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Research Article

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Metal complex of glyoxalbisisonicotinoylhydrazone: Synthesis, spectroscopic characterization and antimicrobial activity

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ABSTRACT

Hydrazone are an important class of compounds found in many synthetic and pharmaceutical products. Due to their importance in synthetic and pharmaceutical chemistry, the present research paper reports Synthesis of Glyoxalbisisonicotinoylhydrazone(GINH), Melting point, Elemental analysis, Spectral study & Antimicrobial activity are studied. A simple, sensitive & specific spectrophotometric method for the determination of Zn(II) is developed based on the colour reaction between zinc (II) and glyoxalbisisonicotinoylhydrazone (GINH). ^{1}H NMR< Effect of diverse ion have been studied respectively. Stability constant of the complex, Dissociation constant & Change in free energy are determined. Composition of the metal & ligand has been determined by Job's variation and mole ratio method. The optimum condition for complete colour development have been established by studying parameters like effect of medium, reagent concentration, time period have been studied.

Keywords : Glyoxalbisisonicotinoylhydrazone , U (VI) , Spectrophotometry , Antimicrobial

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INTRODUCTION

Hydrazones are azomethines characterized by the presence of triatomic grouping. Many of the physiologically active compounds find application [1] in the treatment of several diseases such as tuberculosis, leprosy and mental disorder. On the other hand aroylhydrazones are reported to possestuberculostic activity[2,3] . This is attributed to the formation of stable chelates with transition metal in the cell. Hydrazone have been demonstrated to posses among other antimicrobial, antitumoralactivities.There has been growing interest in studying hydrazones and their metal complexesdue to their application as antifungal[4-6] , antibacterial [4-7] ,anticonvulsant [8] ,anti-inflammatory [6] ,antimalarial [9] , analgesic [10] , antiplatelets[11] antituberculosis[12] , anticancer activities [13] . Hydrazones act as herbicides, insecticides, nematocides, rodenticidesand plant growth regulators, plasticizers and stabilizers for polymers, andpolymerization initiators and antioxidants. In analytical chemistry, hydrazonesare used in the detection, determination and isolation of compounds containing acarbonyl group [14] .More recently, they have been extensively used for the detectionand determination of several metals [15] .Metal complexes of 2-acetylpyridine benzoylhydrazonewere synthesized and crystallographically characterized [16] . TheMn(II), Fe(III), Ni(II), Co(II) and Zn(II) complexes of 2,6-diformyl-4-methylphenolbis(benzoylhydrazone) were prepared and characterized by elemental and spectroscopic measurements [17] . The Co(II), Mn(II), Cu(II) complexes of 2-acetylpyridinesalicyloylhydrazone and 2-benzoylpyridine salicyloylhydrazone were alsosynthesized and characterized[18].Moreover, zinc(II) complexes of 2-benzoylpyridinephenylhydrazone,2-benzoylpyridineparachlorophenylhydrazone and 2-benzoylpyridinepara-nitrophenylhydrazone were prepared and characterized by elemental, spectral and single-crystal X-ray diffraction analyses [19] . Much work onmetal complexes

of hydrazoneswith different functional groups has been reported[20] .However, little research has been devoted to metal complexes of hydrazoneligands; hence, the synthesis, spectroscopic characterization and antimicrobial activities of Metal Complex of Glyoxalbisisonicotinoylhydrazide were studied. Hydrazones and their derivatives constitute a versatile class of compounds in organic chemistry. Hydrazones areimportant compounds for drug design, as possible ligands for metal complexes, organocatalysisand also for the syntheses of heterocyclic compounds [21] .Isonicotinoylhydrazones are antitubercular; 4-hydroxybenzoic acid[(5-nitro-2-furyl)methylene]-hydrazide (nifuroxazide) is an intestinal antiseptic; 4-fluorobenzoic acid[(5-nitro-2-furyl)methylene]-hydrazide[22]and2,3,4-pentanetrione-3-[4-[[(5-nitro2furyl)methylene]hydrazino]carbonyl]phenyl]-hydrazone[23].The potential analytical applications of hydrazone derivatives have been reviewed [24] .Hydrazones are important class of known analytical reagents [25-30] . They react with many metal ions forming colour complexes and act as chelating agents. Isonicotinoylhydrazones are antitubercular, 4-hydroxybenzoic acid [(5-nitro-2-furyl)methylene]-hydrazide (nifuroxazide) is an intestinal antiseptic, 4-fluorobenzoic acid [(5-nitro-2-furyl0methylene]-hydrazide[31] and 2,3,4-pentanetrione-3-[4-[[(5-nitro-2-furyl)methylene] hydrazine] carbonyl] phenyl]-hydrazone[32] N_1 -4(4-methoxybenzamido) benzoyl]-N_2 –[(5-nitro-2-furyl) methylene] hydrazine, was synthesized . Isonicotinic acid hydrazide(isoniazid 1 NH) has very high in vivo inhibitory activity towards. Tuberculosis H37Rv. These compounds were reported to have inhibitory activity in mice than 1 NH [33].

