

**SENSITIVE SPECTROPHOTOMETRIC DETERMINATION OF THORIUM (IV)
USING DIACETYL MONOXIME ISONICOTINOYL HYDRAZONE (DMIH)**

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ABSTRACT: Thorium (IV) forms a yellow Coloured water soluble complex with Diacetyl Monoxime Isonicotinoyl hydrazone (DMIH) reagent in acidic buffer of P^H 5.0 with λ_{\max} at 352 nm. The molar absorptivity and sandell's sensitivity are $2.265 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$ and $0.0022 \mu\text{g} / \text{cm}^2$ respectively. The Beer's law validity range 1.16–13.92 $\mu\text{g} / \text{mL}$. Thorium (IV) forms (M: L) 1:1 complex with DMIH and stability constant of the complex is 7.0265×10^6 . The derivative spectrophotometric determination of Th (IV)) was carried out by measuring peak height method. The developed derivative spectrophotometric method was employed for the determination of Thorium (IV) in synthetic samples of alloy. The effect of various diverse ions was also studied.

Key words: Diacetyl Monoxime Isonicotinoyl hydrazone (DMIH), Derivative Spectrophotometry, Thorium (IV)

INTRODUCTION

Thorium is a naturally occurring white metal. It is contaminated with the oxide and slowly tarnishes in air and become gray 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 common being the rare earth thorium-phosphate mineral, Monazite, which contains up to 12% of Thorium oxide. Thorium and rare earths are often co-exist in their mineral 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 used in lenses for cameras and scientific instruments. Thorium-232 decays very slowly (its half life period is about three times the age of earth) but other thorium isotopes occur in thorium and Uranium decay in chains. Most of these are short lived and hence much more radioactive than Thorium-232, although on mass basis, they are negligible. India is believed to have 25% of the world's Thorium reserves.

Thorium has been utilising as a nuclear fuel, since it is more abundant in earth crust than Uranium. Small amounts of Thorium can cause dermatitis while larger amounts result in lung, pancreas and 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 with Thorium. Only a very few organic reagents are available for the spectrophotometric determination of Thorium. Among all the reagents Thoron-I¹ and Arsenazo-III² were sensitive reagents for the determination of Thorium. Wang³ and his coworkers determined thorium in food samples spectrophotometrically. Kavalentis⁴ et al, and Sivaramaiah et al, used hydrazone reagents for the spectrophotometric determination of Thorium (IV).

Singh⁵ and others reviewed the potential application of hydrazone derivatives for the spectrophotometric determination of metal ions. Some hydrazone reagents⁶⁻⁸ were used for the spectrophotometric determination of metal ions. The oximes and hydrazones are the most important spectrophotometric reagents for the determination of metal ions. Complex formation reactions are of great use in determining metal ions at the micro level or even nano gram level. In this context organic reagents occupy a better place over inorganic reagents because of their complexing ability with metal ions giving highly coloured stable compounds. Among the large number of available organic reagents, the oximes and hydrazones became important spectrophotometric reagents for the determination of metal ions. In the light of good analytical characteristics of hydrazones, the author has developed a method for the spectrophotometric determination of Thorium (IV) using an organic reagent namely Diacetyl Monoxime Isonicotinoyl hydrazone (DMIH).

The author has reported the zero and first order derivative spectrophotometric determination of Thorium (IV) in aqueous medium in this paper. The review also reveals that a very few reagents⁹⁻¹⁷ were used as chromogenic reagents for the determination of Thorium (IV) which are given in the table (5) for the comparison purpose. The present paper describes a new, very simple, rapid and sensitive derivative spectrophotometric determination of Thorium (IV) in aqueous medium.

EXPERIMENTAL

Spectrophotometric measurements were made in an shimadzu 160 A microcomputer based UV – Visible spectrophotometer equipped with 1.0 cm quartz cells, an ELICO LI- 120 digital P^H meter was used for P^H adjustments. All reagents used were of AR grade unless otherwise stated. All solutions were prepared with distilled water. The standard stock solution 0.01 M was prepared by dissolving 0.5702 gram of Thorium Nitrate (Th(NO₃)₄ 5 H₂O) Loba Chemicals Ltd in doubly distilled water in a 100mL standard flask

The reagent Diacetyl Monoxime Isonicotinoyl Hydrazone (DMIH) was prepared by simple condensation of Diacetyl Monoxime and Isonicotinic hydrazide in 1:1 mole ratio and its structure is given in fig - 1.

