



Determination of Thorium (IV) by Simple Spectrophotometric Technique

Aparna Bhardwaj

Assistant professor, Department of Chemistry, Mithibai College, Vile Parle (W), Mumbai, **INDIA**

Email: dr.aparna73@rediffmail.com

Accepted on 1st August 2017, Published online on 27th September 2017

ABSTRACT

A simple and sensitive spectrophotometric method has been developed for the determination of Thorium (IV) using Bromophenol Blue dye as a reagent. Thorium (IV) forms an Orange Yellow coloured water soluble complex with the reagent in acidic medium at pH 3.0. The molar absorptivity and Sandell's sensitivity of coloured species are $1.6 \times 10^5 \text{ dm}^3 \cdot \text{mol}^{-1} \text{ cm}^{-1}$ and $0.00625 \mu\text{g cm}^3^{-1}$ respectively. Beer's law is obeyed in the range $0.232\text{-}2.32 \mu\text{g mL}^{-1}$ of thorium (IV) at λ_{max} 455 nm. Thorium (IV) forms 1:4 complexes and the effect of interferences was studied. The merits and demerits of several other spectrophotometric methods for Thorium (IV) are also discussed.

Keywords: Spectrophotometric technique, Thorium (IV), Bromophenol blue.

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.

The mentioned element can be determined by many instrumental techniques based on different principles including mass spectrometry with inductively coupled plasma [10, 11], electrochemical methods [12- 15],

atomic emission spectrometry with inductively coupled plasma [16, 17], atomic absorption spectrometry [18], chromatography [19-24] and others. A necessary part of most analytical determinations of elements in real matrices is separation and preconcentration. To achieve this goal a number of effective procedures have been developed, for example [25-35]. Concerning spectrophotometric determination of Th a specific group of methods has been studied. To the most promising ones belong the disodium Arsenazo III method [21] which has been successfully applied for determination of thorium at $\mu\text{g g}^{-1}$ level in Ore samples with a precision of $\pm 0.04\%$, the Eriochrome Cyanine R method [36] proposed for determination of Th(IV), La(III) and Y(III) in natural water samples and in some ore samples; the 2,4-dihydroxybenzaldehyde isonicotinoylhydrazone method [37]. To the less frequently cited reagents proposed for spectrophotometric determination of thorium belong 2-(2,5-disulfonic-4-methoxyphenylazo)-7-(2-hydroxyl-5-carboxyl phenylazo)-1,8-dihydroxynaphthalene-3,6 disulfonic acid [38], DCB-Arsenazo [39] and Arsenazo III [40], however none of them became a generally accepted one.

The present paper deals with a sensitive and selective method for the Spectrophotometric determination of thorium (IV) at trace levels using Bromophenolblue as analytical reagent.

MATERIALS AND METHODS

An UV- visible spectrophotometer (ELICO, Model SL-159) with quartz cells of 1.0 cm path length was used for absorbance measurement. An ELICO digital pH (Model LI-120) with combined glass calomel electrode was used for pH measurements. All chemicals used were of AR grade (Merck). A stock solution of thallium nitrate, $[\text{Th}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}]$ of 1.0×10^{-2} M was prepared by dissolving the requisite amount of thorium (IV) in distilled water. The standard stock solution of Bromophenol Blue of 1.0×10^{-2} M concentration was prepared in aqueous alcohol (40% v/v). The standard stock solutions of various salts (as source of diverse ions), each of 1.0×10^{-2} M, were prepared in doubly distilled water.

Recommended Procedure: An aliquot of solution containing $2.3203 \mu\text{g mL}^{-1}$ thorium (IV) was taken in a 10 mL measuring flask, and 4 mL of 1.0×10^{-5} M of the reagent was added to it. The contents were diluted to the mark with aqueous alcohol (40% v/v), keeping the pH constant, the absorption spectrum of the resultant Orange yellow coloured thorium (IV)- Bromophenolblue complex was recorded against blank from which the value of λ_{max} was obtained. The optimum experimental conditions in regard to (1); the concentration of the reagent (Bromophenol Blue); (2) the concentration of the Thorium(IV); (3) the pH of the medium; and (4) ascertaining the λ_{max} of the Thorium (IV) Bromophenol Blue complex were established.

RESULTS AND DISCUSSION

The absorption spectrum of the Thorium (IV)- Bromophenol Blue complex in aqueous alcohol was studied over the wave length range 340-550 nm. The Orange yellow coloured complex exhibited absorption maximum at 455 nm, (Fig.1) where reagents shows negligible absorption at this wavelength. The effect of the quantity of the reagent on the intensity of colour was also studied. It was found that minimum 4 - fold excess of the reagent was required for full colour development. The colour develops instantaneously on mixing the two solutions and remains stable for 24 h. The optimum pH for the formation of this complex is 4.0.