Uranium(VI) forms highly soluble carbonate complexes at alkaline pH.Uranium is a heavy, silvery-white, ductile and slightly paramagnetic metal, whichis pyrophoric when finely divided. It is slightly softer than steel and reacts with coldwater when present in a finely divided state. In air it easily oxidizes and becomescoated with a layer of oxide. Thus in nature uranium mainly occurs in oxidized form.Uranium is about as abundant as molybdenum and arsenic and more plentiful thanmercury, antimony, tungsten and cadmium. It occurs in numerous minerals and isalso found in lignite, monazite sands, phosphate rock and phosphate fertilizers. Inores it occurs as uranite (UO_2), pitchblende (U_3O_8□) or as secondary minerals(complex oxides, silicates, phosphates, vanadates). Uranium is the heaviest naturallyoccurring element and is found at an average concentration of 0.0003% (3 mg/kg)in the earth's crust. In seawater the concentration is about 3.0 g/l. Due to its presence in soil, rocks, surface and underground water, air, plants, and animals it occursalso in trace amounts in many foods and in drinking water. The daily intake of uranium is estimated to be 1–2 g in food and 1.5 g in

water consumed [34] .The human body contains approximately 56 gof uranium, 32 g (56%) are in the skeleton, 11 g in muscle tissue, 9 g in fat, 2g in blood and less than 1 g in lung, liver and kidneys[35] . Theuranium in the human body is derived mostly from uranium in food, especially fromvegetables, cereals, and table salt [36,37].Uranium is a very reactive element readily combining with many elements to form a variety of complexes. Uranium (VI) forms a complex with dipicolinic acid (2, 6-pyridinedicarboxylic acid), which can be highly sensitiveand selective determined by ACSV using a hanging mercury drop electrode [38] ..Metal complexes ofthe Schiff base 2,5-dihydroxyacetophenoneisonicotinoylhydrazone (LH_2) was studied [39] .Numerous uranium complexes and their mixed chelates have been studied [40,41]. A large number of complexes with varying geometries of dioxouranium(VI), UO_2^{2+}oxocations are possible [42] . The coordination numbers ranging from 7 to 12 for metal chelates of UO_2(VI) has been reported [43,44] The present paper describes a new, very simple, rapid and sensitive spectrophotometric determination of uranium (VI) with Glyoxalbisisonicotinoylhydrazide (GINH).