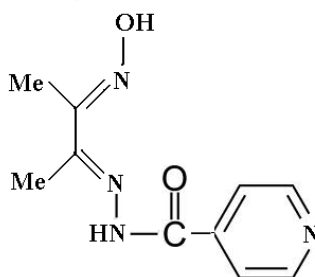


Fig 1. Structure of Diacetyl Monoxime Isonicotinoyl Hydrazone (DMIH)

The reagent solution (0.01 M) was prepared by dissolving 0.22 grams of DMIH in 100 mL of dimethyl Formamide. The reagent is stable for 48 hours. Buffer solutions were prepared by mixing 1 M hydrochloric acid – 0.2 M sodium dihydrogen phosphate.

Reaction with metal ions

The reactions of some important metal ions were tested at different P^H values. The samples were prepared in 10 mL volumetric flasks by adding 3 mL of buffer P^H (1.0 – 7.0), 0.5 mL of metal ion (1X 10⁻³ M) and 0.5 mL of DMIH (1 X 10⁻² M) solutions. The solution mixture was diluted up to the mark with distilled water. The absorbance was measured in 300–600 nm range against reagent blank .The results are summarised in Table –1.

Recommended Procedure

Determination of Th (IV) (Zero order spectrophotometry): An aliquot of the solution containing 1.16–13.92 µg /mL of Th (IV), 3 mL of buffer solution of P^H 5.0 and 0.5 mL of 0.01 M DMIH reagent were taken in a 10 mL volumetric flask and the solution was diluted up to the mark with distilled water. The absorbance of the solution was recorded at 352 nm in a 1.0 cm cell against reagent blank prepared in the same way but without Th (IV) metal solution. The measured absorbance was used to compute the amount of Th (IV) from the calibration plot.

Determination of Th (IV) by first order derivative spectrophotometry: The first order derivative spectrum was recorded for the above solution of Th (IV)–DMIH with a scan speed having degrees of freedom 9 in a wavelength range 300-600 nm. The derivative spectrum was measured by peak height (h) method at 405 nm. The peak height (h) at 405 nm is proportional to the concentration of Th (IV). Therefore the peak heights were measured at this wavelength for the construction of calibration plots.

RESULTS AND DISCUSSION

Diacetyl Monoxime Isonicotinoyl Hydrazone (DMIH) reagent can be easily prepared like any other Schiff base reagent. This new chromogenic reagent DMIH was not used for spectrophotometric determination of Th (IV) so far. The reactions of some important metal ions with DMIH are summarised in table-1. The colour reactions are mainly due to the complex formation of DMIH with divalent, trivalent, tetravalent and hexavalent metal ions like Hg (II), Ru (III), Au (III), Th (IV), Mo (VI) and U (VI) in acidic buffer medium to give intense coloured complexes.

Table-1: Analytical Characteristics of Diacetyl Monoxime Isonicotinoyl hydrozone (DMIH)

SI No	Metal Ion	P ^H	λ_{\max} (nm)	Molar absorptivity (L.mol ⁻¹ cm ⁻¹) X10 ⁴
1	Ru (III)	4.5	346	1.4
2	Hg (II)	5.5	351	2.23
3	U (VI)	3.25	364	1.63
4	Th (IV)	5.0	352	2.265
5	Au (III)	4.5	361	1.5
6	Mo (VI)	5	346	1.93

Determination of Th (IV) using DMIH:

Th (IV) reacts with DMIH in acidic medium to give yellow coloured water-soluble complex. The colour reaction between Th (IV) and DMIH is instantaneous even at room temperature in the P^H range 1.0 -7.0. The absorbance of the yellowish coloured species remains constant for more than two hours. The maximum colour intensity is observed at P^H 5.0.

It is observed that a 5 fold molar excess of reagent is more than sufficient for full colour development. The order of addition of buffer solution, metal ion and reagent has no adverse effect on the absorbance. The complex formation reaction between Th (IV) and DMIH has been studied in detail based on the composition of the complex as determined by using Job's and molar ratio methods. Some of the important physico-Chemical and analytic characteristics of Th (IV) and DMIH are summarised in table -2.