The system adheres to Beer's law in the range $1.0 \times 10^{-6} - 1.0 \times 10^{-5}$ M of the thorium (IV) with optimum range of $0.23203 - 2.3203 \mu\text{g mL}^{-1}$ of the metal (Fig.2). The molar absorptivity calculated over the range studied was $1.6 \times 10^5 \text{ dm}^3 \cdot \text{mol}^{-1} \text{ cm}^{-1}$, while Sandell's sensitivity was $0.00625 \mu\text{g cm}^3^{-1}$. The standard deviation and coefficient of variance as determined of a series of measurements made according to the optimum conditions were 0.00092 and 0.57 respectively. This speaks the volume for the precision for the present spectrophotometric method for the determination of thorium (IV) using Bromophenolblue as the analytical reagents. It is worthwhile to mention here that this method has an edge over some recent

spectrophotometric methods for the determination of thorium (IV) using other reagents. Further, the mole ratio method gives the composition of this thorium (IV)- Bromophenol Blue complex as 1:4. The effect of diverse ions on the spectrophotometric determination of thorium (IV), using Bromophenol Blue as the reagent has been studied in the terms of tolerance limit which was set as the amount ($\mu\text{g mL}^{-1}$) of the diverse ions causing an error of $\pm 1\%$ (refer to Table 1). It has been concluded that the following cations and anions do not interfere in the spectrophotometric determination of the thorium (IV).

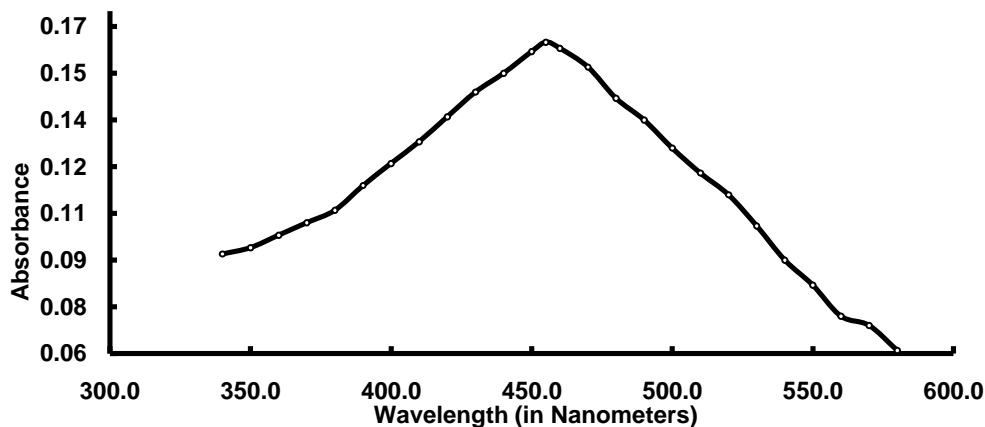


Figure 1: Absorption Spectrum of Thorium (IV)-Bromophenol Blue Complex system in aqueous alcoholic medium (40%, v/v)

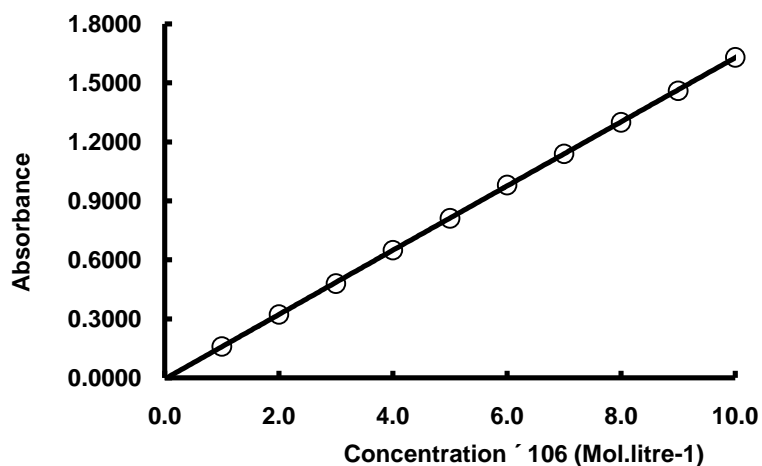


Figure 2. Plot of Absorbance vs Molar Concentration of Thorium (IV) in Thorium (IV)-Bromophenol Blue Complex System at $\lambda_{\text{max}} = 455 \text{ nm}$

Table 1: Effect of diverse ions on the spectrophotometric determination of Thorium (IV) using Bromophenol Blue as the reagent. Thorium (IV) = $1.16015 \mu\text{g mL}^{-1}$