EXPERIMENTAL SECTION

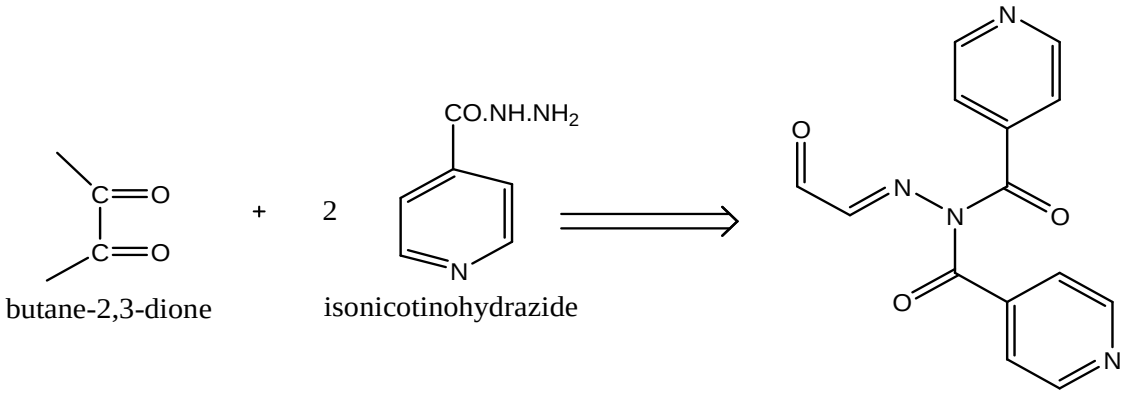
An Elico UV-visible spectrophotometer model UV_SL 164 equipped with 1 cm quartz cell is used for spectrophotometric measurements. An Elico pH meter LI-610 is used for pH measurements. The chemicals used are of analytical reagent grade. Perkin Elmer 221 IR spectrophotometer using KBr pellets techniques is used for IR studies. X-RD was taken on PW 3710 diffractometer using CuK2 radiation has been taken on the instrument BRUKER AC 300F NMR spectrophotometer 300HZ with $CDCl_3$ solvent. Elemental analysis and antimicrobial activity was done in laboratory approved by Central Government for AGMARK.

Synthesis and Characterisationof GINH

Synthesis of GINH

Glyoxalbisisonicotinoylhydrazone(GINH) synthesized by refluxing 1 : 2 butane-2,3-dione and isonicotinohydrazide about 72 hrs. It was then filtered and recrystalized in water in presence of 2 M HCL.

Reaction



Glyoxal bis isonicotinoyl hydrazone

The colour is orange yellow. The recrystallized product has melting point is 235-239^{0}C & molecular weight by formula is 294.00

Characterisationof GINH

Elemental Analysis of GINH

The elemental analysis of GINH was done in laboratory approved by Central Government for AGMARK. It shows the result of elemental analysis in Table 1.

Absorption Spectra of GINH

The absorption spectra of GINH was recorded against a blank solution containing buffer (PH=4.5) and is shown in Fig 1. Absorption spectra was recorded in the wavelength range 270-420 nm. The GINH shows an absorption maximum at 320 nm. At 320 nm wavelength the molar absorptivity of GINH is 1.6190 x10^4 L.mol^{-1}.cm^{-1}. Fig 2. Shows the absorption spectra of U (VI)-GINH.

Effect of Reagent concentration of GINH

Effect of reagent concentration was recorded by keeping same amount of concentration of uranium but different concentration of Glyoxalbisisonicotinoylhydrazone (GINH) at pH 4.5. At 320 nm wavelength absorbance was measured. Fig 3. Shows the effect of reagent concentration**.**

Job's method of continous variation of GINH

For Job's method number of solutions were prepared by keeping same molar concentration of U (VI) andGlyoxalbisisonicotinoylhydrazone (GINH) constant while the ratio varied in different solutions. At 320 nm wavelength absorbance was measured . Fig.4 indicate that the formation of complex is 1:2.

Antimicrobial Activity of GINH

Antimicrobial Activity of GINH has done in the laboratory approved by Central Government through AGMARK, The result are noted in Table 2.

Physico-chemical Characteristic of U (VI)-GINH

Physico-chemical and Analytical characteristic of U (VI)-GINH was studied and given in Table 3.

Effect of diverse ion of GINH

Effect of diverse ion was studied for U (VI)-GINH complex using metal U (VI) & GINH An error upto 2 % in absorbance was considered to be tolerable Table 4. It conclude that Cu (II) , Pb (II), Ti (IV) ,Cr (VI) & Ti (I) strongly interfere while Ba (II) , Mn (II) Na,,K do not interfere. Anion like EDTA, IPO_4& $C_2O_4^{-2}$ strongly interfere while thiocynatesalicylate do not.