Table-2: Some of Physico- Chemical and analytical characteristics of Th (IV) –DMIH Complex

Characteristics	Results
λ_{\max} (nm)	352
P ^H Range (Optimum)	4.0-6.0
Mole of reagent required per mole of metal ion for full colour development	5 folds
sMolar absorptivity (L.mol ⁻¹ cm ⁻¹)	2.265 X10 ⁴
Sandell's sensitivity ($\mu\text{g}/\text{Cm}^2$)	0.00221
Beer's law validity range ($\mu\text{g}/\text{mL}$)	1.16 – 13.92
Optimum Concentration Range ($\mu\text{g}/\text{mL}$)	2.32- 11.6
Composition of complex (M: L) obtained in job's and mole ratio method	1:1
Stability Constant of the complex	7.026 X10 ⁶
Standard Deviation for 10 determinations	0.0004
Relative Standard Deviation	0.0617

Derivative spectrophotometry is an important useful technique as it decreases the interference i.e increases the tolerance limit value of the foreign ions. Therefore it may be useful for the determination of metal ions having overlapped spectra. The recommended procedure has been used for the determination of Th (IV). The zero order and first order derivative spectra of Th (IV) Complex of DMIH are given in Fig 2 and 3 respectively.

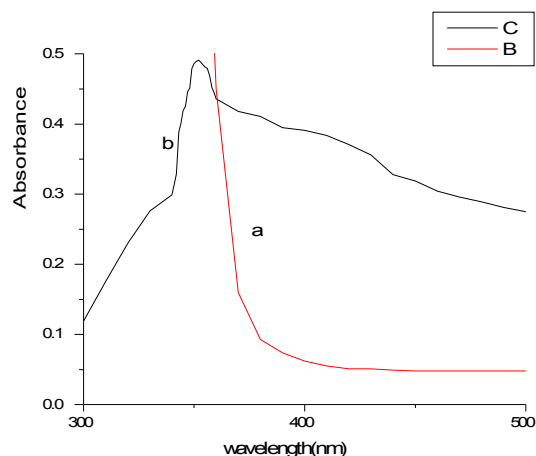


Fig 2. Zero order absorption spectra of (a) reagent DMIH 1×10^{-2} M vs Water blank at P^H 5.0 (b) Th (IV) – DMIH complex vs reagent blank at P^H =5.0 , Th(IV) = 1×10^{-3} M; DMIH = 1×10^{-2} M

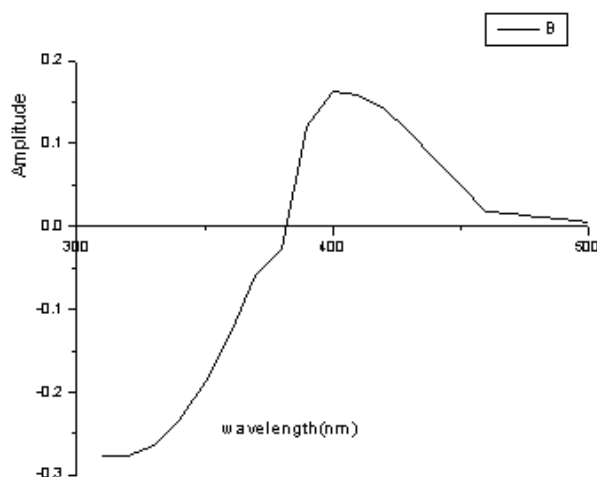


Fig 3. First Order Derivative Spectrum of Th (IV) – DMIH Complex Vs Reagent Blank at P^H = 5.0, Th (IV) = 1×10^{-3} M, DMIH = 1×10^{-2} M

Effect of Diverse ions: The effect of various diverse ions in the determination of Th (IV) was studied to find out the tolerance limit of foreign ions in the present method. The tolerance limit of foreign ions was taken as the amount of foreign ion required to cause an error of $\pm 2\%$ in the absorbance or amplitude. The results are given in table-3. The data obtained in the derivative method is also incorporated.

