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Direct and derivative spectrophotometric determination of thorium (IV) with 2-hydroxy-3-methoxybenzaldehyde isonicotinoyl hydrazone (HMBAINH)

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ABSTRACT

A simple, sensitive and rapid spectrophotometric method was developed for the determination of thorium(IV) using 2-hydroxy-3-methoxybenzaldehydeisonicotinoylhydrazone (HMBAINH) as an analytical reagent. The metal ion forms a fluorescent yellow colored complex with HMBAINH in aqueous dimethyl formamide medium at pH 5.0. The complex showed absorption maximum at 395 nm in the pH range 4.0-6.0. Beer's law was obeyed in the range of 0.58 – 11.60 $\mu\text{g mL}^{-1}$ of Th(IV). The molar absorptivity and Sandall's sensitivity of the method were $1.4 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$ and $0.0167 \mu\text{g cm}^{-2}$ respectively. The interference of various diverse ions was studied. The 1:1 (Metal: Ligand) complex was fairly stable (stability constant 2.17×10^5). First and Second order derivative spectrophotometric methods were also developed for the determination of Thorium (IV) which showed greater sensitivity and selectivity. The proposed methods were applied for the determination of Thorium (IV) in monazite sand samples and in gas mantle samples.

Keywords: Thorium (IV), Direct and derivative spectrophotometry, HMBAINH

INTRODUCTION

The principal oxidation state of thorium is only +4. Th(IV) forms complexes of variable geometries with different ligands. They include dodecahedral $[\text{Th}(\text{NO}_3)_6]^{2-}$ C.O No: 6; fluorite structure (ThO_2), C.O No: 8; square antiprism (ThL_4), C.O No: 8; capped square antiprism $[\text{Th}(\text{trop})_4]$, C.O No: 9 and irregular icosahedrons $[\text{Th}(\text{NO}_3)_6]^{2-}$ C.O No: 12[1]

Among the various chromogenic agents reported for the determination of thorium (IV), most of them were found to be non-selective involving in serious interference from the diverse ions. Arsenazo III [2-4] is found to be nonselective and gives non-reproducible results. Thoron I method is less sensitive and less selective than Arsenazo III method. Zr(IV) and Hf(IV) seriously interfere in this method[5,6] A survey of recently reported spectrophotometric methods for the determination of thorium has been made and presented in table 7. Majority of the reported methods require prior removal of closely associated metal ions and hence lack selectivity. In the present investigation simple, sensitive, non-extractive direct and derivative spectrophotometric method for the determination of thorium using HMBAINH is reported.

MATERIALS AND METHODS

2.1. Apparatus

The absorbance and pH measurements were made on a Perkin Elmer (LAMBDA25) spectrophotometer controlled by a computer and equipped with a 1cm path length quartz cell and Phillips digital pH meter (model L1 613) respectively.

2.2. Reagents

2.2.1. 2-hydroxy-3-methoxybenzaldehyde iso-nicotinoylhydrazone(HMBAINH):

The reagent was synthesized by condensing equimolar solutions of 2-hydroxy-3-methoxy benzaldehyde in methanol and isonicotinic acid hydrazide adopting the described procedure (Brown et al., 1975) (m.p.224⁰c) The stock solution of the reagent (1×10^{-2} M) was prepared by dissolving 0.271g in 100 ml of dimethyl formamide (DMF). Working solutions were prepared by diluting the stock solution appropriately with DMF.

2.2.2. Thorium (IV) solution

A stock solution (1×10^{-2} M) of Thorium(IV)solution was prepared by dissolving 0.57g of $\text{Th}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$ (Loba) in 100ml volumetric flask with distilled water. Solutions of lower concentrations were prepared by successive dilution of the stock solution.

