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A chelating reagent, 2, 3, 4-trihydroxy acetophenoneoxime(THAPO) used for selective and sensitive kinetic spectrophotometric determination of thorium(IV) from ores

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ABSTRACT

A complexing agent, 2,3,4-trihydroxyacetophenoneoxime (THAPO) was prepared and developed a selective and sensitive kinetic direct spectrophotometric method for the determination of thorium(IV). The method sensitivity is calculated in terms of molar absorptivity (3.179 x10^4 L mo1^{-1} cm^{-1}) and Sandell's sensitivity (0.0073 µg cm^{-2}), which explains that the method is more sensitive. The developed method is more precise and accuracy, which is found by standard deviation (0.0014), relative standard deviation(0.52%), absolute error(0.00057) and confidence limit(± 0.27). The metal and ligand forms 1:1(M:L) complex and its stability constant is calculated by Asumu's and Edmonds and Birnbaum's method. This developed method was applied for the determination of thorium (IV) from thorite ore and checked the validity of the method by comparing the obtained results with AAS method.

Key words: Oxime, kinetic spectrophotometry, thorium(IV) and thorium ore.

INTRODUCTION

Thorium, especially ^{232}Th finds extensive application in nuclear fuels. It is also used in dissipating static electricity and gas mantle industry. Thorium and its compounds are hazardous causing environmental pollution**.** 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 [1-3]. In aqueous solutions, thorium ions exist in stable tetravalent state and do not take part in redox reactions. There are various methods, such as gravimetric, volumetric and colorimetric methods for the determination of thorium. However, colorimetric method have unique place in determination of thorium at micro level. But, gravimetric and volumetric methods are used at macro levels only. Though colorimetry is a sensitive technique, there are very few reagents used for the colorimetric determination of thorium(IV) [4-5]. Among these, the most widely used reagent for determination of thorium is thoron. The proposed method when compared with other spectrophotometric methods shown in Table 1 was found to be more sensitive and selective.

Table1. Comparison of the present method with other spectrophotometric methods for the determination of Thorium(IV).

Reagent	λ_{max}**(nm)**	**Molar absorptivity** x10^4 L mo1^{-1} cm^{-1}	**Reference**
2-hydroxy-1,4-naphthaquinone Lawsone (LAS)Mepazine hydrochloride	440	0.27	6
Disodium salt of 2-(2-hydroxy-3,6-disulfo-1-naptylazo)-benzene arsenic acid	544	1.69	7
2,4-dihydroxybenzaldehyde isonicotinoyl hydrazone.	390	2.20	8
Calixearene hydroxamic acid (CPCHA)	450	2.20	9
1-(2’thiazolylazo)-2-naphthol	555	3.14	10
2,3,4-trihydroxyacetophenoneoxime (THAPO)	325	3.179	Present method

In the present study, a new colorimetric reagent, 2,3,4-trihydroxy acetophenone oxime(THAPO) has been prepared for the selective determination of thorium(IV) from its ores by sensitive kinetic spectrophotometric method.

EXPERIMENTAL SECTION

Reagents: It is suggested that 4.0 g of 2,3,4-trihydroxy acetophenone are taken in a round bottomed flask and treated with 10 ml of alcohol and 100 ml of water followed by 4g of hydroxylamine hydrochloride. The mixture is refluxed for about 10 minutes and cooled. The contents are neutralized to pH 7 with a mixture containing 1g of sodium hydroxide and 1.5g of sodium carbonate. The product is cooled in ice for six hours filtered, washed thoroughly with ice cold water and recrystallised twice from hot water using animal charcoal. Colorless, needle shaped crystals are obtained; yield 2.5 g. The purity of the reagent is checked by melting point.

0.025M thorium(IV) solution is prepared by dissolving 3.675 g of thorium nitrate [$Th(NO_3)_4.6H_2O$] in distilled water containing a few drops of nitric acid. The solution is made upto 250 ml and standardized gravimetrically by employing the iodide method.0.1moles/L Hydrochloric acid and 0.1moles/L Potassium chloride, 2.0 moles/L Sodium acetate and 2.0 moles/L acetic acid solutions are prepared in distilled water and suitable portions of these solutions are mixed to get the desired pH using a pH meter. All the chemicals used in the present work are of the analytical grade unless specified here.

Instruments: Determination of metal ion concentration is carried out by Shimadzu 2450 UV-VIS spectrophotometer equipped with 1.0 cm quartz cell and was adjusted the pH of solution with an Elico LI-120 digital pH meter. A Perkin-Elmer 170-30 atomic absorption spectrometer was used for the comparison of results.

General procedure: An aliquot of working (5.0 ml of 4.31 x 10^{-4} moles/L) thorium(IV) solution is transferred into a 25.0 ml standard flask. To this solution, 5.0ml(2.155 x 10^{-3} moles/L) of THAPO in ethanolic solution (30%, i.e., five fold excess) are added, followed by 1.0 ml of 0.04% v/v hydrogen peroxide and 5.0 ml of pH 3.5 sodium acetate-acetic acid buffer solutions. The mixture is made up to the mark with distilled water and determined the absorbance of complex against the reagent blank at 325 nm wavelength.

Preparation of ore sample: About 100 mg of the powdered ore is weighed accurately and decomposed by evaporating with concentrated hydrochloric acid. The mixture is diluted with hot water. The precipitate is filtered, washed and the filtrate is treated with hydrogen sulfide to separate lead and tin. The excess of hydrogen sulfide is removed by boiling. A few drops of concentrated nitric acid is added to the solution to form thorium nitrate. The solution is made up to 100 m1. The solution is further diluted to get lower concentrations.

