Research Article

Determination of Thorium (IV) by Derivative Spectrophotometric Technique.

G.V.S.Vallinath*, K.B.Chandrasekhar and N.Devanna

Department of chemistry, Jawaharlal Nehru Technological University, Anantapur-515002, Andhra Pradesh, India.

ABSTRACT

A simple and sensitive spectrophotometric method has been developed for the determination of Thorium (IV) using newly synthesized reagent 3,5-Dimethoxy-4-hydroxybenzaldehyde isonicotinoyl hydrazone (DMHBIH). Thorium (IV) forms an Yellow coloured water soluble complex with the reagent in acidic medium pH 3.0. The molar absorptivity and Sandell's sensitivity of coloured species are 4.84×10^4 L.mol^{-1} cm^{-1} and 0.0083 μg/cm^2 respectively. Beer's law is obeyed in the range 0.580-5.80 μg/ml of Thorium(IV) at λ_{max} at 390 nm. Thorium (IV) forms a 1:1 complex and stability constant of the complex is $4.176 \times 10^{6.}$ the developed derivative spectrophotometric method has been satisfactorily applied for the determination of Thorium (IV) in monazite sand.

Key words:
Thorium(IV), 3,5-dimethoxy-4-hydroxybenzaldehyde isonicotinoylhydrazone(DMHBIH), derivative spectrophotometry.

INTRODUCTION

Thorium is a naturally occurring white metal. It is contaminated with the oxide. Thorium slowly tarnishes in air, becoming grey and eventually black. Thorium is found in small amounts in most rocks and soils. Soils commonly contain an average of 12 ppm of thorium. Thorium occurs in several minerals, the most being the rare earth thorium-phosphate mineral, monazite, which contains up to about 12% thorium oxide. Thorium and rare earths are often co-exists in their minerals, products. Thorium found numerous applications in light bulb elements, lantern mantles, arc light lamps, welding electrodes and heat-resistant ceramics. Glass containing thorium oxide has high refractive index and dispersion and is used in lenses for cameras and scientific instruments. Thorium is utilized as nuclear fuel. Small amounts of thorium can cause dermatitis while larger amounts results in lung, pancreas and blood cancer. Exposure to thorium internally leads to increased risk of liver diseases. Determination of thorium is a problem in analytical chemistry due to similar behaviour of rare earths and thorium. Spectrophotometric methods for the determination of metal ion in microgram level continue to be interesting than other analytical methods. Only few organic reagents are available for the spectrophotometric determination of thorium. [1-9] Each chromogenic system has its own advantages and disadvantages with respect to selectivity, sensitivity and rapidity. In general, solvent extraction technique is used in most of the methods. However, organic solvents used for the extraction are often carcinogenic, toxic and causes environmental pollution.

Hydrazones are important organic analytical reagents for the spectrophotometric determination of metal ions in microgram quantities. They react with many metal ions forming colour complexes and act as chelating agents. The potential applications of hydrazone derivatives for the spectrophotometric determination of metal ions have been reviewed by Singh et al..[10] The great interest towards derivative spectrophotometry is due to the increased resolution of spectral bands, allowing the detection and location of the wavelengths of poorly resolved components of complex spectra and reducing the effect of spectral background interferences. Hydrazone reagents are widely used in our laboratories for the derivative spectrophotometric determination of metal ions.[11-13] In the light of good analytical characteristics of hydrazones, herein we report zer and first order derivative spectrophotometric determination of thorium (IV) using 3,5-dimethoxy-4-hydroxybenzaldehydeisonicotinoylhydrazone (DMHBIH) is proposed.

EXPERIMENTAL

Apparatus:

All absorption measurements were made in a shimadzu 160A, microcomputer based UV-Visible spectrophotometer equipped with 1.0cm quartz cells. The instrumental parameters were optimized and the best results were obtained with scan speed fast, slit width of 1nm and $\Delta\lambda=2$nm for first order derivative mode in the wavelength range 350-650nm. ELICO L1-120 digital pH meter was used for the pH adjustments.