2.2.3. Buffer solutions

Buffer solutions of various pH values were prepared by mixing 1 M hydrochloric acid and 1 M of sodium acetate (pH 1.0-3.0), 0.2 M acetic acid and 0.2 M sodium acetate(pH 3.5-7.0) 0.2 M acetic acid and 1 M sodium acetate (pH 7.0) and 2M ammonium chloride and 2M ammonium hydroxide (pH8.0-10.0) solutions in appropriate ratios. The pH of the solutions was checked with pH meter.

2.2.4. Preparation of sample solutions

Preparation of Monazite sand sample[7]:

The monazite sand was collected from the Arabian Sea coast at Mangalore. 1.0 g of the monazite sand was mixed with 5ml of concentrated sulphuric acid and heated at 250⁰C for about 4 hours to digest the monazite sand. The resultant viscous paste was dissolved in distilled water by heating at 45⁰ C for half an hour. The resultant solution was filtered and thorium from the filtrate is precipitated as hydroxide by adding ammonia solution. The precipitate was filtered off and dissolved in minimum quantity of dil.HCl and then diluted to 25ml.

Preparation of gas mantle sample[7]:

0.5 g of gas mantle sample was accurately weighed and placed in a 100ml beaker. 10ml of con HNO_3 was added and gently boiled for 20 minutes. The residue was diluted with 10 ml of distilled water and filtered. The resultant solution was diluted to 250ml in a volumetric flask with distilled water.

3. Procedure

3.1. Direct spectrophotometry:

In each of a set of 10 ml volumetric flasks, 4 ml of buffer solution (pH 5.0), and 0.3 ml of HMBAINH (1×10^{-2} M) were taken and various volumes of 1×10^{-3} M thorium (IV) solution were added. The resultant solutions were made upto the mark with distilled water. The absorbance was measured at 395 nm against the reagent blank. The calibration plot was prepared by plotting the absorbance against the amount of thorium (IV).

3.2. Derivative spectrophotometry:

First and second order derivative spectra were recorded for the above solutions with a scan speed of fast (nearly 2400 nm min⁻¹) and split width of 1 nm with nine degrees of freedom in the wavelength region 350-600 nm. The derivative amplitudes were measured at 430 nm, for the first derivative and at 445 nm for the second derivative curves and plotted against amount of thorium (IV) to obtain the calibration plots.

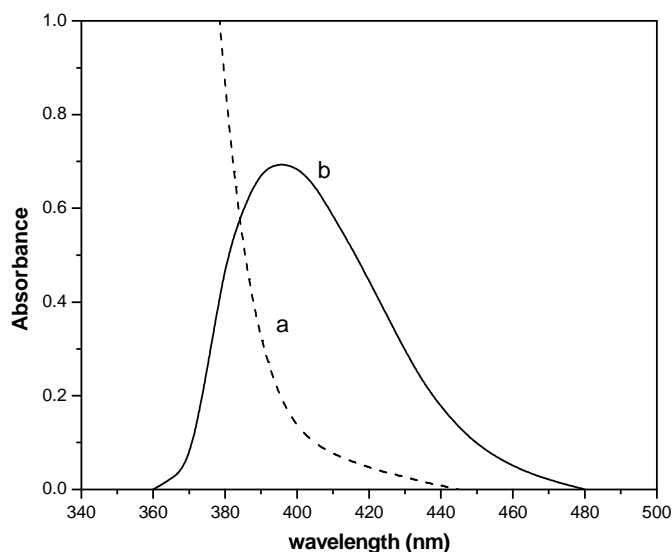
RESULTS AND DISCUSSION

4.1. Direct method:

4.1.1. Absorption spectrum:

The absorption spectra of HMBAINH and [Th(IV)-HMBAINH] in aqueous dimethylformamide were measured against buffer and reagent blank respectively. The thorium complex absorbs strongly at 395 nm where the reagent negligible absorbance fig.1. As the absorption was maximum at 395 nm, the analysis of Th(IV) was carried out by measuring the absorbance at 395 nm against the reagent blank.

