

Spectrophotometric Determination of Uranium Using Tris-[2,4,6-(2-hydroxy-4-sulpho-1-naphthylazo)]-s-triazine, Trisodium Salt (THT)

SONIA VERMA¹, SAPANA GARG² and PRATAP SINGH KADYAN^{2*}

¹A.I.J.H.M (PG) College, Rohtak-124001, India

²Department of Chemistry, M.D. University, Rohtak 124001, India
pskadyan@rediffmail.com

Received 11 March 2013 / Accepted 30 April 2013

Abstract: A sensitive and selective spectrophotometric method is proposed for the rapid determination of uranium using tris-[2,4,6-(2-hydroxy-4-sulpho-1-naphthylazo)]-s-triazine, trisodium salt (THT). An addition of dilute solution of uranyl ions to the aqueous solution of THT resulted to form a water soluble dark red colored complex absorbing maximum at 540 nm in the pH range 3.8-6.0. Beer's law is valid over concentration range 0.0-6.2 ppm with molar absorptivity and Sandell's sensitivity of 6.1×10^4 L mol⁻¹cm⁻¹ and 0.0039 µg cm⁻², respectively. The molar composition of the complex is 2:3 (M:L) as determined by Job's method of continuous variations. The tolerance limits for interfering ions have been investigated. All variables have been studied in order to optimize the reaction conditions. The efficiency of the proposed method is shown by the successful determination of traces of uranium in some synthetically made samples of ores.

Keywords: Spectrophotometry, Uranium, THT, Triazine

Introduction

The geographical distribution of uranium is of interest because the element is used in the production of energy in nuclear reactors. It is of interest to geochemists because it belongs to the rare earth elements and its geochemical pathways have not been studied as rigorously as those of the transition metals (*e.g.* copper, lead, zinc, cadmium *etc.*). The stable oxidation state is uranium(VI) in oxygenated water and its predominant form in the uranyl ion, which is complexed by carbonate in carbonate-bearing water¹. Uranium(VI) occurs in sea water as anionic carbonate complexes and has a very long residence time of $2-4 \times 10^6$ years². Considerable interest has developed in the determination of trace uranium in environmental sites as well as in nuclear industry facilities.

Numerous methods for the spectrophotometric determination of uranium based on the use of balmic acid, morin, sodium fluoride, pyrogallol red, pyrogalllic acid *etc.* have been reported³⁻¹⁰, but most of them require a solvent extraction step and entail various disadvantages in terms

of reproducibility, simplicity, rapidity and sensitivity. Heterocyclic azo compounds have attracted much attention as they are sensitive chromogenic reagents in addition to being important complexing agents. These dyes have been useful in the spectrophotometric determination due to its good selectivity and sensitivity over a wide range of pH and because they are relatively easy to synthesize and purify.

This paper reports, a water soluble tris-[2,4,6-(2-hydroxy-4-sulpho-1-naphthylazo)]-s-triazine, trisodium salt (THT) as an analytical reagent for the micro-determination of uranium(VI), whereas a very limited number of heterocyclic azo dyes find their uses for the determination of uranium(VI). Comparatively this reagent has been found as a sensitive reagent for uranium(VI).

Experimental

A Bausch and Lomb Spectronic 2000 spectrophotometer with 10 mm matched glass cells was used for recording spectra and a Beckman pH meter was used for pH measurements.

Reagents

Tris-[2,4,6-(2-hydroxy-4-sulpho-1-naphthylazo)]-s-triazine, Trisodium salt (THT) solution

THT as synthesized earlier¹¹, was used as a 1×10^{-3} M solution prepared by dissolving 0.9 g in 1 L of double distilled water. Solutions more than a week old were discarded.

Standard uranium(VI) solution

A stock solution of uranyl ion was prepared by dissolving appropriate amounts of uranyl nitrate (AnalaR) in double distilled water. The solution was standardized as uranyl oxinate¹².

Acetate buffer, pH 4.0

An acetate buffer solution¹² was prepared by mixing 800 mL of 0.2 N acetic acid and 200 mL of 0.2 N sodium acetate solution in a 1 L measuring flask. All other reagents were of analytical grade and doubly distilled water was used throughout.

General procedure

To a suitable volume of sample containing 15-105 μg of uranyl ions, add 2 mL of 1×10^{-3} M THT solution followed by 2.0 mL of acetate buffer solution (pH 4.0) and make up the volume to 25 mL with double distilled water. Measure the absorbance at 540 nm against a corresponding reagent blank prepared under identical conditions.

