DIRECT, DERIVATIVE SPECTROPHOTOMETRIC DETERMINATION OF MICRO AMOUNTS OF THORIUM (IV) BY 2-AMINOACETYL-3-HYDROXY-2-NAPHTHOIC HYDRAZONE (AHNH)

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Abstract

2-aminoacetyl-3-hydroxy-2-naphthoic hydrazone (AHNH) is a new chromogenic reagent used for the determination of thorium (IV) by simple, rapid, sensitive, selective, direct and derivative spectrophotometricmethod. 2-aminoacetyl-3-hydroxy-2-naphthoic hydrazone forms a dark orange coloured thorium (IV) - 2-aminoacetyl-3-hydroxy-2-naphthoic hydrazone complex shows maximum absorbance at 425 nm at pH 6.0. The reagent blank shows negligible absorbance. Hence, the analytical studies were carried out at 425nm. The method obeyed Beer's law validity in the range 0.581-5.813 μg mL^{-1}. The molar absorptivity and Sandell's Sensitivity are calculated and found as $2.75 x 10^3$ l mol^{-1} cm^{-1} and 0.00835μg cm^{-2}. The composition of the complex has 1:2 and stability constant of the complex was calculated as $3.63x10^3$. The effect of various diverse ions also incorporated. A first order derivative spectrophotometric method was developed for the determination of thorium (IV) which was found to be more sensitive than zero order method. The proposed method has been successfully applied for the determination of trace level of thorium in monazite sand.

Keywords: *2-aminoacetyl-3-hydroxy-2-naphthoic hydrazone, Thorium (IV), Spectrophotometry, monazite sand.*

1.Introduction

Thorium is a naturally occurring radioactive element of extraordinary long life time. Thorium is first of all a worthwhile potential raw material for fissile nuclear fuel production. Thorium is found in small amounts in most rocks and soils. Thorium occurs in several minerals, the most being the rare earth, thorium-phosphate mineral, monazite, which contain up to about 12% thorium oxide. Thorium found numerous applications in light bulb elements, lantern mantles, light lamps, welding electrodes and heat-resistant ceramics. 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 earth and thorium. Spectrophotometric methods for the determination of metal ion in microgram level continue to be interesting than other analytical methods. A survey of literature revelas that only few reagents are available for the spectrophotometric determination of thorium. Among all the available reagents Thoron [1] and Arsenazo-III [2] were sensitive reagents for the determination of thorium. Wang [3] and his co-workers determined thorium in food samples spectrophotometrically. Kavalentis [4] et al, and sivaramaiah et al [5] used hydrazone reagent for the determination of thorium. Few other reagents are available for the spectrophotometric determination of thorium [6-11]. In the light of good analytical characteristics of hydrazones, the author has developed a method for the spectrophotometric determination of thorium(IV), using a organic reagent 2-aminoacetyl-3-hydroxy-2-naphthoic hydrzone.

2. Materials and methods

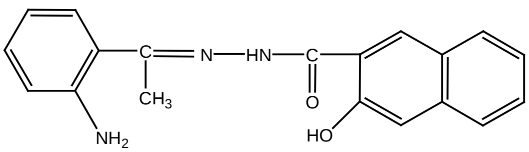
2.1 Instrumentation:

The absorbance and pH measurements were made on a Perkin Elmer UV Lamda 50 double beam spectrophotometer (UV-Visible) controlled by a computer fitted with 1cm path length quartz cells and an ELICO digital pH meter of (Model LI 613) respectively.

2.2 Reagents and Chemicals:

(a) Preparation of 2-aminoacetyl-3-hydroxy-2-naphthoic hydrazone (AHNH)

Equimolar solutions of 2-amino acetophenone in methanol and 3-hydroxy-2-naphthoic hydrazide in hot aqueous ethanol were refluxed for two h on water bath and cooled. The yellowish brown colored solid obtained. The structure of ligand as shown in **Fig.1**. It was then filtered, washed and dried. The product showed a melting point of 274-276^{0} C which was found to be different from those of the reactants indicating the formation of the new product.