**Fig.1 Absorption spectra of (a) HMBAINH vs buffer blank
(b) [Th (IV) – HMBAINH] v/s reagent blank**
 [Th (IV)] = 5×10^{-5} M
 [HMBAINH] = 1.5×10^{-3} M
 pH = 5



4.1.2. Effect of pH:

Studies on the effect of variation in pH on the absorbance of the yellow coloured [Th(IV)-HMBAINH] solution showed that the coloured complex exhibits maximum and constant absorbance in the pH range 4.0 - 6.0. Therefore, the studies were carried out at pH 5.0.

4.1.3. Effect of reagent concentration:

Color intensity of the experimental solution was found to increase with the increase in the reagent concentration attaining maximum colour intensity in the presence of 30-fold excess of the reagent. Hence the required reagent concentration (30fold excess) was maintained throughout the studies.

4.1.4. Validity of Beer's law:

The absorbance data measured for experimental solutions containing different known amounts of thorium (IV) fitted into a straight line equation $A_{395} = 0.0602C + 0.0017$. Beer's law was obeyed in the concentration range $0.58 - 11.6 \mu\text{g mL}^{-1}$ of thorium. The molar absorptivity, Sandell's sensitivity, detection limit, determination limit, relative standard deviation, correlation coefficient and other statistical data of the direct method were evaluated and presented in table 4.

4.1.5. Effect of foreign ions:

The effect of various anions and cations on the absorbance of the experimental solution was studied and their tolerance limits were determined. The amount of foreign ion that brings about a change in absorbance by $\pm 2\%$ was taken as its tolerance limit. The results are given in table 1, which reveal that the proposed method is selective in the presence of masking agents, table 2.

4.1.6. Stoichiometry and stability constant:

The stoichiometry of [Th(IV)-HMBAINH] complex in solution was determined by Job's continuous variation method, molar and slope ratio methods and obtained as 1:1 (Metal:Ligand). The stability constant of the complex was calculated from the experimental data of Job's method as 2.17×10^5 .

4.1.7. Applications:

To substantiate the validity of the proposed direct method, Different aliquots of the prepared Monazite sample solution were taken, the pH was adjusted to 5.0 and then treated with the required amount of hydrazone reagent. By measuring the absorbance of the resultant solution, the amount of the thorium was evaluated from the predetermined calibration plot and compared with that obtained by AAS method. The results are presented in table 3.

Table.1. Tolerance limits of foreign ionsAmount of Th(IV) taken = 1.74 $\mu\text{g mL}^{-1}$ pH = 5.0

Foreign ions	Tolerance limit ($\mu\text{g mL}^{-1}$)	Foreign ions	Tolerance limit ($\mu\text{g mL}^{-1}$)
Iodide	1270	Ba(II)	1510
Thiosulphate	1120	Na(I)	1379
Sulphate	960	K(I)	1368
Phosphate	940	Ca(II)	1202
Bromide	800	Sr(II)	1051
Thiourea	760	Mg(II)	850
Nitrate	620	La(III)	347
Thiocyanate	580	Te(IV)	345
Tartrate	512	W(VI)	284
Chloride	354	Se(IV)	276
Carbonate	326	Y(III)	267
Citrate	316	Cd(II)	142
EDTA	272	Mn(II)	121
Fluoride	190	Hg(II)	65
Oxalate	96	Ir(III)	39
		Pb(II)	29
		Ce(IV)	20
		Ti(IV)	18
		Zr(IV)	15
		Au(III)	15
		Sn(II)	14
		Co(II)	Interfere
		Mo(VI)	Interfere
		Ni(II)	Interfere
		Cr(VI)	Interfere
		Fe(II)	Interfere
		Cu(II)	Interfere
		Pd(II)	Interfere
		V(V)	Interfere