Reagents :

*Corresponding Author
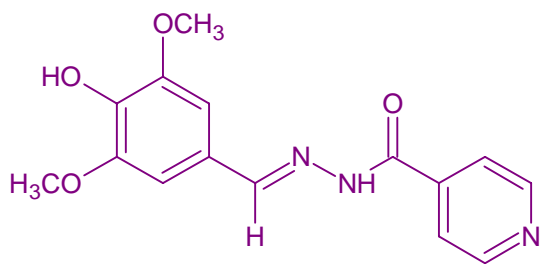Email: vallinath999@gmail.com
Mobile :+91-98495-15835

Fig.1. Structure of 3,5-Dimethoxy-4-hydroxybenzaldehyde isonicotinoylhydrazone (DMHBIH)

All chemicals used were of A.R grade unless stated. All solutions were prepared with doubly distilled water. The

Table-1. Analytical Characteristics of 3,5-Dimethoxy-4-hydroxybenzaldehyde isonicotinoylhydrazone

Metal ion	Ph	Λ_{max} (nm)	Molar absorptivity (ε) $(L.mol^{-1}cm^{-1}) \times 10^4$
Ru(III)	4.25	390	1.7
Fe(III)	4.0	386	1.875
Cu(II)	9.0	440	3.37
Th(IV)	3.0	390	4.84*

*Present work

standard Thorium (IV) solution (0.01M) was prepared by dissolving accurately weighed 0.5702 g of Thorium nitrate pentahydrate($Th(NO_3)_4.5H_2O$, LOBA CHEMIE)

Table-2: Physico-Chemical and Analytical Characteristics of [Th(IV)-DMHBIH] Complex

Characteristics	Results
Colour	Yellow
λ_{max}(nm)	390
p^H range (optimum)	2.0-3.0
Mole of reagent required per mole of metal ion for full colour development	10 folds
Molar absorptivity($L.mol^{-1}cm^{-1}$) (ε)	4.84×10^4
Sandell's sensitivity($\mu g/cm^2$)	0.0083
Beer's law validity range($\mu g/ml$)	0.580-5.80
Optimum concentration range($\mu g/ml$)	0.9282-4.6408
Composition of complex(M:L) obtained in Job's and mole ratio methods	1:1
Stability constant of the complex	4.176×10^6
Standard deviation	0.00011
Relative standard deviation (%)	0.03

in a 100 ml. of doubly distilled water. The resultant solution was standardised gravimetrically.[14] Working solutions were prepared by diluting the stock solution to an appropriate volume. Buffer solutions were prepared by using 0.1M HCl, 0.1M NaOH, 0.1M disodium hydrogen phosphate and 0.1M potassium dihydrogen phosphate.

Synthesis of 3,5-dimethoxy-4-hydroxybenzaldehydeisonicotinoylhydrazone:

The reagent 3,5-dimethoxy-4-hydroxybenzaldehydeisonicotinoylhydrazone(DMHBIH) was synthesized by refluxing equimolar amounts of 3,5-dimethoxy-4-hydroxybenzaldehyde and isonicotinoylhydrazone. In a 250 ml round bottomed flask hot ethanolic solution of 3,5-dimethoxy-4-hydroxybenzaldehyde(1.8212g, 0.01 mole) and hot ethanolic solution of isonicotinoylhydrazone(1.3714g,

Table 3. Tolerance limit of foreign ions in the determination of 2.90 µg/ml Thorium (IV)

Ion added	Tolerance limit µg/mL	Ion added	Tolerance limit µg/mL
Bromide	3196.16	Pb^{2+}	103.6
Iodide	2538	Hg^{2+}	100.3
Urea	1500	Co^{2+}	88.4
Chloride	1064	Zn^{2+}	65.39
Tetraborate	970	Ca^{2+}	60.15
Sulphate	940	Sn^{2+}	59.35
Oxalate	880	Cd^{2+}	56.21
Nitrate	620	Zr^{4+}	45.61
Acetate	590	Ni^{2+}	29.34
Thiocyanide	581	U^{6+}	12.0
Phosphate	475	Ag^+	11.0
Ascorbic acid	176.13	Mo^{6+}	9.59
Tartarate	148	As^{3+}	7.5
Thiourea	115	Sb^{3+}	6.08
Fluoride	95	Pd^{2+}	5.32
Ba^{2+}	206	Ru^{3+}	5.05
W^{6+}	184	Al^{3+}	2.69
Sr^{2+}	175.2	Cr^{3+}	2.59
Mn^{2+}	110	V^{5+}	2.54
Bi^{3+}	104.5	Cu^{2+}	0.63 1.27*
		Fe^{3+}	2.8,3.8†

* masked by thiourea 245 µg/ml., † masked by fluoride 180 µg/ml.