RESULTS AND DISCUSSION

The rate of catalyzed oxidation of THAPO is influenced by pH of the solution, concentration of the reagent, presence of hydrogen peroxide, temperature of the system and foreign ions associated with it. Hence, the above factors are studied in detail to establish suitable conditions for higher sensitivity and selectivity in the determination.

Absorption spectra of the reagent and complex: An aliquot of 5.0 ml of 4.31 x 10^{-4} moles/L thorium(IV) solution is transferred into a 25 ml standard flask. To this solution, 5.0 ml of 2.155 x 10^{-3} moles/L solution of THAPO in ethanolic solution (30%, i.e., five fold excess) are added, followed by 1.0 ml of 0.04% v/v hydrogen peroxide and 5.0 ml of pH 3.5 sodium acetate-acetic acid buffer solutions. The mixture is made up to the mark with distilled water. Then the spectrum of the complex is recorded against the reagent blank (Figure1). It is observed that the complex has λ_{max} at 325 nm. The absorbance of the reagent at this wave length is minimum and hence further absorbance measurements of the complex are made at 325 nm.

Effect of pH: A mixture containing 5.0 ml of 4.31 x 10^{-4} moles/L thorium(IV) solution and 5.0 ml of 2.155 x 10^{-3} moles/L reagent solution is treated with 1.0 ml of 0.04% v/v hydrogen peroxide. The pH of the solution is adjusted to the required value, either by adding dilute hydrochloric acid-potassium chloride solution, or sodium acetate- acetic acid buffer. Then the solution is made upto 25 ml with distilled water. The absorbance is measured at 325 nm against the reagent blank. The experiment is repeated for different pH values from 1.0-6.0 and drawn a plot (Figure 2) between pH and absorbance shows that the absorbance is maximum and constant in the pH range of 3.0-4.0. Hence, further studies are made at pH, 3.5.

Effect of hydrogen peroxide: An aliquot of 5.0 ml of 4.31 x 10^{-4} moles/L thorium(IV) solution is transferred into a 25 ml standard flask and to it are added 5.0 ml of pH 3.5 buffer, 5.0 ml of 2.155 x 10^{-3} moles/L reagent and 1.0 ml of required hydrogen peroxide solutions.

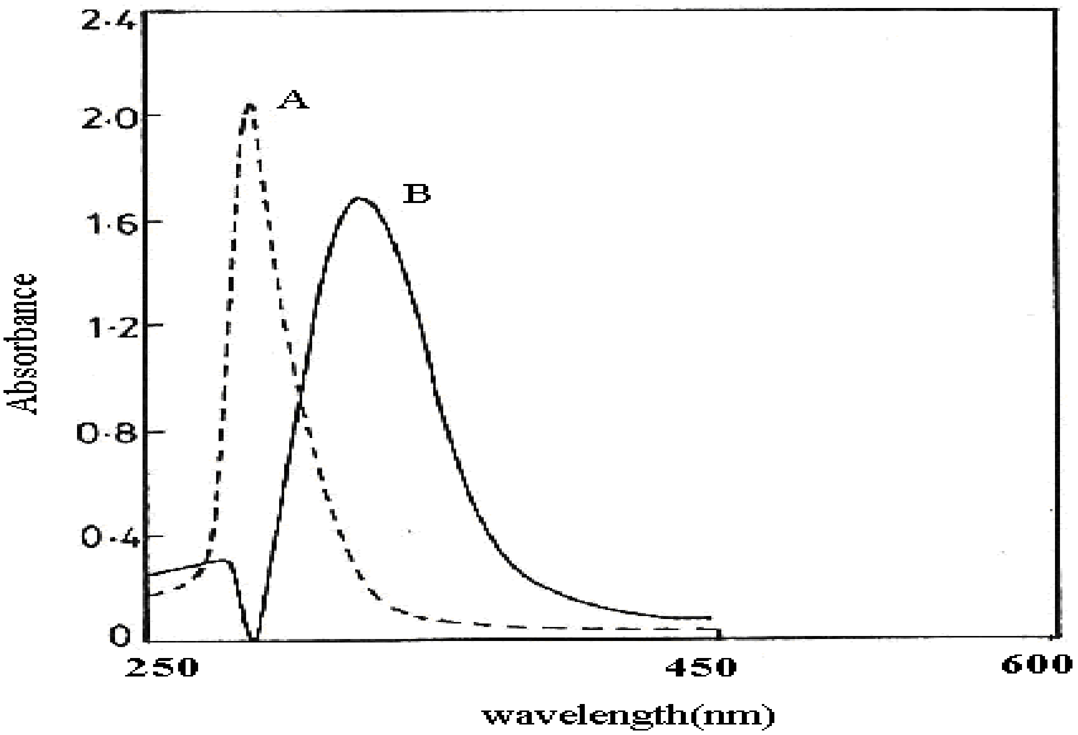

Fig. 1: Absorption spectrum of reagent (A) and Th-THAPO complex (B)