S. No.	Diverse ions	Added as	Amount of adverse ion added ($\mu\text{g mL}^{-1}$)	Th (IV) found ($\mu\text{g mL}^{-1}$)	Relative error (%)
1	NO_2^-	NaNO_2	114.96	1.1098	4.34
2	NO_3^-	NaNO_3	309.26	1.1569	0.28
3	CH_3COO^-	CH_3COONa	144.00	1.1513	0.76
4	Cl^-	KCl	178.00	1.1615	-0.11
5	Br^-	KBr	192.26	1.1399	1.74
6	I^-	KI	313.50	1.1657	-0.47

7	CO ₃ ²⁻	CaCO ₃	299.67	1.1632	-0.25
8	SO ₄ ²⁻	K ₂ SO ₄	238.08	1.1571	0.26
9	PO ₄ ³⁻	Na ₂ HPO ₄ .12H ₂ O	234.22	0.992	14.4
10	NH ₄ ⁺	NH ₄ NO ₃	899.00	1.1553	0.42
11	Na ⁺	NaNO ₃	115.34	1.1569	0.28
12	Pb ²⁺	Pb(NO ₃) ₂	259.00	1.1555	0.40
13	Hg ²⁺	HgCl ₂	495.00	1.1617	-0.31
14	Cu ²⁺	Cu(NO ₃) ₂ .3H ₂ O	157.48	1.1571	0.26
15	Cd ²⁺	Cd(NO ₃) ₂	280.33	1.1555	0.40
16	Al ³⁺	Al ₂ (SO ₄) ₃ .16H ₂ O	385.20	1.1552	0.42
17	Fe ³⁺	FeCl ₃	155.00	1.1615	-0.11
18	Cr ³⁺	CrCl ₃ .6H ₂ O	259.05	1.1571	0.26
19	Zn ²⁺	Zn(NO ₃) ₂	490.10	1.1692	-0.77
20	Mn ²⁺	MnSO ₄ .H ₂ O	137.26	1.1386	1.86
21	Ni ²⁺	Ni(NO ₃) ₂ .6H ₂ O	293.30	1.1632	-0.25
22	Co ²⁺	Co(NO ₃) ₂ .6H ₂ O	144.80	1.6445	-0.37
23	Ba ²⁺	BaCl ₂ .2H ₂ O	343.00	1.1615	-0.11
24	Sr ²⁺	Sr(NO ₃) ₂	215.50	1.1634	-0.28
25	Ca ²⁺	Ca(NO ₃) ₂	291.84	1.1569	0.28
26	Mg ²⁺	Mg(NO ₃) ₂ .6H ₂ O	59.30	1.1532	0.60
27	K ⁺	KCl	965.00	1.1615	-0.11

CONCLUSIONS

The proposed method for the determination of thorium (IV) offers advantage of simplicity rapidity, sensitivity and reasonable selectivity over the other methods. The developed colour is stable for 24 h. The major advantage of the proposed method is that the maximum colour intensity is obtained instantaneously at room temperature without the need for heating and also a high tolerance limit for the interfering ions in thorium determination. Because no extraction step is required, the use of organic solvents, which are generally toxic pollutants, is avoided. The proposed method does not involve any stringent reaction conditions and can be favorably compared with other methods. The sensitivity in terms of the molar absorptivity and precision in terms of the standard deviation of the present method are very reliable for the determination of thorium(IV).