2-aminoacetyl3-hydroxy-2-naphthoic hydrazone

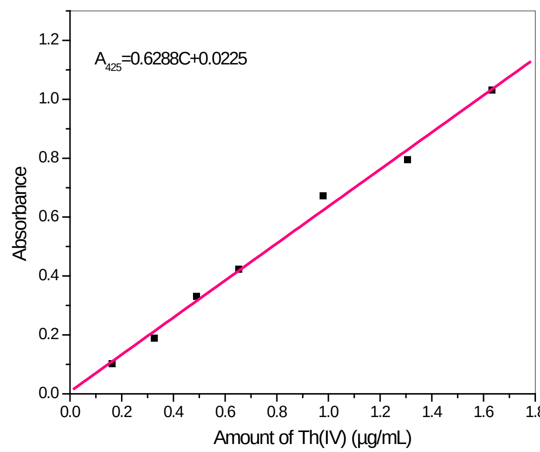
Fig.1. Structure of ligand

(b) Thorium (IV) solution:

1.10g of monazite sand was digested in 30ml of concentrated sulphuricacid, leached and filtered. The filtrate was collected in a 500ml standard flask and made up to the mark with distilled water. Thorium from the solution was separated by reverse phase extraction chromatography [12]. The separated thorium was dissolved and diluted to 100ml with distilled water. An aliquot of the dark orange coloured solution was taken and the thorium (IV) content of the solution was determined.

3. Results and Discussion

The absorption spectrum of Th (IV)-AHNH complex showed maximum absorbance at 425nm where the reagent showed negligible absorbance.



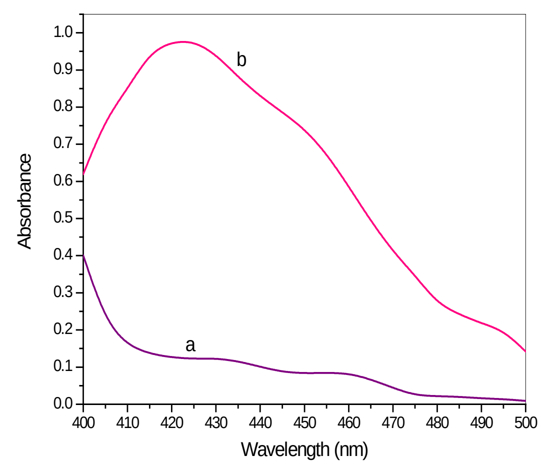


Fig.3. Absorbance Vs amount of Th (IV) (μg/mL)
[AHNH]= 2.5×10^{-4} M
pH= 6.0; λ= 425 nm

Fig.2. Absorption spectra of
a) AHNH Vs buffer blank
b) [Th (IV)] – AHNH Vs reagent blank
[Th (IV)] = 2.5×10^{-4} M: [AHNH] = 2.5×10^{-3} M
pH = 6.0

The typical spectra are presented in **Fig 2**.The absorbance was found to be maximum and constant in the pH range 4.0 -7.0. Therefore, the analytical studies were carried out at pH 6.0. A 10 fold molar excess reagent was found to be necessary to obtained maximum colour intensity for a given amount of metal ion.

Composition and stability of the complex:

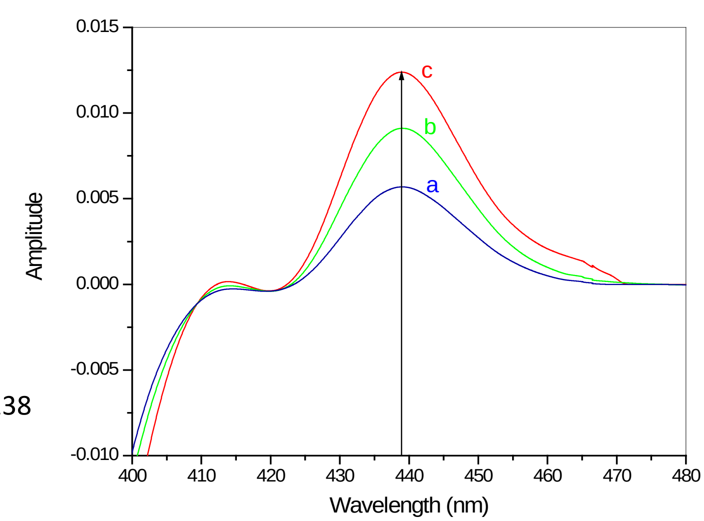
The composition of the complex was determined using Job's continuous variation method. The results indicate a 1:2 stoichiometry between the metal ion and the reagent. The stability constant of the complex was determined as $3.632x10^3$.

Validity of Beer's law:

The results are presented in the form of a plot of absorbance vs amount of Th (IV) and shown in **Fig.3**. The straight line plot obtained obeys the equationA_{425}=0.6288C+0.0225. The linear plot between the absorbance and the amount of Th (IV) indicates that Beer's law is obeyed in the range of 0.581-5.813 μ g/mL of Th (IV). The molar absorptivity and Sandell's sensitivity are $2.78 \pm 0.002 \times 10^3$ 1 mol^{-1} cm^{-1} and 0.0083 µg/mL. The correlation coefficient (γ) of the calibration equation of the experimental data is 0.9998.