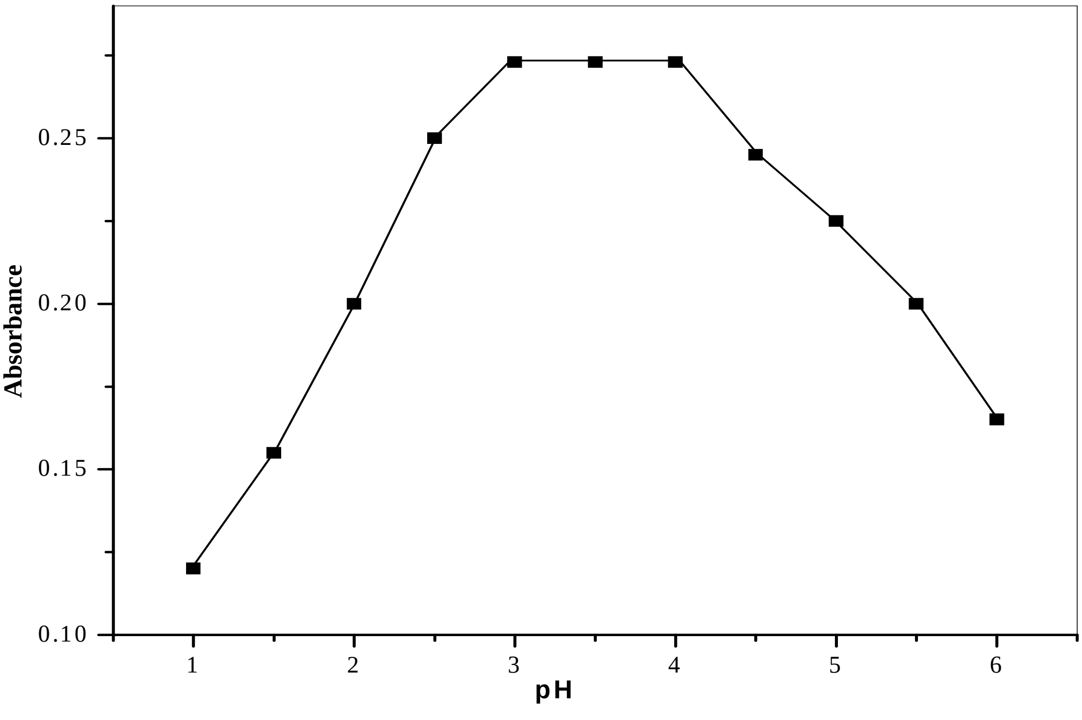

Fig. 2: Effect of pH on absorbance of Th(IV)-THAPO complex.

The solution is made upto the mark with distilled water. The absorbance of the oxidised compound is measured at 325 nm after 15 minutes. The experiment is carried out by using varying percentages of hydrogen peroxide and the results are shown in Figure 3.

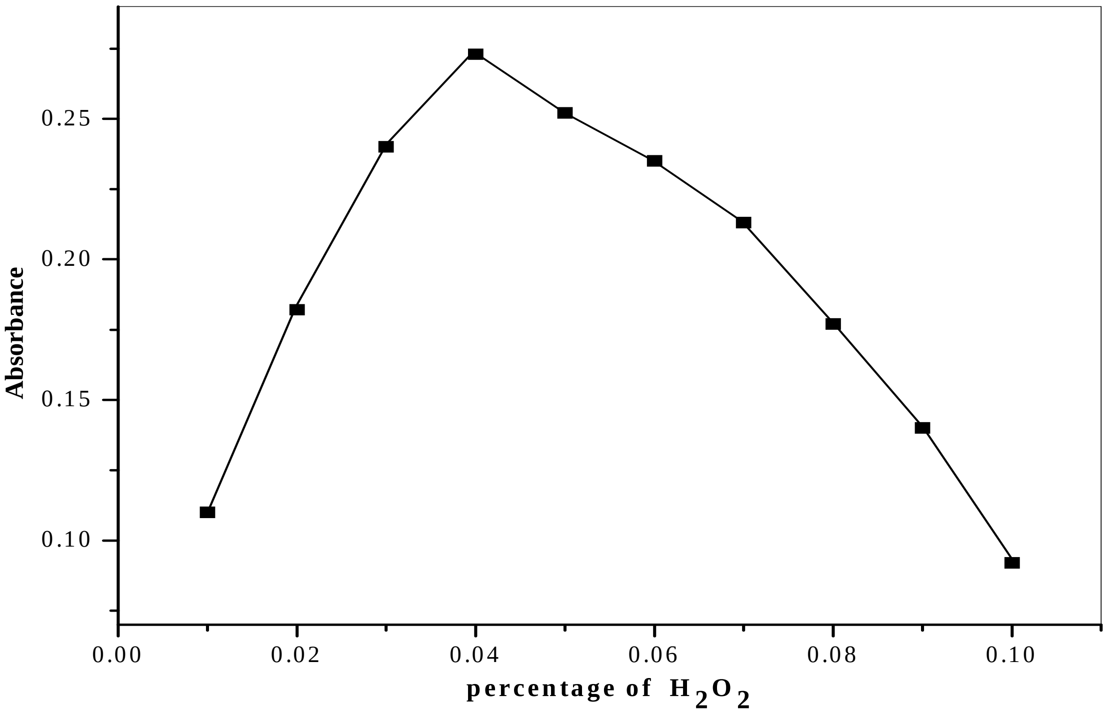

Fig. 3: Effect of H_2O_2 on absorbance of Th(IV)-THAPO complex.