REFERENCES

- [1] Y.K. Agarwal, U. Dayal, *J. Radioanal. Nuclear chem.*, **1985**, 19(2), 323.
- [2] J. Korkisch, G.E. Janauer, *Microchimica Acta*, **1961**, 49(4), 537.
- [3] Y. Chen, Z. Li, Z. Zhu, J. Pan, *J. Analyst*, **1999**, 124(11), 1839.
- [4] M. Tarek, M. Zaki, A.Y. El-Syed, *Analytical let*, **1995**, 28(8), 1525.
- [5] J. Korkisch, G.E. Janauer, *Microchimica Acta*, **1961**, 49(6), 880.
- [6] S. Meng, M. Tian, Y. Liu, Y. Guo, Y. Fan, *J Anal. Chem*, **2007**, 62(10), 946.
- [7] G.S. Manku, *Microchimica Acta*. **1972**, 60(6), 811.
- [8] Neena Nashine, MK. Deb, R.K. Mishra, *Fresenius J. Anal.Chem*, **1996** 335(1), 34.
- [9] C.D. Sharma, M.C. Eshwar, *J.Radioanal. Nuclear. Chem*, **1985**, 91(2), 323.
- [10] Y. Zheng, B. Weinman, T. Croninc, M.Q. Fleisher, R.F. Anderson, *Appl. Geochem.*, **2003**, 18, p. 539-549.
- [11] P.Grinberg, S. Willie, R. Sturgeon, *Anal. Chem.*, **2005**, 77, 2432-2436.
- [12] S.Liu, J. Li, M. Xun, P. Gao, *Anal. Lett*, **2003**, 36, 1381-1392.
- [13] S.Chandra, H. Agarwal, Ch.K. Singh, *Anal. Sci.*, **2007**, 23, 469-473.
- [14] L.Ju-Nan, Y. Fe-Yun, J. Zhong-Min, F. Jun-Jie, *Microchim. Acta*, **2007** 143, 287-292.
- [15] S. S. M.Hassan, M. E. Elneem, M. A. Y. Attawiya, *Electroanalysis*, **2008**, 20, 2063-2069.
- [16] O. Fujino, S. Umetani, *Anal. Chim. Acta*, **2000**, 420, 65-71.
- [17] S. Thangavel, S. M. Dhavile, K.Dash, S.C. Chaurasia, *Atom. Spectrosc*, **2010**, 31, 92-96.
- [18] M. A. Castro, J. A. Aller, A. McCabe, W. E. Smith, D. Littlejohn, *J. Anal. At. Spectrom.*, **2007**, 22, 310-317.
- [19] W. A .AL-SWAHI, R. DAHL, *J. Chromatogr. A*, **1995**, 706, 175-181.
- [20] P. A. Jackson, J. Carnevale, H. Fuping, P. R. Haddad, *J. Chromatogr. A*, **1994**, 671, 181-191.
- [21] S. I. El-Dessouky, E. H. Borai, *J. Radioanal. Nucl. Chem.*, **2006**, 268, 247-254.
- [22] M. J. Shaw, P. R. Haddad, *Environ. Int.*, **2004**, 30, 403-431.
- [23] P.G. Jaison, N. M. Raut, S. K. Aqqarwal, *J. Chromatogr. A*, **2006**, 1122, 47-53.
- [24] J. B. Truscott, P. Jones, B. E. Fairman, H. E. Evans, *J. Chromatogr. A*, **2001**, 928, p. 91-98.
- [25] E. H. Borai, A. S. Mady, *Int. J. Radiat. Applic. Instrum., Part A*, **2002**, 57, 463-469.
- [26] V. K. Jain, S. S. Sait, P. Shrivastav, Y. Agarwal, *Sci. Technol.*, **1998**, 33, p. 1803-1818.
- [27] F. A. Aydin, M. Soylak, *Talanta*, **2007**, 72, 187-192.
- [28] S. R. Yousefi, S. J. Ahmadi, F. Shemirani, M. R. Jamali, M. Salvati-Nisari, *Talanta*, **2009**, 80, 212-217.
- [29] M. S. De Carvalho, M. L. F. Dedomingues, J. L. Mantovano, J. W. S. D. Dacunha, *J. Radioanal. Nucl. Chem.*, **2002**, 253, p. 253-256.
- [30] C. M., Rozmari, C, A. G. Ivsi, Z. Grahek, *Talanta*, **2009**, 80, 352-362.
- [31] N. S. Patkar, A. S. Burungale, R. J. Patil, *RJC*, **2009**, 2, 825-032.
- [32] V. G. Maiorov, A. I. Nikolaev, O. P. Adkina, G. B. Mazunina, *Radiochemistry*, **2006**, 48, 576 - 579.
- [33] R. Bose, D. S. R.Murthy, G.Chakrpani, *J. Radioanal. Nucl. Chem.*, **2005**, 265, 115-122.
- [34] B "Uy "Uktiryaki. S., Say, R., Ers "Oz, A., Birlik, E., Denizli, A. *Talanta*, **2005**, 67, 640-645.
- [35] Z. Talib, M. Eral, C .Hi` , "U "Osonmez, *J. Environ. Radioactiv*, **2009**, 100, 139-143.
- [36] A. M., Abdallah, M. A. Kabil, A. M. Akl, D. S. Ismael, *J. Iran. Chem. Soc.*, **2004**, 1, 79-87.
- [37] S Sivarmaiah, P. R. Reddy, V. K. Reddy, T. S. Reddy, *J. Radioanal. Nucl. Chem.*, **2000**, 245, 367-370.
- [38] S. Meng, M. Tian, Y. Liu, Y. Guo, Y. Fan, *J. Anal. Chem.*, **2007**, 62, 946-950.
- [39] A. T.Kandil, H. F. Faramawy, R. M, Amin, *Egypt. J. Chem.*, **2007**, 50, 709-714.
- [40] Q. Z. Zhai, X. X. Zhang, L. Chen, *Asian J. Chem.*, **2008**, 20, 5187-5191.

AUTHOR ADDRESS

1. Dr. Aparna Bhardwaj

Assistant Professor, Dept. of Chemistry,

Mithibai College, Vile Parle (W), Mumbai

E-mail; dr.aparna73@rediffmail.com, Mobile No. 9819975654