Table2. Elimination of interference by addition of masking agents

Masking agent ($\mu\text{g mL}^{-1}$)	Foreign ion	Tolerance ($\mu\text{g mL}^{-1}$)
SCN ⁻ : 500	Co(II)	70
PO ₄ ³⁻ : 600	Ni(II)	80
	Sn(II)	100
	V(V)	160
Thiourea: 600	Pd(II)	100
S ₂ O ₃ ²⁻ : 800	Cu(II)	150
Tartrate: 400	Fe(II)	250
	Cr(VI)	100
	Mo(VI)	55

Table3. Determination of thorium in Monazite sand samples

Sample	Amount of thorium ($\mu\text{g mL}^{-1}$) \pm SD *		Relative error (%)
	Present method	AAS Method	
S1	2.26 \pm 1.50	2.20 \pm 0.56	2.72
S2	4.83 \pm 2.30	4.90 \pm 2.14	-1.43
S3	3.34 \pm 2.88	3.26 \pm 0.56	2.45

* Average of three determinations

4.2. Derivative methods:

In order to improve the sensitivity and selectivity of the proposed method, the absorbance data was derivatized once and twice and plotted against the wavelength which gave the resultant first and second order derivative curves respectively. The derivative amplitudes at certain wavelengths were found to be proportional to the amount of thorium thus obeying Beer's law. Therefore, the method was exploited to develop first and second order derivative spectrophotometric methods for the determination of thorium.

4.2.1. Derivative curves:

The first and second order derivative curves recorded in the wavelength region 350-600 nm, are shown in figures 2 and 3 respectively. The derivative amplitudes were measured by peak zero method. The first order curves showed maximum amplitudes at 430 nm and second order curves exhibited maximum amplitude at 445 nm.

Fig.2 First order derivative spectra of [Th (IV) - HMBAINH]
Amount of Th (IV) ($\mu\text{g mL}^{-1}$): a - 2.32; b - 4.64; c - 6.96; d - 9.28; e - 11.60

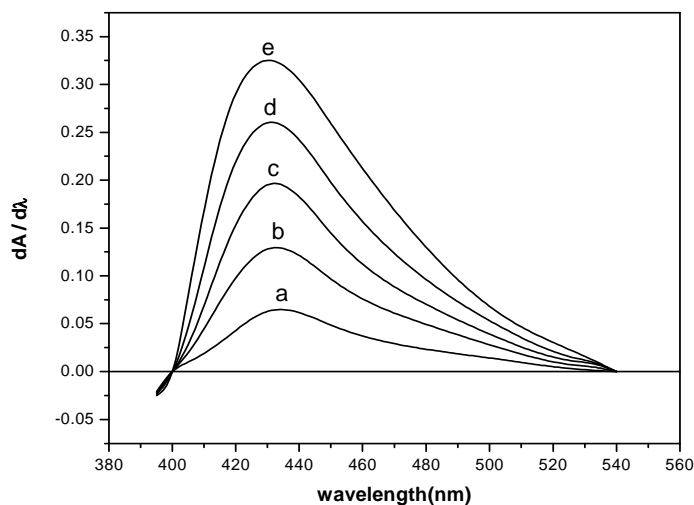
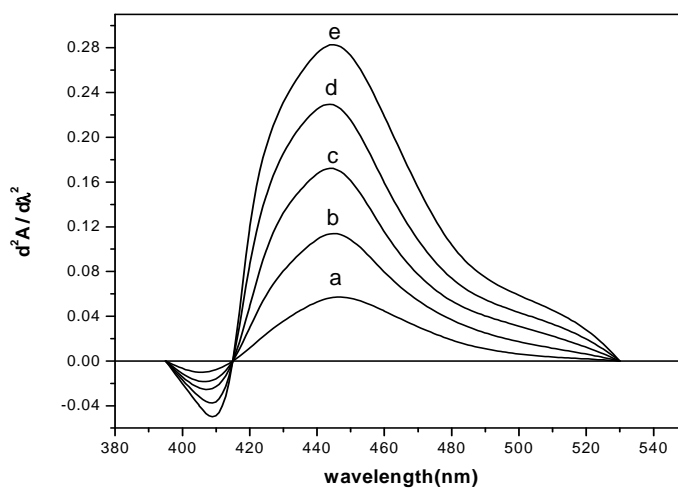