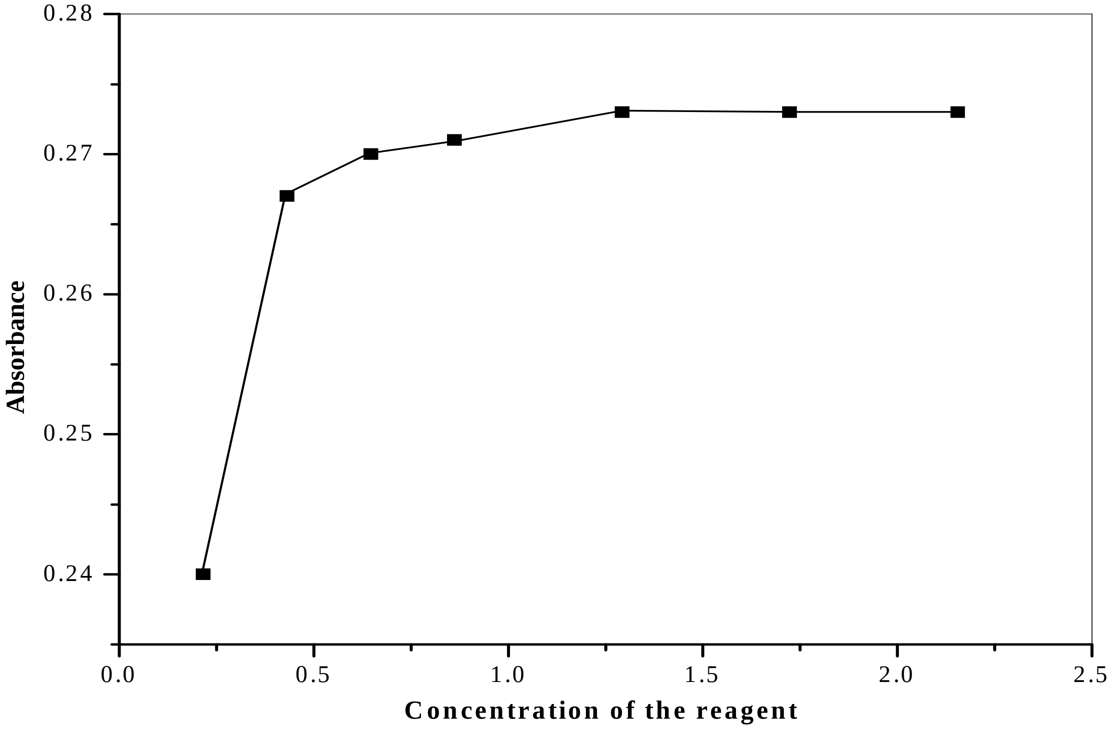

Fig.4: Effect of reagent concentration on absorbance of Th(IV)-THAPO complex.

The catalysed oxidation is slow below 0.04% v/v hydrogen peroxide; further increase in the concentration of hydrogen peroxide reduces the absorbance. The maximum absorption is at 0.04% v/v hydrogen peroxide. Hence, further studies are carried out by employing 1.0 ml of 0.04% v/v hydrogen peroxide solution.

Effect of reagent concentration: The intensity of the colour varies with the concentration of THAPO in the reaction mixture. Hence, it is found necessary to fix the optimum concentration of the reagent required in the investigation. Keeping the concentration of metal ion, percentage of H_2O_2 and buffer solutions at constant level and changing the concentration of (0.2155 x 10^{-3} moles/L - 2.155 x 10^{-3} moles/L) reagent in various solutions, the experiment is repeated as described earlier. Absorbance values are recorded in each case at 15th minute and drawn the plot between reagent concentration and absorbance as shown in Figure 4. It is found that absorbance increases with increase in the concentration of the reagent upto 3-folds excess to that of metal. There is no further increase in the rate of oxidation when the concentration of the reagent is more than 3-folds excess.

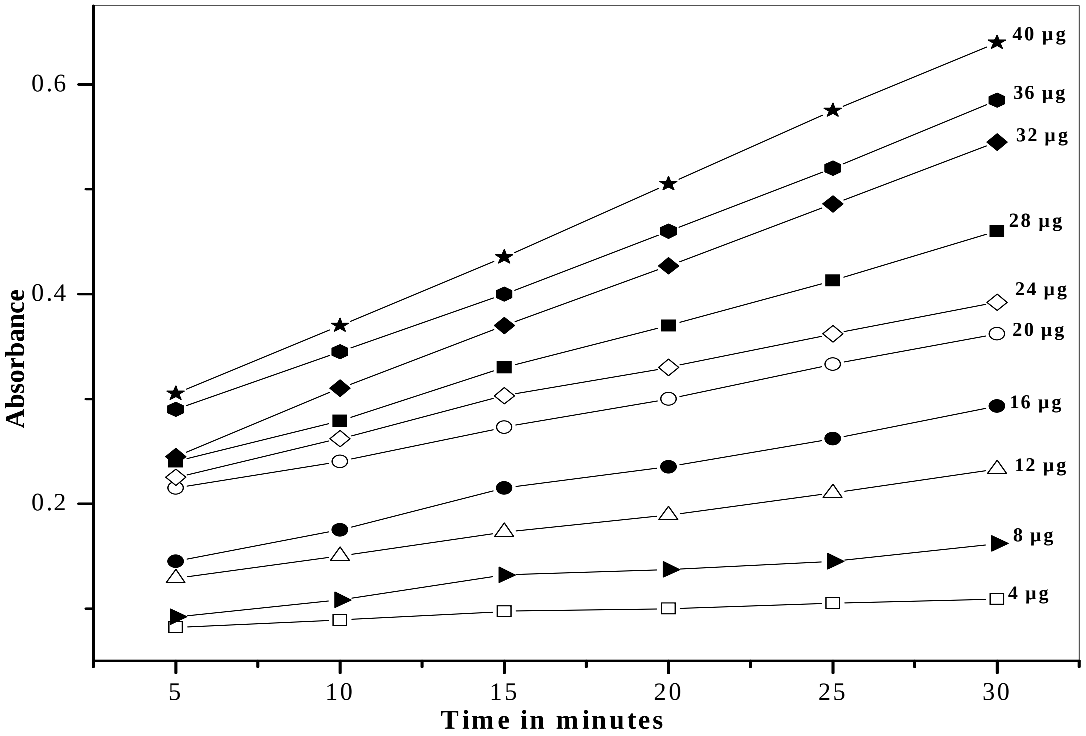

Fig. 5: Variation of absorbance with time for different concentration of Thorium(IV).