0.01mole) were mixed and refluxed using water condenser for 3 hours. On cooling the reaction mixture, a greenish yellow coloured product separated out, Which was collected by filtration and washed with double distilled water. The resulting hydrazone was recrystalized using 50% ethanol (yield,76%, mp 221⁰C). The structure of DMHBIH was confirmed based on the IR, NMR and Mass spectral data and is given in Figure-1.

Table 4. Determination of Thorium (IV) in monazite sand.

Amount of Th(IV) taken (µg/ml)	Amount of Th(IV) found* (µg/ml)			Error(%)		
	Zero order method	First derivative method	Second derivative method	Zero order method	First derivative method	Second derivative method
1.0	0.962	0.973	0.998	+3.80	+2.70	+0.20
1.5	1.444	1.475	1.488	+3.73	+1.66	+0.80
2.5	2.516	2.508	2.510	-0.64	-0.32	-0.40

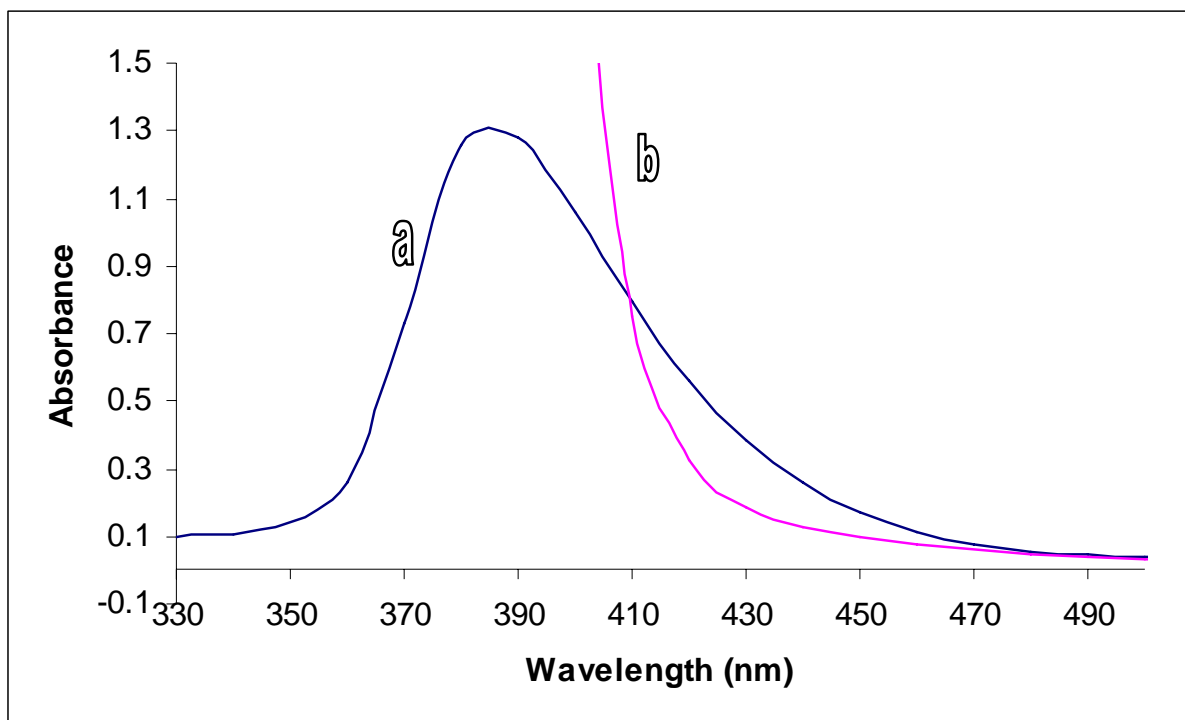**average of best three determinations among five determinations