Table- 3: Tolerance limit of Foreign Ions in the determination of 5.015 µg / mL of Th (IV)

Ion Added	Tolerance Limit (µg / mL)		Ion Added	Tolerance Limit (µg / mL)	
	Zero Order	First Derivative		Zero order	First Derivative
Mn ⁺²	82.35	54.9	Sb ⁺³	121.8	121.8
Cr ⁺³	78	52	Cd ⁺²	112.4	112.4
Ascorbic Acid	176	264	Ag ⁺	107.9	161.85
Mo ⁺⁶	143.95	95.9	Sr ⁺²	87.6	87.6
Urea	60.06	90.9	Sn ⁺²	118.7	178.05
Tartarate	423	282	Al ⁺³	40.47	26.98
Sulphate	144	144	Bi ⁺³	104.5	208.98
Phosphate	95	95	Ba ⁺²	137.3	137.3
Nitrate	93	93	Zn ⁺²	98.1	65.4
Acetate	88.5	88.5	Zr ⁺⁴	91.2	136.8
Oxalate	67	134	U ⁺⁶	238	238
Thio Urea	114	114	W ⁺⁶	91.9	183.8
Fluoride	28.5	28.5	Ca ⁺²	60	60
Iodide	126.9	126.9	Ni ⁺²	88.05	88.05
Bromide	119.85	79.9	Pd ⁺²	106.4	159.6
Chloride	53.25	53.25	V ⁺⁵	76.35	50.9

Applications.

The proposed method was applied for the determination of Th (IV) in Monazite sand sample. The sample was brought into solution by adopting the standard procedure.

Ore sample:

1.10 grams of ore sample was digested in 30 mL of concentrated Sulphuric acid, leached and filtered. The filtrate was collected in a 500 mL standard flask and made up to the mark with distilled water. The Thorium metal from the solution was separated by reverse phase extraction chromatography. The separated metal was dissolved and diluted to 100 mL with distilled water.

Recommended procedure for analysis of the sample:

A known aliquot of the sample solution was taken in a 10 mL standard flask containing 3 mL of buffer solution and a suitable aliquot of the reagent DMIH was added. The contents were made up to the mark with distilled water. The absorbance of the complex was measured at a selected wavelength λ_{\max} against the reagent blank prepared in a similar way. The amount of Th (IV) present in the sample was computed from a pre determined calibration plot and the results were presented in table- 4.

Table-4: Estimation of Thorium (IV) (µg / mL) in Monazite sand sample

Sample (µg / mL)	Amount of Th (IV) (µg / mL)		
	Taken	Found *	Relative Error (%)
Monazite Sand	2.0	1.981	+0.95
	2.5	2.471	+1.16
	3.5	3.496	+0.114

* Average of best three determinations among five determinations

Table (5) - Comparison of some earlier Spectrophotometric methods for the determination

Conclusion

The present method using DMIH as a spectrophotometric reagent for the determination of Thorium (IV) in aqueous medium is sensitive and simple. The determination of Th (IV) using

Reagent	λ max (nm)	PH	Molar Absorptivity (L.mol ⁻¹ cm ⁻¹)	Extractio n/ Aqueous	Beer's law Range	Ref
2,4-dihydroxy benzaldehyde Isonicotinoyl Hydrazone	390	5.5	2.20 X 10 ⁴	-	2.30-7.0	9
(O-Hydroxy Phenyl) Mono and Dimethylene Phoporic Acid	-	--	-	-	-	10
2-hydroxy-1, 4-napthaquinone Lawsone (LAS)	440	2.1-3.6	0.27 X 10 ⁴	-	5.8-3.2	11
5-(2-hydroxy -4, 5-dinitrophenylazo)-4hydroxy 2,7-napthalene disulphonic acid	620	-	12.3 X 10 ⁴	-	-	12
H-acid Schiff alkali	560	-	9.28 X 10 ⁴	-	-	13
Disodium salt of Arsenazo-III	654	2M H ₃ PO ₃	3.07 X 10 ⁵	Maintain ed at 24 o C	1.60 mg/g	14
3,5-dibromo Salicylfluorone	557	8.8-10.2	2.19 X 10 ⁵	----	0- 7.0 mg/25mL	15
5-[(5-bromo-2-pyridyl)-azo]-5-diethylamino Phenone	590	-	12.7 X 10 ⁴	----	-	16
Eluorophosphonazo -DBF	632	-	13.4 X 10 ⁴	-	-	17
Diacetyl Monoxime Isonicotinoyl Hydrazone (DMIH) Th (IV)	364	3.25	1.63 X 10 ⁴	---	1.19-14.28 (μg / mL)	Present Method

DMIH is not laborious and there is no need of heating the components or extraction. Further the reagent is easy to synthesise using available chemicals. Moreover the present method is simple, rapid, reasonably sensitive and selective for the determination of Thorium (IV)

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