RESULTS AND DISCUSSION

U (VI) forms orange yellow colour complex with Glyoxalbisisonicotinoylhydrazone(GINH) .

Table 1. Elemental Analysis of GINH

Sr.No.	Chemical Analysis	Percentage Found	Percentage Expected
1)	Carbon	52.89	57.14
2)	Hydrogen	03.76	03.40
3)	Nitrogen	22.27	23.13
4)	Oxygen	16.00	16.33

Table 2 : Antimicrobial Activity of GINH

Sr.No.	Antimicrobial	Activity
1)	K. pneumonia	Nil
2)	V. chloerease	Nil
3)	S. typhi	Nil
4)	S. aureus	Nil
5)	S.flexneri	Nil
6)	B. subtilis	Nil

Table 3: Physico-chemical & Analytical Characteristic of U (VI) -GINH

Sr.No.	Characteristics	Result
1)	Absorption spectra	435 nm
2)	Molar extinction coefficient ($L.mol^{-1}.cm^{-1}$.)	3.763×10^3
3)	pH range (optimum)	4.5
4)	Reagent required for maximum complexation	2.0 ml
5)	Beer's law validity range (ppm)	10 ppm
6)	Compositon of complex (M:L) obtained in job's & molar ratio method	1:2
7)	Sandell's sensitivity ($\mu g/cm^{-2}$)	0.0150
9)	Dissociation constant of complex	3.171×10^{-13}
10)	Stability constant	0.9534×10^{12}
11)	Change in free energy	-82.15 KJ/mole

Table No.4 Tolerance limit of diverse ions in the determination of Uranium (VI)

Sr. No.	Metal ion	Metal in added form	Tolerance limit ppm	Sr. No.	Metal ion	Metal in added form	Tolerance limit ppm
1)	Ba (II)	$BaCl_2$	None	17)	Mn (II)	$MnCl_2$	none
2)	Na (I)	NaCl	None	18)	Mg (II)	$MgSO_4$	1000
3)	Ti (I)	TiCl	1	19)	Be (II)	$BeSO_4$	200
4)	Pb (II)	$PbCl_2$	1	20)	Te (IV)	Na_2TeO_3	10
5)	Fe (II)	$FeSO_4$	200	21)	W (VI)	$Na_2WO_4.H_2O$	10
6)	Cu (II)	$CuCl_2$		22)	Cr (VI)	$K_2Cr_2O_7$	2
7)	Ti (IV)	K-titanyl oxalate	1	23)	Bi (III)	$Bi(NO_2)_3$	10
8)	V (V)	Vanadium sulphate	200	24)	$S_2O_3^{-2}$	$Na_2S_2O_3$	50
9)	Hg (II)	$HgCl_2$	200	25)	$C_2O_4^{-2}$	$H_2C_2O_4$	4
10)	Ca (II)	$CaCl_2$	200	26)	CH_3COO^-	CH_3COONa	30
11)	Ni (II)	$NiCl_2$	400	27)	HPO_4^{-2}	Na_2HPO_4	2
12)	Co (II)	$CoCl_2$	1000	28)	EDTA	Na-EDTA	2
13)	Zn (II)	$ZnCl_2$	400	29)	SCN^-	NH_4SCN	None
14)	Cd (II)	CdCl	None	30)	Citrate	Citric acid	100
15)	Ce (IV)	$Ce(SO_4)_2$	400	31)	Salicylate	Salicyclic acid	None
16)	K (I)	KCl	none	32)	Tartarate	Sodium tartarate	200

The absorption spectra of GINH at pH 4.5 was 320 nm while for U (VI)-GINH was 435 nm. At 320 nm wavelength the molar absorptivity of GINH is 1.6190×10^4 $L.mol^{-1}.cm^{-1}$. The molar extinction coefficient of complex was $3.763 \times 10^3 L.mol^{-1}.cm^{-1}$. The reagent required for maximum complexation was 2.0 ml. The elemental analysis of GINH shows carbon 52.89 % hydrogen 03.76 %, nitrogen 22.27 % and oxygen 16.00 %. Antimicrobial Activity of GINH was studied by K. pneumonia , V. chloerease, S. typhi , S. aureus , S. flexneri& B.