Fig.3. Second order derivative spectra of [Th (IV) - HMBAINH]
Amount of Th (IV) ($\mu\text{g mL}^{-1}$): a - 2.32; b - 4.64; c - 6.96; d - 9.28; e - 11.60



4.2.2. Determination of thorium (IV).

The derivative amplitudes of the first and second order curves measured at 430 nm and 445 nm were plotted against the amount of thorium figures 4 and 5. The curves were found to be linear obeying Beer's law in the range $0.29 - 12.76 \mu\text{g mL}^{-1}$ at 430 nm (first order) and 445 nm (second order). The other analytical and statistical results of the derivative methods are presented in table 4.

Fig 4. Beer's law plot for first derivative data
[HMBAINH] = 1.5×10^{-3} M pH = 5

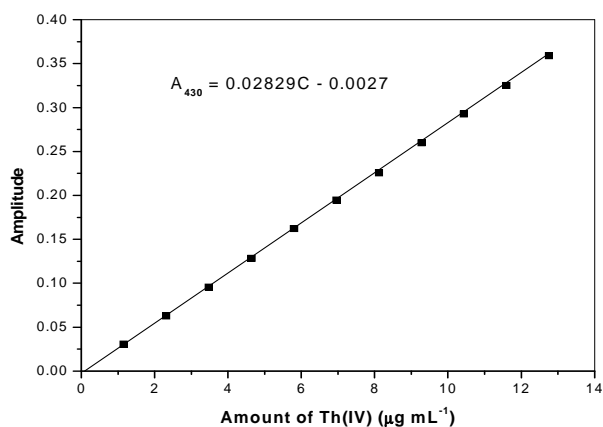


Fig. 5. Beer's law plot for second derivative data
[HMBAINH] = 1.5×10^{-3} M
pH = 5.0

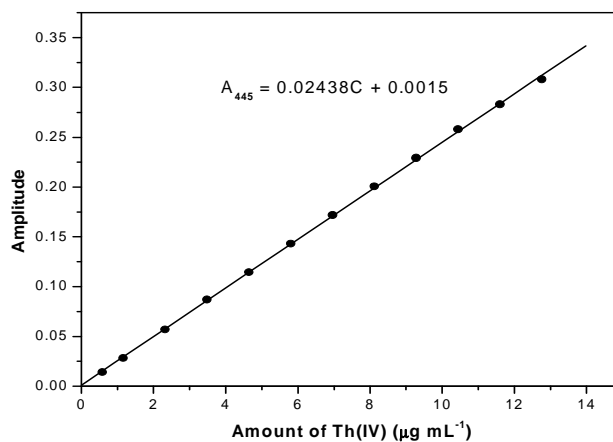


Table 4. Analytical characteristics of [Th (IV) – HMBAINH]

Parameter	Direct method 395nm	First derivative 430nm	Second derivative 445nm
Beer's law range ($\mu\text{g mL}^{-1}$)	0.58 – 11.6	0.29 – 12.76	0.29 – 12.76
Molar absorptivity, ϵ ($\text{L mol}^{-1} \text{cm}^{-1}$)	1.4×10^4	-	-
Sandell's sensitivity ($\mu\text{g cm}^{-2}$)	0.0167	-	-
Angular coefficient (m)	0.0602	0.0302	0.0261
Y- intercept (b)	-0.0018	-0.0012	-0.0016
Correlation coefficient (r)	0.9999	0.9999	0.9998
Relative standard deviation	0.92%	0.45%	0.59%
Detection limit ($\mu\text{g mL}^{-1}$)	0.159	0.079	0.092
Determination limit ($\mu\text{g mL}^{-1}$)	0.478	0.239	0.276
Composition (Metal: Ligand)	1 : 1	-	-
Stability constant	2.17×10^5	-	-

4.2.3. Effect of diverse ions:

The tolerance limits of some metal ions which showed serious interference in direct method were evaluated in derivative methods and shown in table 5. It can be seen from the table that the tolerance levels of all the tested ions are much higher in derivative methods than in the zero order method.