Results and Discussion

THT is a multi-dentate water-soluble heterocyclic azo dye (Figure 1) and is very sensitive towards uranium(VI) ions. It gives an intense dark red colour with uranium(VI) (in the form of uranyl ions) with maximum absorbance at 540 nm (Figure 2). The color development is maximum and constant at pH 3.8-6.0 (acetate buffer). Many base metals show very weak interactions or color reactions at this pH with THT. Moreover, EDTA and cyanide are tolerated in fair concentration and have been used to mask most of the interfering transition metals, if any, during the determination of uranium(VI). Rare earths, zirconium, molybdenum and tungsten do not interfere at all in the uranium(VI) determination, while manganese(II) interfere seriously. Phosphate quantitatively decomposes the thorium complex of THT but since fair amount of phosphate is tolerated (~30 fold) in the determination of uranium(VI) ions, thorium(VI) therefore has been masked up to 6- fold excess with respect to uranium (VI) using phosphate.

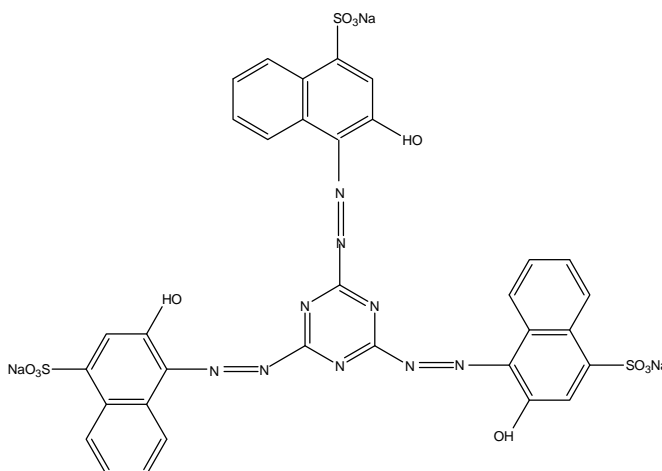


Figure 1. Chemical structure of tris-[2,4,6-(2-hydroxy-4-sulpho-1-naphthylazo)]-s-triazine, trisodium salt (THT)

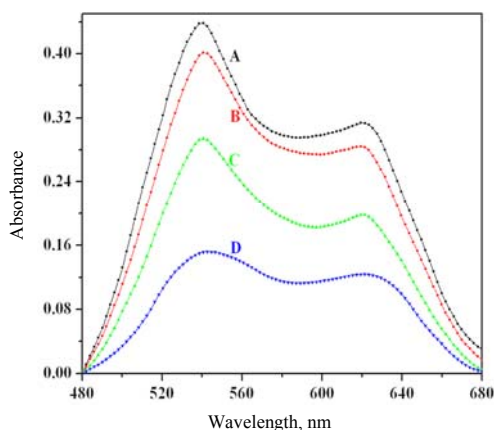


Figure 2. Absorption spectra of U(VI)-THT complexes at different pH with U(VI): 8×10^{-6} M and THT 4×10^{-5} M; curve A at pH, 3.8-6.0; B pH, 7.0; C pH 3.2; D pH 2.7

Physicochemical characteristics of the uranium(VI)-THT complex

Absorbance data recorded for a series of solution containing 2×10^{-4} M uranyl ion and varying amounts of reagents at pH 4.0, showed that a 2-fold molar excess of THT was required for full complexation. However, in further studies, at least 5-fold molar excess of THT was maintained.

The concentration range over which Beer's law was obeyed and the optimum concentration range for the accurate determination of metal ion were 0.0-6.2 ppm and 0.6-4.20 $\mu\text{g mL}^{-1}$ respectively. The composition of the complex was 2:3 (metal to ligand) as determined by Job's method of continuous variations. The complex was not extractable in non aqueous organic solvents, thereby showing the ionic character. Sandell's sensitivity of the colour reaction was 0.0039 $\mu\text{g cm}^{-2}$ of uranium (VI) with a molar absorptivity (ϵ) of 6.1×10^4 $\text{L mol}^{-1} \text{cm}^{-1}$. Table 1 gives a comparison of the sensitivities of some methods used for the determination of uranium(VI).

Table 1. Comparison of sensitivities of various spectrophotometric reagents for uranium(VI)