Applicability of the method: An aliquot of thorium(IV) solution is transferred into a 25 ml volumetric flask. 5.0 ml of sodium acetate - acetic acid buffer (pH 3.5), 5.0 ml of 2.155 x 10^{-3} moles/L reagent solution and 1.0 ml of 0.04% v/v hydrogen peroxide solutions are added to the same flask. The solution is made up to the mark and the absorbance is measured for every five minutes, using a reagent blank at 325 nm, upto 30 minutes. The experiment is carried out as explained above by varying the concentration of metal ion (4.0 to 40.0 µg/ml), at constant concentration of reagent, buffer and hydrogen peroxide. The results are shown in Figure 5. Slope values (tan θ) are calculated for each curve. It is noted that the rate of the catalyzed reaction increases with increase in the concentration of thorium.

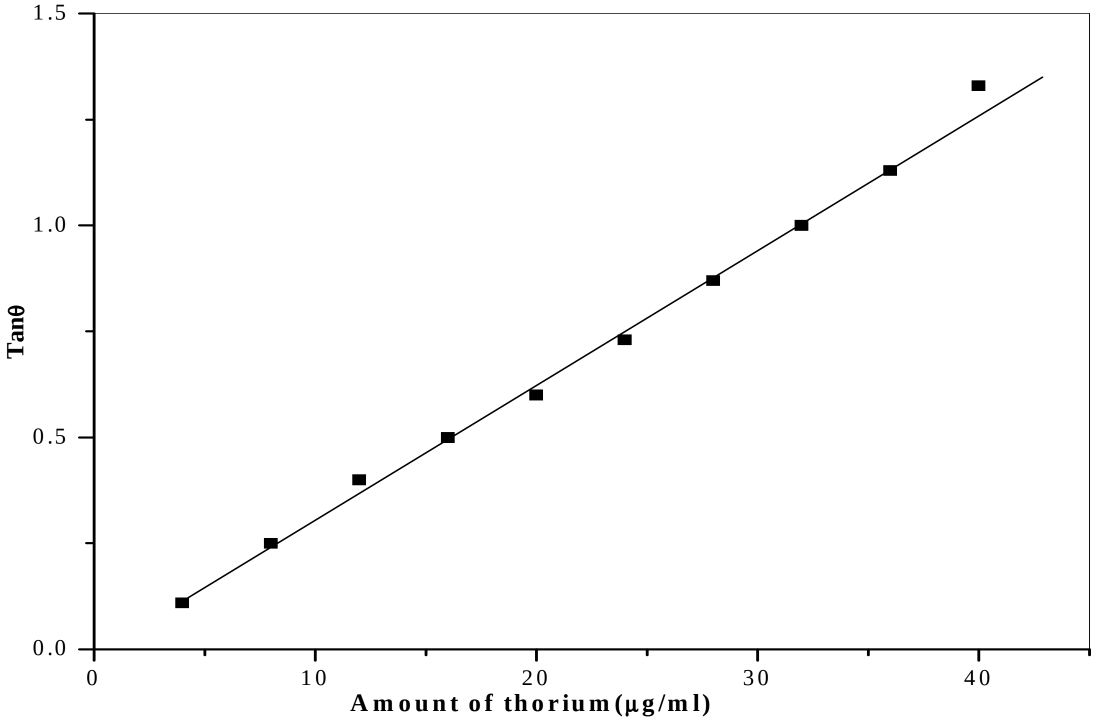

Fig. 6: Calibration curve for the determination of by Thorium(IV) by tangents method.

