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Research Article

Direct Spectrophotometric Determination of Th (IV) in Monazite sand Using 5-Bromo-2-hydroxy -3-methoxybenzaldehyde-4-hydroxy benzoichydrazone

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Abstract

5-Bromo-2-hydroxy-3-methoxy benzaldehyde-p-hydroxybenzoichydrazone and thorium(IV) react to give a yellow coloured soluble complex [Th(IV)-5-BHMBHBH] in acidic buffers. The absorbance is maximum in the pH range 1.5-2.5. The complex solution shows λ_{max} at 400 nm. The system obeys Beer's law in the range 1.16- 18.5 µg/ml. The linear plot obeys the equation A_{400} = 0.03783C + 0.0007 and correlation coefficient (γ) is 0.9999. The molar absorptivity and Sandell's sensitivity are 0.8766×10^{4} L mol^{-1} cm^{-1} and 0.00264 µg/cm^{2} respectively. The standard deviation for ten determinations of 9.28 µg/ml of Th(IV) is 0.00379. The effect of various foreign ions on the colour intensity is also studied. Job's method indicate that formula of the complex is 1:1 and its stability constant is 1.273×10^{6}. The method is a simple, sensitive, accurate and selective direct spectrophotometric procedure for the determination of thorium (IV). The present method is applied for the determination of thorium in monazite sand.

Keywords: Th(IV), Spectrophotometry, 5-Bromo-2-hydroxy-3-methoxybenzaldehyde-p-hydroxy benzoic hydrazone (5-BHMBHBH), monazite sand.

INTRODUCTION

Berzelius discovered thorium in 1828 and named as Thor, the Scandinavian god of war. Thorium occurs in +4 oxidation state. Thorium is a naturally occurring radioactive element of extraordinary long life time. Thorium is a worthwhile potential raw material for fissile nuclear fuel production. Most rocks and soils contain thorium in trace quantities. Of various minerals in which thorium occur, thorium phosphate, monazite sand contains about 12% of thorium oxide. In minerals thorium and other rare earths exist together as well as in waste water. Thorium finds several applications in the manufacture of lantern mantles, light lamps, welding electrodes and ceramics. Humans when exposed to thorium have increased risk liver diseases. The analytical chemistry of thorium is complicated because of its similar behavior as that of other rare earths. Hence, determination of thorium in different matrices requires methods with high accuracy and high detection limits spectrophotomeric methods for the determination of metal ions in microgram level continues to be interesting over other analytical methods.

Many instrumental techniques such as mass spectrometry with inductively coupled plasma[1,2], electrochemical methods[3-6], atomic emission spectrometry with inductively coupled plasma[7,8], atomic absorption spectrometry[9], chromatography[10-13] and others for employed for the determination of thorium. But these techniques are costly and need expertise for their operation. In view of the low cost and easy handling spectrophotometric methods for determination of thorium in the analysis of the environmental samples[14-21] have been developed.

A survey of literature reveals that only few reagents are available for the spectrophotometric determination of thorium. Among all the available reagents Thoron-I[22] and Arsenazo-III[23] are sensitive reagents for the determination of thorium. Meng S[24] and co-workers determined thorium in food samples spectrophotometrically. Kavalentis[25] used hydrazones for the determination of thorium.

The potentialities of hydrazones have been reviewed by Singh et al[26]of In view of the potentialities of hydrazones as analytical spectrophotometric reagents and as no parahydroxybenzoichydrazone are used for the spectrophotometric determination of Th(IV), the author has developed a new spectrophotometric method for determination of thorium (IV), using 5-bromo -2-hydroxy-3-methoxybenzaldehyde-4-hydroxybenzoichydrazone.

MATERIALS AND METHODS

The chromogenic reagent, 5 - bromo - 2 - hydroxy-3 - methoxy benzaldehyde - p – hydroxyl benzoic hydrazone was synthesized in the laboratory by condensing 5 - Bromo- 2 - hydroxyl - 3 – methoxy benzaldehyde and p – hydroxyl benzoic hydrazide. A 0.01M DMF solution of the reagent is used in the studies.

A 1.0 x 10^{-2}M solution Th(IV) is prepared by dissolving in appropriate amounts of $ThNO_3$ $6H_2O$(AR BDH) in double distilled water , made up to the mark with distilled water in a 100 ml standard flask and standardized gravimetrically[27] . Working solutions are prepared by diluting the stock solution.

Buffer solution of pH 2.0 was prepared by mixing 1.0M sodium acetate and 1.0M HCl solutions in suitable proportion and the pH was adjusted by a pH meter.

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 pH meter of (Model LI 613) respectively.

Procedure:

To each a set of 10 ml volumetric flasks, 5 ml of buffer solution (pH 2.0), 0.5 ml of 5-BHMBHBH (1 x 10^{-2}M) in DMF,1.5 ml of DMF and varying amounts of Th(IV) were added and diluted to 10 ml in distilled water. The absorbance of these solutions was measured at 400 nm. A straight line is obtained which corresponded to the equation A_{400} = 0.03783C + 0.0007. (C is the amount of thorium in µg/ml) .