Reagent	λ_{\max} , nm	Molar absorptivity ($l\ mol^{-1}\ cm^{-1}$)	References
2-Hydroxy-3-methoxybenzaldehyde isonicotinoyl hydrazone	374	1.05×10^4	[13]
2-(2-Thiazolylazo)- <i>p</i> -cresol	588	1.31×10^4	[14]
Pyrocatechol violet	650	9.5×10^4	[15]
1,4-Dihydroxy-9,10- anthracenedione	600	1.19×10^4	[16]
<i>o</i> -Chlorophenyl fluorone	560	1.42×10^4	[17]
5-(<i>p</i> -Carboxyphenylazo)-8- hydroxyquinoline	470	4.39×10^4	[18]
5-(2- Carboxyphenylazo)-8-quinolinol	524	1.035×10^4	[19]
5,14- <i>N, N'</i> - Hydroxyphenyl – 4, 15-dioxo-1,5,14,18 –tetraaza hexacosane (NHDTAHA).	390	1.0×10^4	[20]
2-Hydroxy-1-naphthaldehyde isonicotinoyl hydrazone	430	9.6×10^3	[21]
Diacetyl monoxime isonicotinoyl hydrozone (DMIH)	364	1.63×10^4	[22]
Di-2-pyridyl ketone benzoyl hydrazone	377	2.02×10^4	[23]
1-(2-Quinolylazo)-2,4,5-Trihydroxybenzene	560	1.9×10^4	[24]
Tris-[2,4,6-(2-hydroxy-4-sulpho-1-naphthylazo)]- <i>s</i> -triazine, trisodium salt (THT).	540	6.1×10^4	This work

Effect of diverse ions

In the determination of uranium(VI) at the 1.9 $\mu\text{g/mL}$ level; chloride, bromide, iodide, nitrate, nitrite, sulphate, sulphite, thiosulphate, sulphide, thiocyanate, citrate, tartrate, borate, thiourea, thiosemicarbazide, alkaline earths, lanthanides, aluminium(III), chromium(III), vanadium(V), molybdenum(VI), tungsten(VI), zirconium(IV) and platinum metals did not interfere at all while manganese(II) interfered seriously.

Under the appropriate conditions found for uranium(VI), EDTA and cyanide are tolerated in fair concentration and have been used to mask most of interfering transition metals. Phosphate quantitatively decomposed the thorium complex of THT and hence ~30-fold excess of phosphate was used to mask 6-fold excess thorium(IV). Uranium(VI) can therefore be determined selectively in presence of many base metals as well as noble metals. Table 2 represents the tolerance limits in ppm of various ions in solution that caused a deviation smaller than $\pm 2\%$ in absorbance for the determination of uranium(VI).

Table 2. Tolerance limits of diverse ions in the determination of 1.9 $\mu\text{g/mL}$ of uranium(VI)

Foreign ions	Tolerance limits, ppm	Masking agents
F ⁻	550	-
CN ⁻	300	-
C ₂ O ₄ ²⁻	250	-
EDTA	500	-
PO ₄ ³⁻	60	-
AsO ₄ ³⁻	10	-
Zn(II)	60	Masked by EDTA
Cd(II)	50	Masked by EDTA

Contd...

Hg(II)	50	Masked by EDTA
Fe(II)	40	” ”
Co(II)	35	” ”
Ni(II)	35	” ”
Cu(II)	50	” ”
Ag(I)	40	Masked by I ⁻
Pb(II)	25	Masked by S ₂ O ₃ ²⁻
In(III)	50	Masked by EDTA or S ²⁻
Bi(III)	30	Masked by S ²⁻
Sb(III)	35	Masked by S ²⁻
Th(IV)	12	Masked PO ₄ ³⁻

Application for determining uranium(VI) in various synthetic ores

Synthetic mixtures of the ores were prepared by mixing the compounds in the same ratio equivalent to the composition of the corresponding ore and dissolving them in concentrated HCl. The mixtures were evaporated to dryness and dissolved in distilled water. The amount of U(VI) was determined following the recommended procedure given above. The results of the analysis obtained are given in Table 3.

Table 3. Estimation of uranium(VI) in synthetic samples of uranium ores

Ores	Amount of uranium taken, ppm or (% composition in ore)	Uranium (VI) found ppm	Mean value, ppm	Standard Deviation (σ)
Pitchblende	U(VI) 47, Pb(II) 3.0, As(II) 0.9, Ca(II) 0.5	46.5, 47.0, 47.0, 46.0, 46.0, 48.5	46.83	0.930
	U(VI) 48, Pb(II) 3.5, As(II) 1.2, Ca(II) 1.0	49.5, 48.0, 48.5, 47.5, 48.0, 48.5	48.33	0.638
Carnotite K ₂ (UO ₂) ₂ (VO ₄) ₂ · 1-3H ₂ O	U(VI) 52, K(I) 9.0, V(V) 12	51.0, 50.5, 52.0, 53.0, 51.5, 53.0	51.83	1.032
Autunite Ca(UO ₂) ₂ (PO ₄) ₂ · 10-12H ₂ O	Ca(II) 5.0, U(VI) 52.0	53.5, 53.0, 52.0, 51.5, 52.0, 50.0	52.00	1.224
Torbernite Cu(UO ₂) ₂ (PO ₄) ₂ · 10H ₂ O	U(VI) 48.0, Cu(II) 6.4	46.5, 47.5, 47.0, 47.0, 48.0, 47.0	47.16	0.516

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