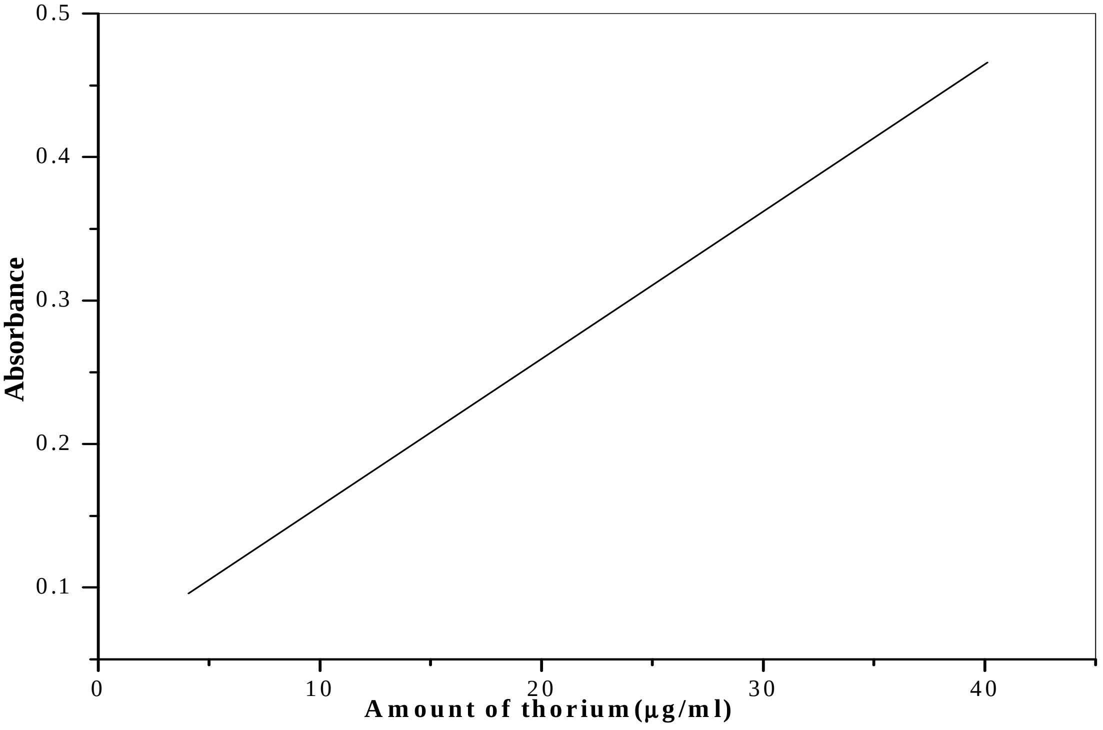

Fig.7: Calibration curve for the determination of Thorium(IV) by fixed time method.

A graph is also plotted between tan θ and concentration. A straight line is obtained in the range of 4.0-40.0 µg of Th(IV)/ml (Figure 6). The determination can also be carried out using fixed time method. A plot is drawn between amount of thorium(IV) and its absorbance as shown in Figure 7.

Sensitivity, precision and accuracy of the method: The molar absorptivity of the Th(IV)-THAPO complex is calculated as 3.179×10^4 L. $mo1^{-1}.cm^{-1}$. The Sandell's sensitivity of the complex is found to be 0.0073 µg. cm^{-2}. These values reveal that the kinetic spectrophotometric determinations of Th(IV) by THAPO in presence of H_2O_2 is highly sensitive, when compared with other spectrophotometric determinations of Th(IV) so far reported. The standard deviation (0.0014), relative standard deviatio (0.52%), confidence limit (± 0.27) and standard error (0.00057) for this method clearly indicates that the precision and accuracy of the method is highly satisfactory (table 2).

Table 2: Precision and accuracy of the method

S.No.	**Amount of thorium(IV) µg/ml**	***Absorbance***
1	20	*0.273*
2	20	*0.275*
3	20	*0.271*
4	20	*0.274*
5	20	*0.273*
6	20	*0.274*
Mean		*0.273*
S.D		*0.0014*
R.S.D		*0.52%*
Standard error		*0.00057*
Confidence limit		*±0.27*

Effect of temperature: The effect of temperature is studied by warming the reaction mixture of 5.0 ml of 4.31×10^{-4} moles/L thorium(IV), 5.0 ml of pH 3.5 buffer, 5.0 ml of 2.155×10^{-3} moles/L reagent and 1.0 ml of 0.04% v/v hydrogen peroxide solutions, on a water bath at 60°C. The absorbance values (15th minute) at 30°C and 60°C are 0.273 and 0.280 respectively. As there is no significant change in absorbance with change in temperature, hence the reaction is carried out only at room temperature.

Composition of the complex

The composition of the complex is arrived by Job's continuous variation and Asmus' methods.

Job's method of continuous variation: The composition of the complex is determined using 4.31×10^{-4} moles/L solutions of thorium(IV) and THAPO. A series of solutions are prepared by mixing 'X' ml of ligand with (1-X) ml of thorium(IV) solution ('X' is varied from 0.1 to 0.95 ml). In all the cases 5.0 ml of sodium acetate-acetic acid buffer (pH 3.5) and 1.0 ml of 0.04% v/v hydrogen peroxide solutions are added. The solutions are made up to 25 ml with distilled water. Absorbance values for all the solutions are measured at 325 nm using the reagent as blank at 15th minute. A plot between absorbance versus mole fraction of THAPO is shown in Figure 8**.** From the graph, the metal ligand composition in the complex is found to be 1:1.