Effect of foreign ions:

The effect of various anions and cations normally associated with Th (IV) on the absorbance of the experimental solution was studied. The tolerance limits of the tested foreign ions which bring about a change in the absorbance by +2% were calculated and presented in table 3. Almost all the tested anions possess high tolerance levels (>100 fold). The data in table 3 indicate that many metal ions and anions do not interfere in the determination of Th (IV). 10 fold excess of each of Mo(VI), Ti(IV), Zr(IV), Cu(II) and 25 fold excess of Fe(III) are masked by ascorbate. It was noticed that all the ions which did not interfere in the zero order determination of thorium (IV) also did not



interfere in the first order derivative method.

Derivative method:

The derivative spectra recorded **(Fig.4)** in the wavelength region 400-500nm for the experimental solutions showed and proportional variable absorbance at 439nm for first order derivative. The analytical results of both direct and derivative methods were summarized and are presented in Table 1. The tolerance limits of first derivative method are presented in Table 3.

Fig. 4. First derivative spectra of Th (IV)-AHNH Vs reagent blank
Th (IV) =a) 2.612 µg/mL; b) 3.918 µg/mL; c) 5.224 µg/mL; pH = 6.0

Table 1: Analytical Characteristics of Th (IV)-AHNH

S. No	**Parameter**	**Zero method**	**Derivative method**
1	Analytical Wavelength (nm)	425nm	439nm
2	Molar absorptivity (L mol^{-1} cm^{-1})	$2.78x10^3$	-
3	Beer's law range (µg mL^{-1})	0.581-5.813	-
4	Sandell's sensitivity (µg cm^{-2})	0.0083	-
5	Y-intercept	0.00752	-0.00178
6	Co-relation coefficient	0.9998	0.999
7	Stability constant	$3.632x10^3$	-
8	Composition (metal: ligand)	1:2	-

4. Applications

Zero and first order derivative method was applied for the determination of thorium(IV) in monazite sand [13].

Determination of Thorium(IV) in Monazite sand

The sample solution was prepared according to the recommended procedure and the results are presented in **Table 2**.

Table 2: Determination of Thorium(IV) in Monazite sand

Amount of Thorium (IV)	**Zero method (µgmL)**	**Error (%)**	**First order derivative method (µg mL)**	**Error (%)**
0.5	0.356	5.64	0.628	4.90
1.0	0.902	19.32	1.452	18.5
1.5	1.398	5.02	1.847	0.259

Table 3. Tolerance limits of foreign ions
Amount of Th (IV) = 3.265 µg/mL, pH=6.0

Ion	Tolerance limit µg/mL	Ion	Tolerancelimit µg/mL
Ascorbae	2632	Mg (II)	1494
Tartarate	2264	Ca (II)	1396
Fluoride	2010	Sr (II)	1292
Chloride	1818	Na (I)	1266
Oxalate	1286	Ba (II)	1195
Bromide	1224	K (I)	418
thiosulphate	1122	W (VI)	58
phosphate	1024	Ir (III)	36
Iodide	986	Mo(VI)	34
Sulphate	884	Zr (IV)	28
Citrate	840	Ni (II)	29
Nitrate	724	Bi (III)	24
Thiocyanate	586	Ce (IV)	22
Carbonate	50	Ti (IV)	20
EDTA	44	Ag (I)	10
		Al(III)	8
		Hg (II)	6
		U (VI)	6
		Co (II)	6
		Cu(II)	4
		Fe(III)*	Interferes

*Masked with ascorbate.

The data presented in the **Table 3**. Shows that a large number of commonly associated cations and anions do not interfere in the determination of thorium (IV). Many metal ions which involve in the zero order will not interfere in their derivative studies.

5. Conclusions

The colour reaction between thorium (IV) and AHNH, thorium (IV) forms dark orange coloured water soluble complex at pH 6.0. The complex shows absorption maximum at 425 nm in direct spectra and first order derivative shows absorption maximum at 439 nm. Various parameters such as effect of pH, reagent concentration and interference of associated foreign ions on the colour formation of thorium (IV) – AHNH complex are studied. Beer's law is obeyed in the range of 0.581-5.813 μg/mL. The composition of the complex is determined by Job's method and molar ratio method. The mole ratio plot confirms the composition as 1:2 [Th(IV):AHNH]. The method is applied for the determination of thorium (IV) from monazite sand.

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