RESULTS AND DISCUSSIONS

The reagent 5-bromo-2-hydroxy-3-methoxy benzaldehyde-4-hydroxy benzoichydrazone (5-BHMBHBH) was used for the spectrophotometric determination of thorium (IV). Thorium (IV) reacts with 5-BHMBHBH to form yellow coloured complex in the pH range 1.5-2.5. The absorption spectra of 5-BHMBHBH and its Th (IV) complex under the optimum conditions shown in Figure1. The Th (IV)-5-BHMBHBH complex shows maximum absorbance at 400 nm, where the reagent has negligible absorbance . The colour formation is instantaneous. It is stable for 60 hours. The analytical measurements were made at pH 2.0. A five fold molar excess of the reagent is sufficient to produce maximum absorbance. The formula of the complex was ascertained from jobs and molar ratio methods as 1:1. The stability constant of the complex is 1.273× 10^6. The analytical characteristics of the complex are given in table-1.

Effect of foreign ions:

The effect of foreign anions and cations on the determination of Th(IV) under optimal conditions were studied and the data are presented in table-2. The data indicate that many metal ions and anions do not interfere in the determination of Th(IV). 10 fold excess of Cu (II) is masked by the hypo solution and 10 fold excess of Fe (III) and Al(III) are masked by fluoride.

Applications

The proposed method is applied for the determination of Th(IV) in monazite sand. The monazite sand was brought into solution by the following procedure.

a) Preparation of monazite sample solution

1.0 g of monazite sand is treated with 30 ml of conc. H_2SO_4, leached and filtered. The filtrate is diluted to 500 ml with distilled water. Th (IV) form the solution is separated by reverse phase extraction chromatography[25]. The separated thorium is dissolved in distilled water and diluted to 100 ml in a volumetric flask. The amount of thorium present in the solution is determined by adopting the general procedure.

CONCLUSION

The proposed method is simple, accurate, sensitive and selective do not involve extraction or heating and also do not use surfactants. The method can be easily applied for the determination of Th(IV) in monazite sample. The results compare well with standard method.

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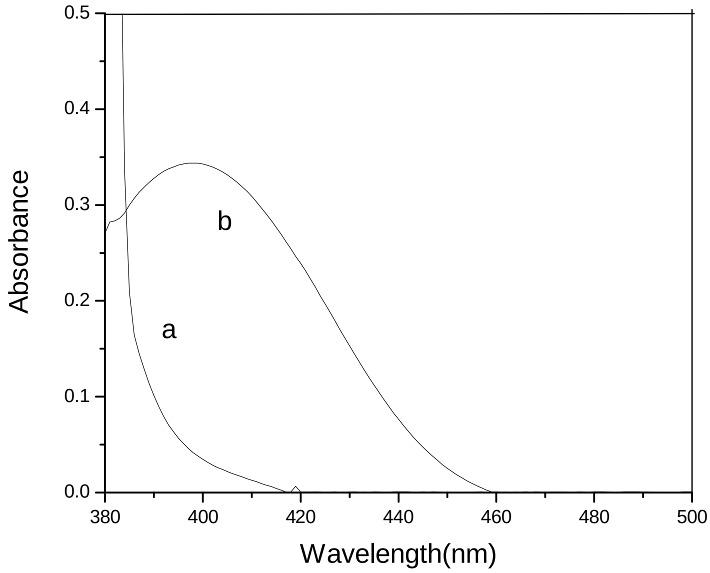

Fig.1
Absorption spectra of
a) 5-BHMBHBH Vs buffer blank
b) [Th (IV)] – 5-BHMBHBH Vs reagent blank
[Th (IV)] = 4.0× 10^{-5} M: [5-BHMBHBH] = 1.0 ×10^{-3} M
pH = 2.0

Table 1.
Analytical characteristics of [Th(IV) – 5-BHMBHBH]

Parameter	Direct method (400 nm)
Beer's law range (μg/m l^{-1})	1.16- 18.5 μg /ml
Molar absorptivity (L mol^{-1}cm^{-1})	0.8766×10^4 L mol^{-1}cm^{-1}
Sandell's sensitivity (μg/c m^2)	0.00264 μg/c m^2
Correlation coefficient (γ)	0.9999
Standard deviation	0.00379
Y- intercept(b)	0.0007
Detection limit(μg/m l^{-1})	0.3006
Composition (Metal :Ligand)	1:1
Stability constant(ß)	1.273×10^6

Table -2
Tolerance limit of foreign ions.
Amount of Th (IV) = 9.28 µg/ml pH = 2.0

Ion	Tolerance Limit (µg/ml)	Ion	Tolerance Limit (µg/ml)
Nitrate	3410	W (VI)	201
Thiourea	2230	Mo (VI)	Interferes
Iodide	1400	Mg (II)	80
Chloride	1171	Ba (II)	60
Bromate	704	Fe (III)	91*
Fluoride	302	Cu (II)	20**
Thiosulphate	275	Ce (IV)	150
Oxalate	154	Mn (II)	12
Tartarate	82	Pb (II)	90
Thiocyanate	66	Cd (II)	70
Phosphate	22	Hf (IV)	27
Ascorbic acid	450	Zn (II)	55
Citrate	480	Nb (IV)	63
EDTA	Interferes	Hg (II)	45
Ni (II)	17	U (VI)	20
Al (III)*	90	La (III)	90
V (V)	54	Co (II)	18

* masked with phosphate;
**masked with thiosulphate,

Table -3
Determination of thorium in monazite sand

Sample	Amount of Thorium(µg mL^{-1}) found*		Error (%)
	Present method	Arsenazo (III) method	
Monazite sand	1.258	1.240	-1.45
	1.817	1.830	0.71
	2.029	2.015	-0.69
	2.195	2.212	0.76

*Average of seven determinations

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