Fig.2. Zero order Absorption spectra (a) Reagent DMHBIH Vs DMF blank
(b)Th(IV)-DMHBIH complex Vs Reagent blank Th(IV)= 5.80 μg/ml ; DMHBIH = 5×10^{-4} M ; pH = 3.0.
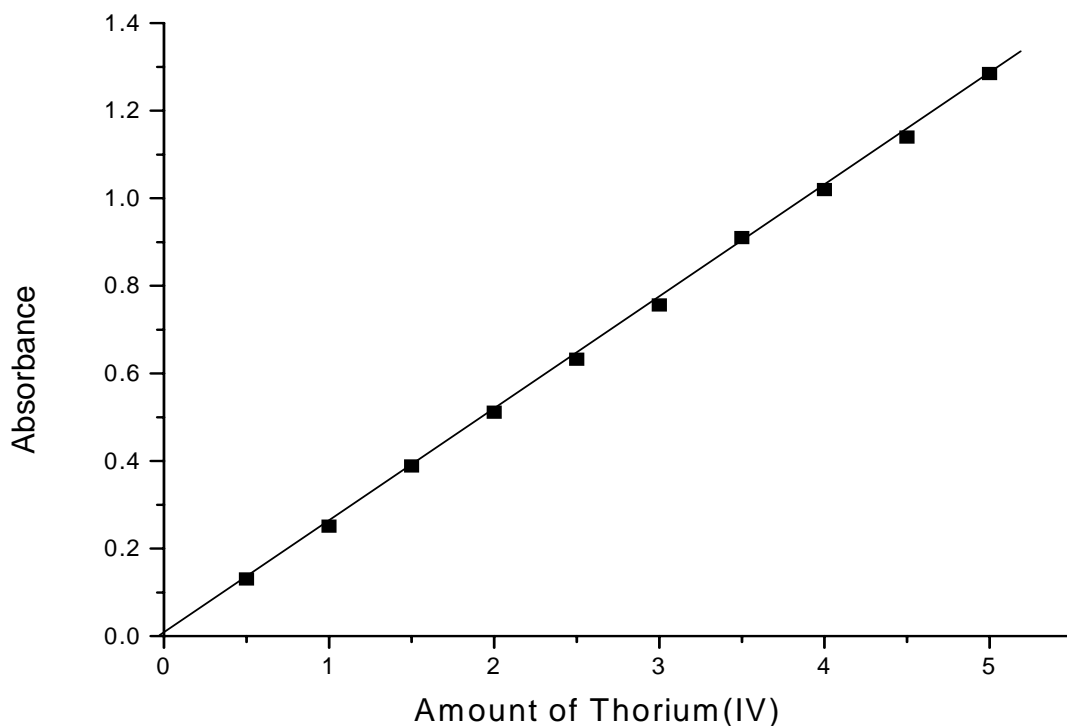

Fig.3. Zero order Beer's law plot of Th(IV)-DMHBIH complex

The reagent solution (0.01 M) was prepared by dissolving 0.3022 g of DMHBIH in 100 ml of Dimethylformamide (DMF). The reagent solution is stable for 48 hours.

Reaction with metal ions:

The reaction of some important metal ions were tested at different pH values. The samples were prepared in 10ml volumetric flasks by adding buffer solution 3.0 ml (pH 1-11), metal ion 0.5 ml of 1×10^{-3}M, Tritonx-100(5%) 0.5ml and HDBIH 0.5 ml of 1×10^{-2}M solution. The mixture was diluted up to the mark with distilled water. The absorbance was measured in 300-700nm range against reagent blank. The results are summarized in Table-1.
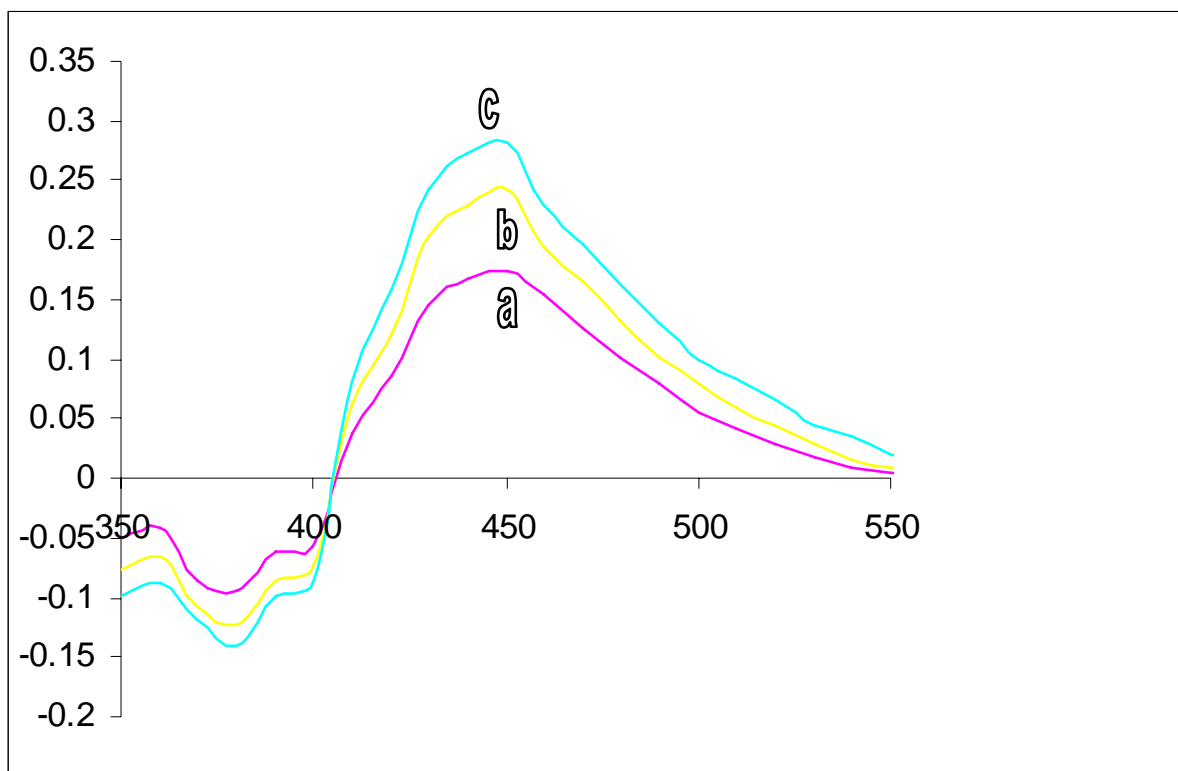
Fig.4. First order Beer's law derivative spectra of Th(IV)-DMHBIH complex (a) 0.788 μg/ml of Th(IV); (b) 1.379 μg/ml of Th(IV); (c) 1.773 μg/ml of Th(IV)
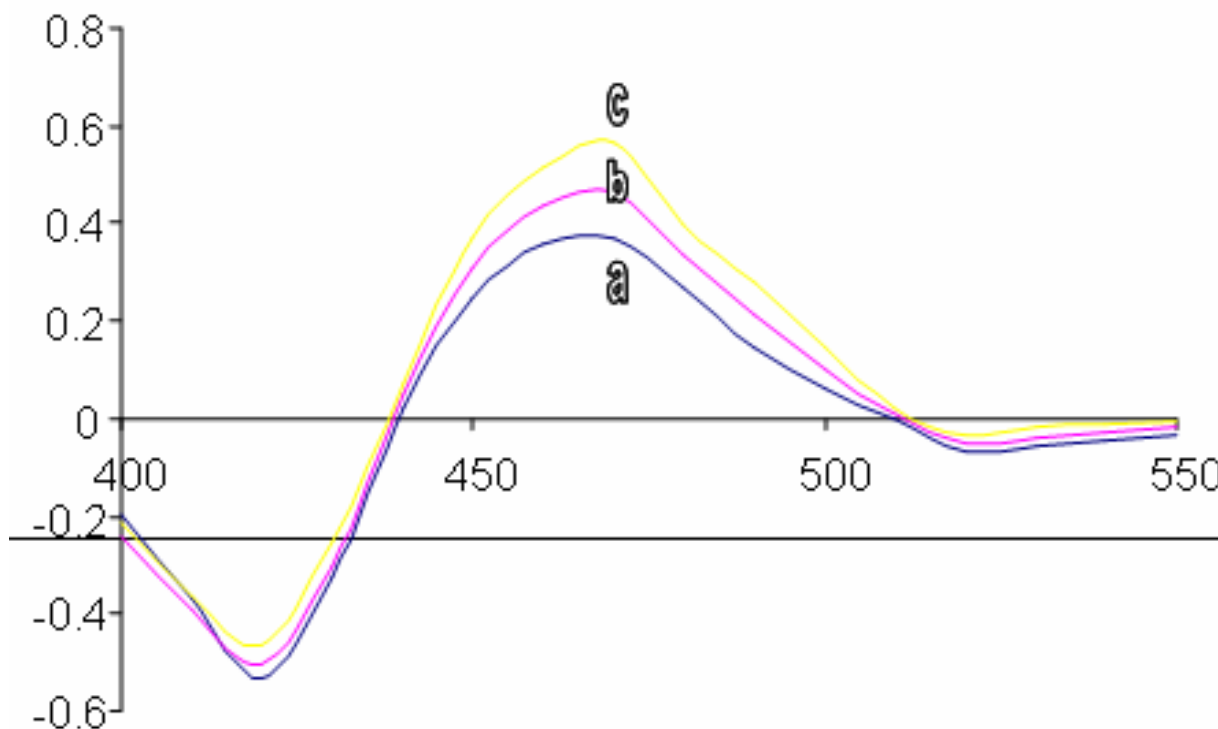