Table 5. Tolerance limits of foreign ions

Diverse ion	Zero order	First derivative	Second derivative
U(VI)	<1 fold	20	25
Fe(II)	<1 fold	22	20
Pd(II)	<1 fold	12	18
Bi(III)	<1 fold	8	22
Ga(III)	<1 fold	14	12
Cu(II)	<1 fold	24	45
V(V)	<1 fold	32	60
Mo(VI)	< fold	18	35

4.2.4. Applications:

The second order derivative spectrophotometric method at 445 nm was employed for the determination of thorium in prepared gas mantle sample. The results obtained are given in table 6.

Table 6. Determination of thorium in gas mantle

Sample	Amount of thorium ($\mu\text{g mL}^{-1}$) \pm SD (n=4)		
	Added	Found	Recovery %
Sample 1	-	1.68 \pm 0.25	-
	0.5	2.23 \pm 1.45	102.29
	1.5	2.98 \pm 0.78	93.7
	2.5	4.26 \pm 1.44	101.9
Sample 2	-	2.15 \pm 0.68	-
	0.5	2.56 \pm 1.32	96.6
	1.5	2.55 \pm 2.10	69.86
	2.5	4.74 \pm 0.86	101.93

Table 7. Comparison of the results

Reagent	Aqueous/ Extraction	Beer's law ($\mu\text{g mL}^{-1}$)	$\epsilon \times 10^4$ L mol ⁻¹ cm ⁻¹	Interference	Ref
2-hydroxy-1-naphthaldehyde-p-hydroxybenzoic hydrazone	Aqueous	1.464-6.96	3.5 x 10 ⁴	Cu(II), Ni(II), Co(II), Zn(II), Bi(III), Fe(II), Al(III), Ga(III), U(VI), In(III)	7
Morin	Aqueous	0-1.2	2.9	Many anions	8
Aniline blue – benzoate	Aqueous	-	0.316	Zr(IV), Mo(VI), Fe(III), PO ₄ ²⁻	9
Alizarin maroon and 5-sulphosalicylic acid	Aqueous	2.3-22.5	1.1	CN ⁻ , NO ₂ ⁻ , HPO ₃ ²⁻ , F ⁻	10
N-Phenyl benzo hydraxamic acid	Extraction	0.5-12.5	1.7	Mo(VI), V(V), W(VI), Mn(III), Cu(II), Zr(IV)	11
Thorin	Aqueous	0-25	1.69	PO ₄ ²⁻ , acetate, cyanide	12
Naphthazarin	Aqueous	1.39-6.0	2.0	EDTA, HPO ₄ ²⁻ , F ⁻ , Al(III), U(VI)	13
Semimethylthymol blue	Aqueous	0.46-4.18	1.44	-	14
Lawsone	Aqueous	5.8-32	0.27	-	15
2-hydroxy-3-methoxy benzaldehyde isonicotinoylhydrazone	Aqueous	0.58-11.6	1.4 x 10 ⁴	U(VI), Fe(II), Pd(II), Bi(III), Ga(III), Cu(II), V(V), Mo(VI)	Present method

CONCLUSION

The results of the present direct and derivative methods were compared with those of some of the already reported methods and presented in table 7. The comparison shows that both the direct and derivative methods proposed are more sensitive than majority of the reported methods. Further, the derivative methods are found to be more selective than large number of the reported methods.

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