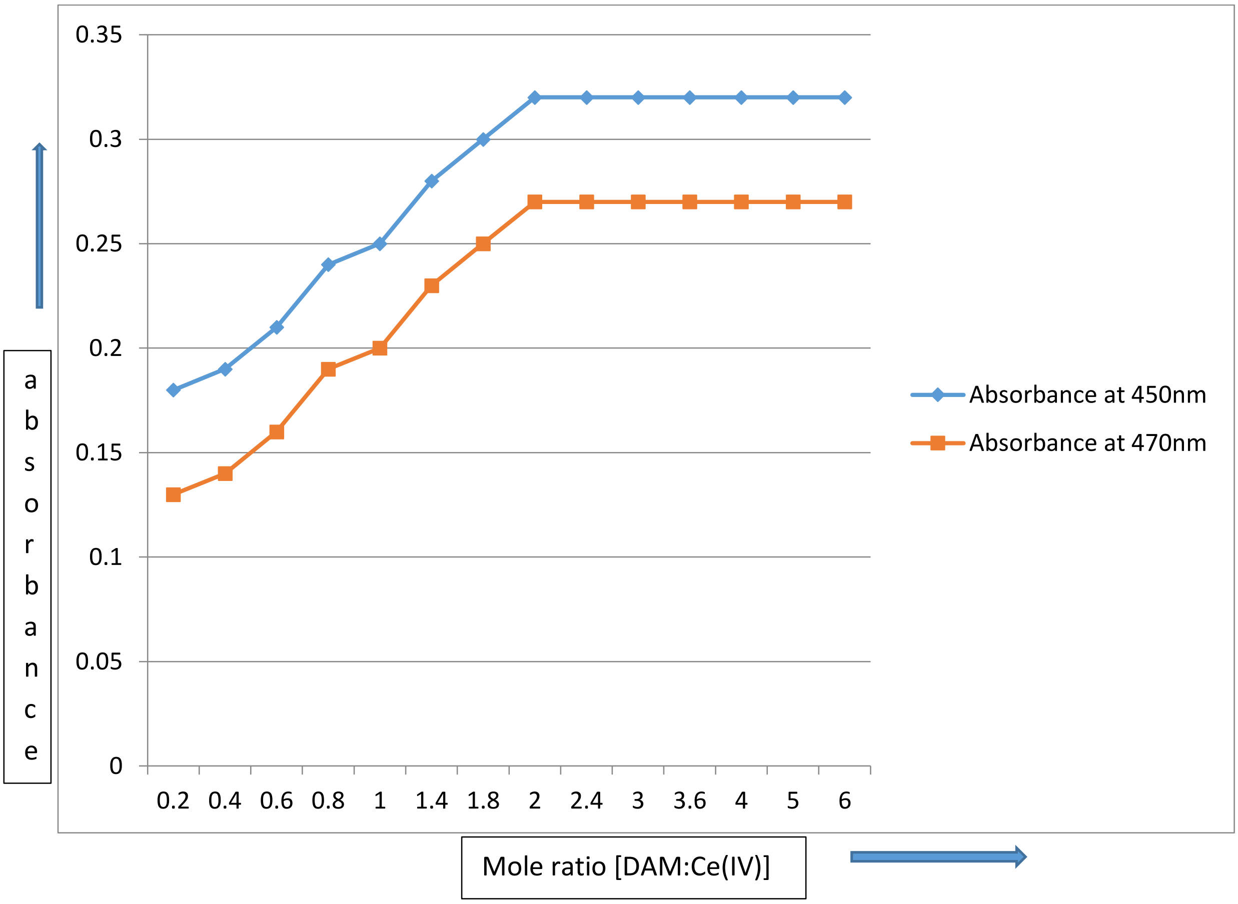

Figure 5: Mole ratio method
*Cerium(IV)= 0.0005M, 0.5ml; DAM= 0.0005M; CurveA = 450nm; Curve B = 470nm.

Table 3
Comparison of the proposed method of determination of Thorium (IV) with some of the existing methods.

S.N.	**Aqueous conditions**	**i)λ_{max} (nm) ii)Extractant**	**Molar Absorptivity ($l\ mol^{-1}\ cm^{-1}$)**	**Interfering ions**
1	Ce(IV), pH 5.5 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone[36]	i)490 nm ii) -	2.1×10^3	Fe(III), Cu(II)
2	Ce(IV), pH 5.0 Pyrogallol red[37]	i)507 nm ii) -	-	Ti(IV),Al(III), V(V), Cu(II),Th(IV), Mo(VI),W(VI),Cr(VI),Sb(III),Zr(IV),Fe(III)
3	Ce(IV), 0.4-2.88M HCl 4-Sulpho-2-aminobenzenethiol[38]	i)560 nm ii) -	8.06×10^3	Fe(II), Fe(III),Cr(VI),Cr(III),Cu(II),Mn(II),Hg(II)
4	Ce(IV), pH 10.2 Methylthymol blue[39]	i)625 nm ii) -	2.7×10^4	Cu(II),Mg(II).Ca(II),Fe(II),Sr(II),Ba(II),Cd(II),Mn(II),Hg(I),Al(III),Zr(IV),V(V),Th(IV),PB(II),Bi(III), Cr(III)
5	Ce(IV), 1M CH_3COOH $K_4[Fe(CN)_6]$[40]	i)425 nm ii) -	6.0×10^3	-
6	Ce(IV), 0.5M H_2SO_4 4,4’- diantipyrylmethane	i)450 nm ii) -	9.1×10^3	34 cations are non-interfering

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