Fig.5. Second order Beer's law derivative spectra of Th(IV)-DMHBIH complex
(a) 0.788 μg/ml of Th(IV); (b) 1.379 μg/ml of Th(IV); (c) 1.773 μg/ml of Th(IV)

Recommended procedures:

Determination of Thorium (IV) (zero order):
An aliquot of the solution containing 0.580-5.80 μg/ml of Thorium (IV), 3.0ml of buffer solution pH 3.0 and 0.5ml of 5×10^{-3}M DMHBIH reagent solution were taken in 10 ml volumetric flask and the solution was diluted up to the mark with doubly distilled water. The absorbance

of the solution was recorded at 390 nm in a 1.0cm cell against reagent blank prepared in the same way. The measured absorbance was used to compute the amount of Thorium (IV) from the predetermined calibration curve.

Determination of Thorium (IV) by First order Derivative Spectrophotometry:

For the above solution of Thorium (IV)-DMHBIH first order derivativespectrum was recorded with a scan speed fast having a degree of freedom 9 in the wave length range from 350-650nm. The first order derivative peak height was measured by peak-zero method at 450nm. The peak height was plotted against the amount of Thorium (IV) to obtain the calibration curve.

Determination of Thorium (IV) by Second order Derivative Spectrophotometry:

For the above solution of Thorium (IV)-DMHBIH second order derivative spectrum was recorded with reference to the reagent blank with 9 degrees of freedom in a wave length range 350-650nm. In the second order derivative spectrum peak height at 470nm was measured from the zero line of spectrum. Calibration plot was constructed by plotting the derivative amplitude against the amount of Thorium (IV).

RESULTS AND DISCUSSION

The reagent 3,5-dimethoxy-4-hydroxybenzaldehydeisonicotinoylhydrazone(DMHBIH) was easily synthesized as any other Schiff base reagent. The new chromogenic reagent DMHBIH was not used for the spectrophotometric determination of Thorium (IV). The colour reactions are mainly due to complex formation of DMHBIH with divalent, trivalent, tetravalent metal ions in aqueous medium. In acidic medium, the ligand presumably co-ordinates the metal ion to give neutral complexes.

Absorption spectra:

The absorption spectra of DMHBIH and [Th(IV)-DMHBIH] complex recorded in optimum conditions against buffer solution and reagent blank are respectively shown in Figure-2. The [Th (IV)-DMHBIH] complex showed the maximum absorbance at 390 nm, where the reagent did not show appreciable absorbance. Therefore analytical wavelength 394 nm was used for all measurements.

It was observed that the colour reaction between Thorium (IV) and the reagent DMHBIH was instantaneous even at room temperature in pH range 2.0-5.0. the study of the effect of pH on the colour intensity of the complex showed that the maximum constant absorbance was obtained in the pH range 2.5-3.5. Therefore pH 3.0 was kept constant throughout the

experiment.

