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RESEARCH ARTICLE

M.Swetha et al, The *Experiment, 2014, Vol. 19(2), 1330-1335*

SENSITIVE SPECTROPHOTOMETRIC DETERMINATON OF THORIUM(IV) USING 5-BROMO SALICYLALDEHYDE ISONICOTINOYL HYDRAZONE(5-BRSAINH).

ABSTRACT

Simple and sensitive direct and derivative spectrophotometric method for the determination of thorium(IV) is reported.The method is based on the formation of yellowish green coloured complex of a stoichometric ratio 1:1 between thorium and 5-bromo salicylaldehyde isonicotinoyl hydrazone(5-BrSAINH) at p^H 5.0. The maximum absorbance of [Th(IV)-5-BrSAINH] complex was measured at 385nm.Under the optical conditions , Beer's law is obeyed over the range 1.16-15.08µg mL^{-1}. The molar absorptivity and sandell's sensitivity are calculated as 1.3342 X 10^4 L mol^{-1} cm^{-1} and 5.8 X 10^{-3} respectively. The proposed method has been succesfully applied for the determination of trace level of thorium in monazite sand.

1. INTRODUCTION

Thorium is a naturally occuring 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 lead 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 anaytical methods.

A survey of literature revelas that only few reagents are available for the spectrophotometric determinationof thorium. Among all the anvailable reagents Thoron-I[1] and Arsenazo-III[3] 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 used hydrazone reagent for the determnation of thorium. Few other reagents are available for the spectrophotometric determination of thorium[5-10]. 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 5-bromo salicylaldehyde isonicotinoyl hydrazone.

2. Materials and Methods

The chromogenic reagent , 5-bromo salicylaldehyde isonicotinoyl hydrazone was prepared in the laboratory by condensing 5-bromo salicyalaldehyde and isonicotinic acid hydrazide in sufficient volume of methanol. 1x10^{-2}M solution of the reagent was prepared by dissolving 0.320gms and making up to the volume in 100ml diethylformamide(DMF). Working solutions were prepared by diluting the stock solution with DMF. 0.01M thorium(IV) solution was prepared by dissolving appropriate amounts of $Th(NO_3).6H_2O$(AR BDH) in 100ml doubly distilled water.The stock solutions were diluted appropriately as required.Other metal ion solutions were prepared from their nitrates or chlorides. Buffer solutions of p^H 1-10 were prepared using appropriate mixtures of CH_3COONa and HCl, CH_3COOH and CH_3COONa, NH_4OH and NH_4Cl. The absorbance and pH measurements were made on a Perkin Elmer (LAMDA 25) UV-Visible spectrophotometer (Model UV-160A) controlled by a computer fitted with 1cm path length quartz cells and an ELICO digital p^H meter of (Model LI 613), respectively.

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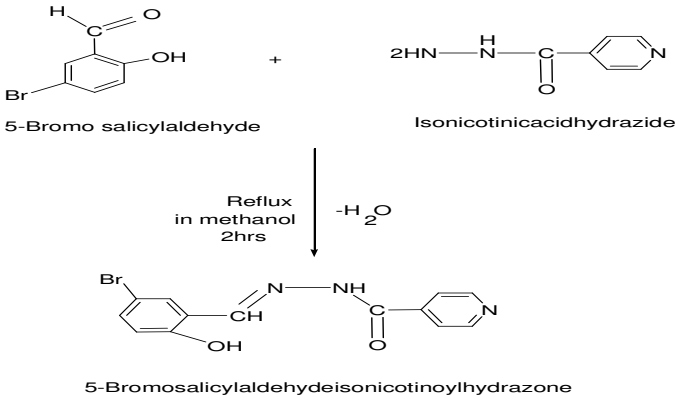

Preparation of sample soluiton

1.10g of monazite sand was digested in 30ml of concentrated sulphuric acid, 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 separatd by reverse phase extraction chromatography[11]. The separated thorium was dssolved and diluted to 100ml with distilled water. An aliquot of the solution was taken and the thorium (IV) content of the solution was determined.

Procedure

To 4ml of buffer solution (p^H 5.0) 0.5ml of 5-BrSAINH($1x10^{-2}$M) taken in each of a set of 10ml volumetric flasks, variable amounts of Th(IV) were added and diluted to the volume with distilled water. The absorbance of these solutions were measured at 385nm against reagent blank and plotted against the reagent blank. A straight line with regression equation A_{385}=0.2843C+0.0014 was obtained in a specific concentration of Th(IV).The composition of the [Th(IV)-5-BrSAINH] complex was found to be 1 : 1. For the derivative spectrophotometric determination of thorium, first derivative spectrum were recorded in the wavelength region 375-550nm with a scan speed of 2400nm per minute with 9 degrees of freedom. For the experimental solutions containing different amounts of the metal ion under optical conditions , the derivative amplitudes were measued at the suitable wavelengths and plotted against the amount of thorium to evaluate the determination ranges in first order derivative method.