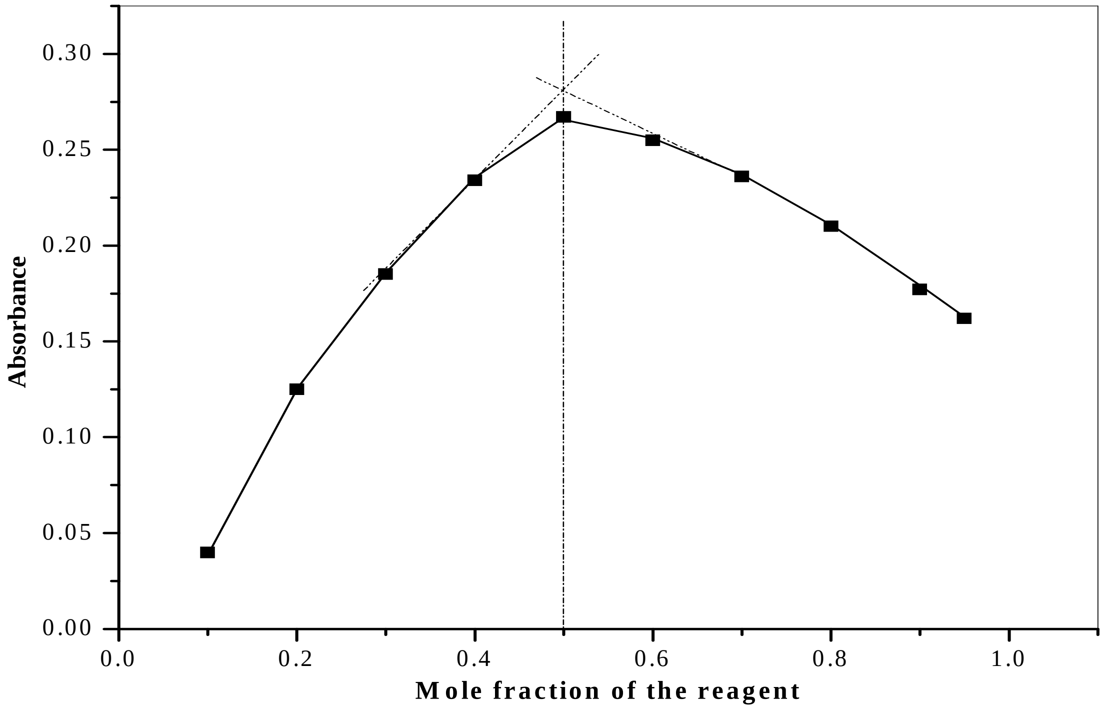

Fig. 8: Job's method of continuous variation for the determination of composition of Th(IV) –THAPO complex.

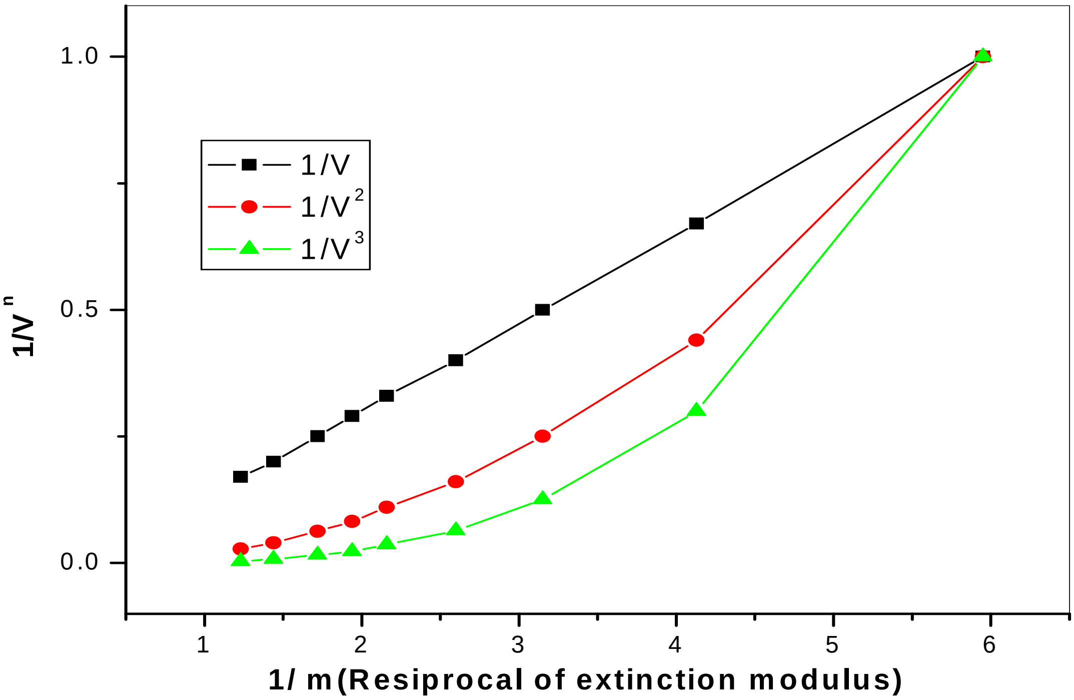

Fig. 9: Asmus' method for the determination of composition of Th(IV)-THAPO complex.

Asmus' method: 1.0 ml of 1 x 10^{-3}moles/L thorium(IV) solution and varying volumes (1.0-6.0 ml) of the reagent solution of concentration 1 x 10^{-3} moles/L are mixed together. To these solutions 5.0 ml sodium acetate-acetic acid buffer (pH 3.5) and 1.0 ml of 0.04% v/v hydrogen peroxide solutions are added. The contents of the standard flasks (25 ml) are made upto the mark with distilled water. Each of the absorbance measurements are made at 325 nm using the reagent blank at 15th minute. The data is recorded in Table 2 along with 1/v, $1/v^2$, $1/v^3$ and 1/m values where 'v' is the volume of reagent and `m' is the extinction modulus. Extinction modulus is calculated as given below:

$$m = A/l$$

where 'A' is the absorbance and 'l' is width of the cell.

The plot is drawn between 1/V and 1/m and shown in Figure 9. This method also indicates that the metal to ligand ratio is 1:1 which is in conformity with Job's method of continuous variation.

Instability constant of thorium(IV)-2,3,4-trihydroxy acetophenoneoxime complex

Asmus' method: The instability constant is calculated from the data obtained in Table 3. From the intercept on y-axis of Figure 9, the instability constant of the complex is calculated making use of the following equation.

$\text{Intercept} = -(b_o/v)^n \cdot 1/k$

Where V= total volume of solution,
b_0= Concentration of reagent

Here the value of 'n' is 1 and the intercept obtained from graph is -0.05. 'K' value obtained by substitution is 8 x 10^{-4} at 30°C.