Order of addition of reactants:

The order of addition of buffer solution, metal ion and DMHBIH reagent had no adverse effect on the absorbance of [Th (IV)-DMHBIH] complex.

Applicability of Beer's law:

From the calibration plots it was observed that the system obeyed Beer's law in the range 0580 to 5.80 μg/ml of Thorium (IV) with excellent linearity. It is presented in Figure-3. The various important analytical characteristics of [Th(IV)-DMHBIH] complex are summarized in Table-2.

Derivative spectrophotometry is a useful technique because it decreases the interference and increases the tolerance limit value of foreign ions and may be advantageously used for the determination of metal ion having overlapping spectra. The recommended derivative procedure was employed for the determination of Thorium (IV).The first order and second order derivative spectral graphs shown in Figure-3 and Figure-4 respectively. This shows that the derivative amplitudes measured at 450nm for first order and 470nm for second order were found to be proportional to the amount of Thorium (IV)

Effect of diverse ions:

The effect of various diverse ions in the determination of find out the 2.90 μg/ml Thorium(IV) was studied tolerance limit of foreign ions in the present method. The tolerance limit of a foreign ion was taken as the amount of foreign ion required to cause an error of ±2% in the absorbance or amplitude. The results are given in Table-3. The data obtained in the derivative method is also incorporated. The data suggest that several associated anions and cations donot interfere when they are present in large excess, such as iodide, nitrate, thiosulphate, thiocyanide, bromide, sodium(I), calcium(II), bismuth(III), tungsten(VI). The tolerance limit values for many anions and cations are more in derivative method. The interference of associated metal ions such as Iron(III) and Copper(II) is decreased by adding masking agents fluoride and thiourea respectively.

APPLICATIONS

The present method was applied for the determination of

Table:5 . Determination of Thorium (IV)

Reagent	λ_{max}(nm)	Molar absorptivity	Reference
2,4-dihydroxybenzaldehyde isonicotinoyl hydrazone.	390	2.20×10^4	18
2-hydroxy-1,4-naphthaquinone Lawsone (LAS)Mepazine hydrochloride	440	0.27×10^4	19
Semi-xylenol	535	3.33×10^4	20
Calixearene hydroxamic acid (CPCHA)	450	2.20×10^4	21
Disodium salt of 2-(2-hydroxy-3,6-disulfo-1-naptylazo)-benzene arsenic acid	544	1.69×10^4	22
1-(2'thiazolylazo)-2-naphthol	555	3.14×10^4	23
3,5-dimethoxy-4-hydroxybenzaldehydeisonicotinoyl hydrazone (DMHBIH)	390	$4.84 \times 10^{4*}$	Present work

*Present work

Thorium (IV) in monazite sand.

Preparation of the sample solution

The sample was prepared by adopting the given procedure. 1.10 g of monazite sand was digested in 30 ml of concentrated sulphuric acid, leached and filtered. The filtrate was collected in a 500-ml standard flask and made up to the mark with distilled water. Thorium from the solution was separated by reverse phase extraction chromatography.[15]

The separated thorium was dissolved and diluted to 100 ml with distilled water. An aliquot of the solution was taken and the Thorium (IV) content in this solution was determined by adopting the recommended procedure. Results are presented in Table-4.

CONCLUSION

The present method using 3,5-dimethoxy-4-hydroxybenzaldehyde isonicotinoyl hydrazone(DMHBIH) as spectrophotometric reagent for the determination of Thorium (IV) in aqueous medium is sensitive and simple. The present method is not laborious and there is no need of heating the components or pre extraction. Although the Arsenazo III[16] and Chlorophosphonazo-III[17] methods are highly sensitive, they suffer from the serious interference of fluoride, sulphate, lanthanum, zirconium, cerium, niobium and uranium. Large amounts of sulphate and moderate amount of the fluoride and phosphate donot interfere in the present method. This method is free from the interference of lanthanum, zirconium, cerium, niobium, uranium and other rare earth metals also. This method is simple and sensitive compared to several other reagents[18-23] presented in Table-5. Further the complex is stable for more time.

ACKNOWLEDGEMENTS

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