3. Results and Discussion

The absorption spectrum of Th(IV)-5-BrSAINH complex showed maximum absorbance at 385nm where the reagent showed negligible absorbance. The typical spectra are presented in Fig 1.The absorbance was found to be maximum and constant in the p^H range 4.5-5.5. Therefore the analytical studies were carried out at p^H 5.0. A 10 fold molar excess reagent was found to be necessary to obtained maximum colour intensity for a given amount of metal ion. The derivative spectra recorded (Fig 2) in the wavelength region 375-550nm for the experimental solutions showed and proportional variable absorbance at 450m for first order derivative. The analytical results obtained in direct and first derivative methods are tabulated in Table 2 and the tolerance limits of first derivative method are presented in Table 3

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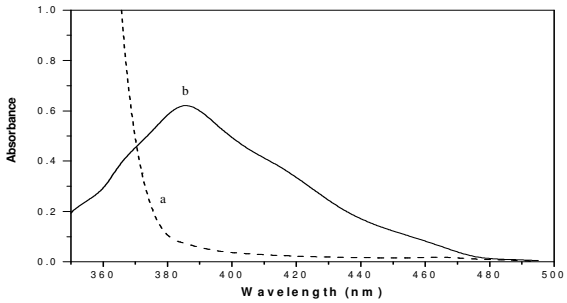

Fig. 1. Absorption spectra of
(a) 5-BrSAINH Vs Buffer blank
(b) [Th)IV) - %-BrSAINH] Vs Reagent blank
[Th(Iv)] = 5 x 10^{-5} M ; [HMBATSC] = 1 x 10^{-3} M pH =

Diverse ion	Tolerance limit (µg mL^{-1})	Diverse ion	Tolerance limit(µg mL^{-1})
Ascorbic acid	1460	Te(IV)	660
Citrate	1210	W (VI)	600
Tartrate	1015	Zr (IV)	580
EDTA	922	Ti (IV)	510
Thiourea	850	K (I)	500
Bromide	800	Na (I)	420
Urea	780	Cd (II)	350
Hypo	775	Li (I)	320
Sulphate	680	Mg(II)	300
Iodide	630	Al (III)	270
Nitrate	610	Ni (II)	210
Acetate	600	Co (II)	200
Thiosulphate	550	Cu(II)	200
Phosphate	460	Pb (II)	190

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Fluoride	440	Mn(II)	180
Formate	410	Ce (IV)	150
Chloride	400	Pd (II)	60
Oxalate	320	U (VI)	60
		Ru(III)	50
		Hg(II)	40
		V(V)	35

Table 1 : Tolerance limits of Diverse ions
Amount of Th(IV) = 1.16µg ml $^{-1}$

The analytical results of both direct and derivative methods were summarized and presented in Table 2 and the tolerance limits of derivative method are presented in Table 3.

S.No	Parameter	Zero method	Derivative method
1.	Analytical Wavelength (nm)	385	450
2.	Molar absorptivity (L mol^{-1} cm^{-1})	1.3342	-
3.	Beer's law range(µg mL^{-1})	1.16-15.08	1.16-19.72
4.	Sandell's sensitivity(µg cm^{-2})	5.8x10^{-3}	-
5.	Angular coefficient (m)	0.2843	0.2378
6.	Y-intercept	0.0014	0.0034
7.	Co-relation coefficient	0.9998	0.9999
8.	Standard deviation	± 0.0068	± 0.0056
9.	Stability constant	9.25 X 10^{6}	
10.	Detection limit	0.0007	0.00235
11.	Determination limit	0.00315	0.0070

Table 2: Analytical Characteristics of Th (IV)-5-BrSAINH

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S.No	Foreign ion	Tolerance limit in folds	
		Zero order (385nm)	First derivative (450nm)
1.	Pd(II)	60	85
2.	U(VI)	60	75
3.	Ru(III)	50	60
4.	Hg(II)	40	60
5.	V(V)	35	55

Table 3 : Tolerance limits of foreign ions

It can be observed from Table 3 that the tolerance limits of metal ions which interfere in zero order method were greatly enhanced in the derivative method indicating the greater selectivity of derivative methods than the direct method.

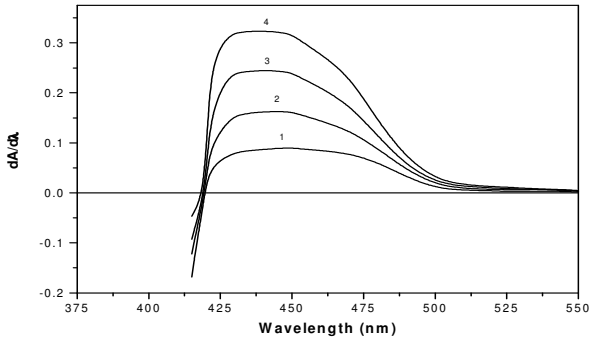

Fig.2: First Order derivative spectra of Th (IV)–5BrSAINH Vs Reagent blank
Th(IV) (µg mL^{-1}) = (1) 1.16; (2) 2.32 (3) 4.64 4) 6.96

Applications

The zero method was applied for the determination of thorium(IV) in monazite sand.

Determination of Thorium(IV) in Monazite sand

The sample solution was prepared according to the recommended procedure and the results are presented in Table 4.

Amount of Thorium(IV) added	Amount of Thorium(IV) added (µg mL^{-1})		Error(%)	
	Zero method	Derivative method	Zero method	Derivative method
1.0	0.958	0.962	4.38	3.95
1.5	1.213	1.224	23.6	22.5
2.0	2.102	1.982	4.85	0.908

Table 4 : Determination of Thorium(IV) in Monazite sand

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CONCLUSIONS

The intensity of the colored species will not be affected by slight variation of the experimental parameters such as concentration of the reagent.Rapid color development, simplicity and selectivity are the advantages of the proposed method The proposed method does not involve extraction, heating or any other stringent reaction conditions and offers the advantage of high color stability (48hrs). The proposed method can be used as an alternative method for the determination of trace amounts of thorium in monazite sand.

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