subtilis. Compositon of complex (M:L) obtained in job's & molar ratio method 1:2 . Sandell's sensitivity is 0.0150 µg/cm^{-2} . Dissociation constant and stability constant of the complex are 3.171x10^{-13}& 0.9534x10^{12} .The change in free energy of the complex has -82.15 KJ/mole. Effect of diverse ion was studied for U (VI)-GINH complex using metal U (VI) & GINH, An error upto 2 % in absorbance was considered to be tolerable . It conclude that Cu (II) , Pb (II), Ti (IV) ,Cr (VI) & Ti (I) strongly interfere while Ba (II) , Mn (II) Na,,K do not interfere. Anion like EDTA, IPO_4& $C_2O_4^{-2}$ strongly interfere while thiocynatesalicylate do not.

Structure of U (VI)- GINH

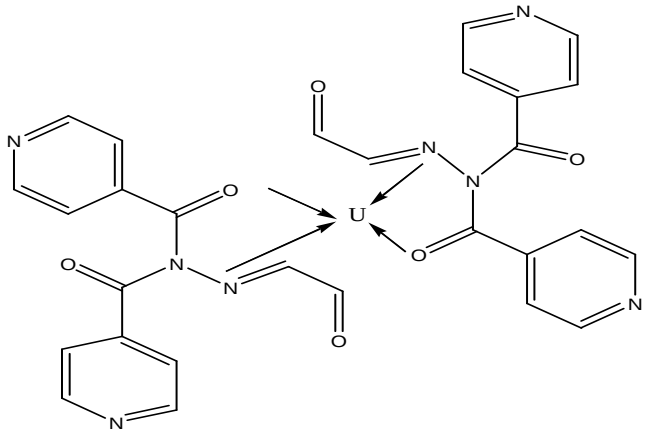


Fig 1 :Absorption Spectra of GINH