Table 3: Asmus Method [Th (IV)] = [THAPO] = 1 x 10^{-3}M

Volume of reagent	Absorbance	1/V	$1/V^2$	$1/V^3$	1/m
1.0	0.168	1.00	1.00	1.00	5.95
1.5	0.242	0.67	0.44	0.30	4.13
2.0	0.317	0.50	0.25	0.125	3.15
2.5	0.385	0.40	0.16	0.064	2.60
3.0	0.463	0.33	0.11	0.037	2.16
3.5	0.515	0.29	0.082	0.025	1.94
4.0	0.581	0.25	0.063	0.016	1.72
5.0	0.694	0.20	0.040	0.008	1.44
6.0	0.813	0.17	0.028	0.004	1.23

Edmonds and Birnbaum's method: Absorbances of solutions containing the fixed amount of thorium(IV), but different known concentrations (0.8- 1.5 x 10^{-4} moles/L) of reagent solutions are measured after making up the volume to 25 ml; pH 3.5 buffer (5 ml) and 0.04% H_20_2 (1 ml) are maintained constant. In each case, the reagent concentration is always taken in excess to that of metal ion concentration. The absorbances are measured at 325 nm against the reagent blank. The average instability constants are calculated by choosing different pairs of solutions. The instability constant of the complex has been found to be 8.092 x 10^{-4} at 30°C.

Effect of foreign ions: The effect of foreign ions on thorium(IV) catalyst in the oxidation of

THAPO by hydrogen peroxide is studied. The absorbances of solutions containing 5.0 ml of 4.31 x 10^{-4} moles/L thorium(IV), varying amounts of interfering ion, 5.0 ml of 2.155 x 10^{-3} moles/L reagent soluton, 5.0 ml of sodium acetate - acetic acid buffer (pH 3.5) and 1.0 ml of 0.04% v/v hydrogen peroxide, are measured at 325 nm (t = 15th minute), against the reagent blank and shown the results in Table 4. The amount of foreign ion required to cause ± 2 per cent error, in the absorbance, is taken as tolerance limit.

Table 4: Effect of foreign ions Amount of thorium(IV) =20 µg/m1

Diverse ion	Added as	Tolerance limit µg/ml
Al(III)	$Al(NH_4)_2(SO_4).12H_2O$	200
Be(II)	$BeSO_4.4H_2O$	600
Ca(II)	$CaCl_2$	400
Cd(II)	$(CH_3COO)_2Cd.2\,H_2O$	20
Co(II)	$CoCl_2.7\,H_2O$	60
Cu(II)	$CuSO_4.5H_2O$	None
Cr(VI)	$K_2Cr_2O_7$	60
Fe(II)	$(NH_4)_2(SO_4).FeSO_4.6H_2O$	60
Hg(II)	$HgCl_2$	20
Mn(II)	$MnSO_4.H_2O$	2000
Mo(VI)	$(NH_4)_6Mo_7O_{24}.4H_2O$	None
Mg(II)	$MgSO_4.7H_2O$	1000
Ni(II)	$(NH_4)_2SO_4.NiSO_4.6H_2O$	20
Pb(II)	$(CH_3COO)_2Pb.2H_2O$	40
U(VI)	$UO_2(CH_3COO)_2.\,H_2O$	120
V(V)	NH_4VO_3	80
W(VI)	$Na_2WO_4.2H_2O$	20
Zr(IV)	$ZrO(NO_3)_2.2H_2O$	40
Bromide	KBr	2000
Chloride	NaCl	1000
Citrate	$Na_3C_6H_5O_7.2H_2O$	None
EDTA	Na_2EDTA	None
Fluoride	NaF	1000
Iodide	KI	1000
Oxalate	$(NH_4)_2C_2O_4.H_2O$	None
Phosphate	$NH_4H_2PO_4$	None
Sulphate	K_2SO_4	None
Tartrate	$(NH_4)_2C_4H_4O_6.4H_2O$	None
Thiocyanate	NH_4SCN	None
Thiosulphate	$Na_2S_2O_3.5H_2O$	None

Determination of thorium in thorite: The mineral thorite contains ThO_2 (58%), SiO_2 (20%), U_2O_3 (1.5%), Fe_2O_3 (4%), PbO (1%), CaO (2%) and rest water. The present method has been applied for the determination of thorium(IV) present in thorite. An aliquot of this solution is treated with 5.0 ml of 2.155 x 10^{-3} moles/L reagent solution. 5.0 ml of sodium acetate-acetic acid buffer (pH 3.5) and 1.0 ml of 0.04% v/v hydrogen peroxide are added to the same flask. The solution is made up to 25 ml with distilled water and the absorbance of the solution is measured at the 15th minute using the reagent blank at 325 nm. The amount of thorium in the ore is found to be 58.25% as ThO_2 after five determinations, which is in agreement with standard oxinate method, 58.05%. The values are also compared with AAS method and the results are tabulated in Table 5.

Table 5: Estimation of thorium(IV) in thorite

S.No.	*Amount of thorium found, μg*	
	THAPO method	*AAS method*
1	0.200	*0.202*
2	0.204	*0.208*
3	0.198	*0.204*
4	0.208	*0.206*
5	0.204	*0.210*
Average	*0.203*	*0.206*

CONCLUSION

The developed spectrophotometric methods for the determination of Th(IV) are not highly sensitive. The present kinetic spectrophotometric method for Th(IV) is proved to be highly sensitive and can be applied for the determination of Th(IV) in thorite ore. Uranium the common element usually present along with thorium, is not interfering even in presence of 6-folds excess. The selectivity of the reagent is further increased judicial use of masking agents to suppress the interference of metal ions like Cu(II) and Mo(VI).

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