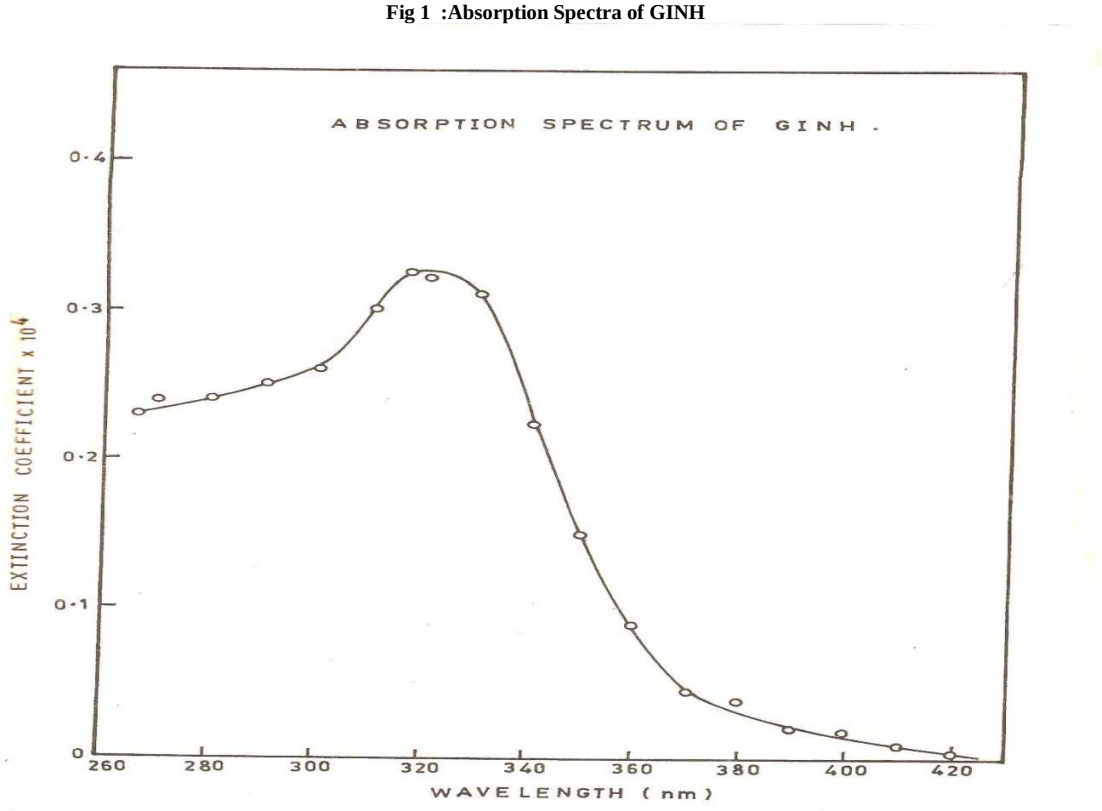


Fig 2 : Absorption Spectra of U (VI)-GINH

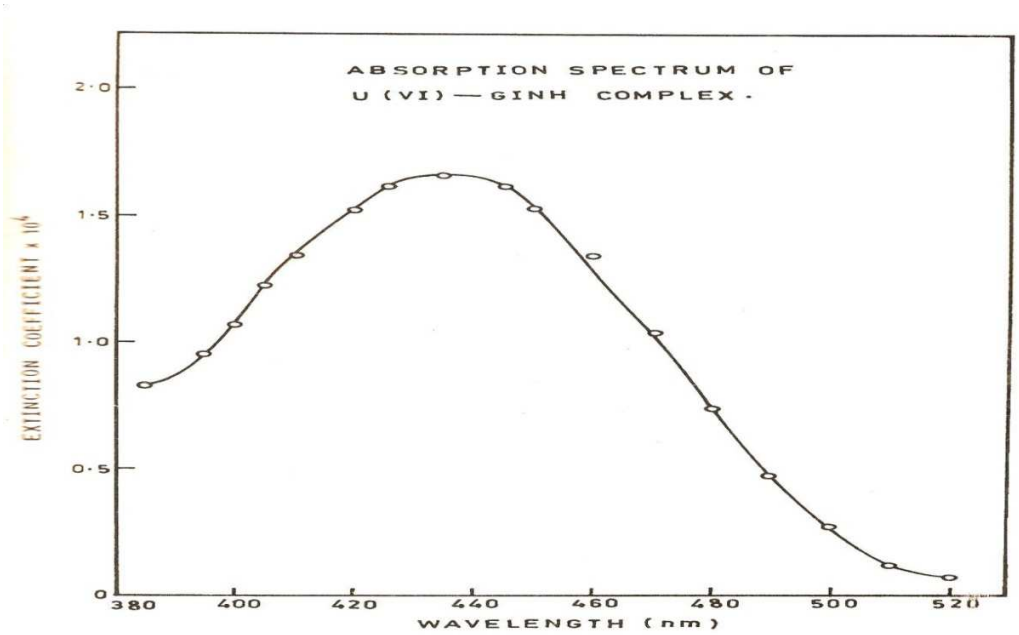


Fig 3 : Effect of Reagent concentration of GINH

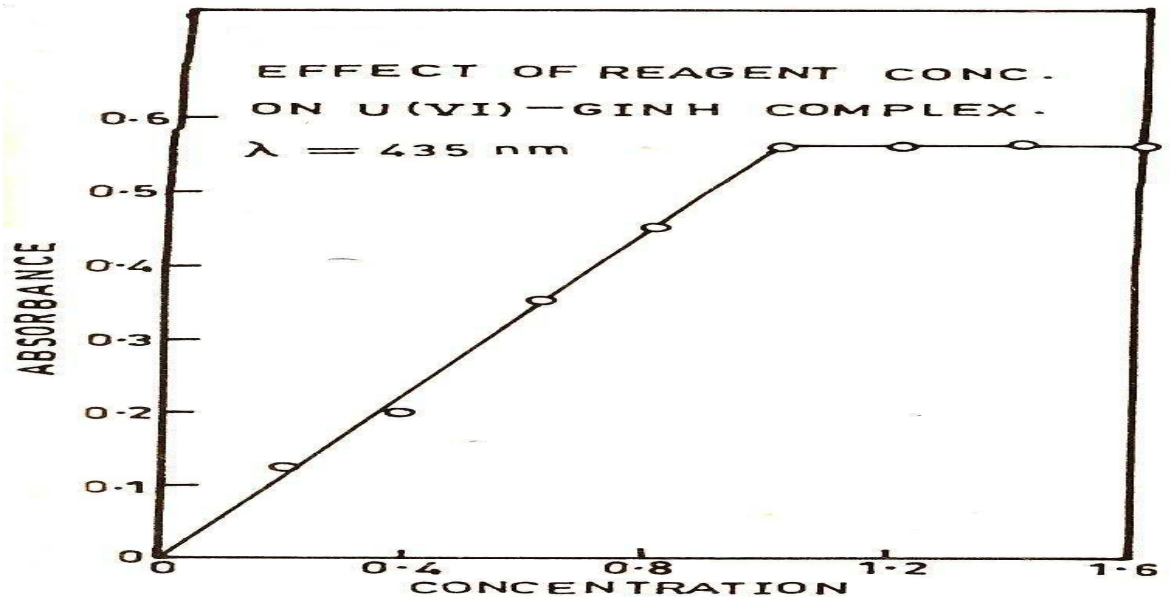
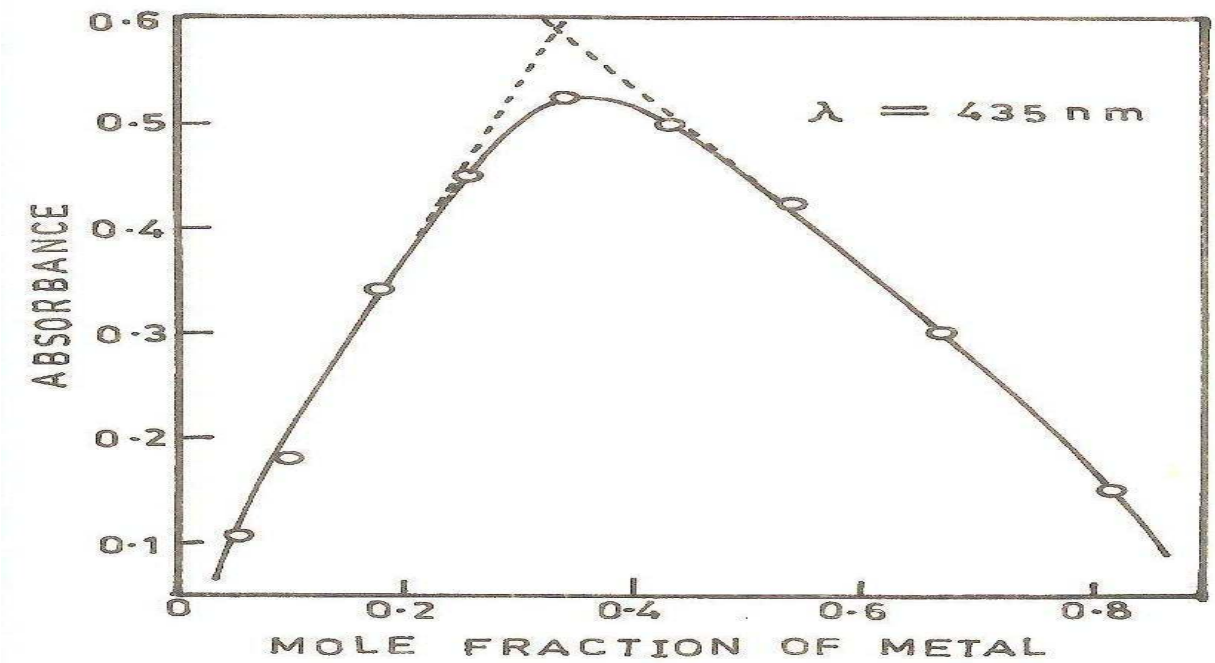


Fig 5. :Job's method of continous variation of F2STSC



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