
CHAPTER - III

SPECTROPHOTOMETRIC DETERMINATION OF
NICKEL(II) WITH 2CHLOROQUINOLINE
3-CARBALDEHYDE THIOSEMICARBAZONE

Photometric Determination of Nickel(II)

Introduction :

Nickel is one of the most commonly used alloying elements. The twentieth century has seen a tremendous development and expansion of the nickel industry with ever more diverse and important uses for nickel, nickel alloys and nickel compounds. Nickel finds many applications in industry including a variety of steels, stainless steel, resistance alloys like nichrome, constantan and manganin, alloys for heating elements and coins. Nickel is extensively used in nickel plating, it is also used for catalyst and hence the determination of nickel is of vital importance.

Although several organic compounds have been proposed for the spectrophotometric determination of nickel, each has its own limitations and many are not available commercially. The most extensively used reagents for photometric determination of nickel(II) are oximes and dioximes; such as, dimethylglyoxime¹⁻³, furil- α -dioxime⁴⁻⁹, 1-hydroxy-2-acetonaphthone oxime¹⁰, Nioxime, Cyclohexane-1,2-dione dioxime¹¹, α -benzoin oxime¹², azonaphthols and dithiols. But in extraction with DMG, 4-isopropyl-1, 2-cyclohexene dionedioxime¹³, cycloheptane 1:2 dionedioxime¹⁴, thiotropolone¹⁵, Quinoxaline-2,3-dithiol^{16,17}, nicotinamidoxime¹⁸, calcichrome¹⁹ and chlorindazon DS²⁰, many cations interfere

seriously and some of all are time consuming due to slow rate of formation of complex. Reagents like 1-(2-pyridylazo)-2-naphthol²¹ and solochrome red ERS²² require elevated temperature for complex formation.

Recently reported reagent for a colourimetric determinations of nickel is 6-Nitroquinoline dithiol²³. Also introduced important reagents are azonaphthols or their substituted derivatives such as PAN²⁴⁻²⁷, or TAN²⁸, isopentyl esters²⁹, and thenoyltrifluoroacetone^{30,31}. Thiobenzoylacetone (3-mercapto-1-phenyl-but-2-en-one)³², 2-mercapto-4-thiochrome³³, thiothenoyltrifluoroacetone³⁴, 2-and 3-hydroxy benzophenone³⁵, sodium purpurin sulphate³⁶.

Among others, the reagents that have been proposed for the photometric determinations of nickel, the following may be mentioned: Alzarín maroon and Eosin³⁷, 5-chloro-2-pyridyl-azo-o-cresol³⁸, 1,5-bis(2-carboxy-methoxy phenyl)-3-phenyl formazan³⁹, 2-(p-sulphophenylazo)-1,8-dihydroxy naphthalene-3,6-Disulphuric acid⁴⁰, 4-hydroxy-3-nitrosonaphthalene-1-sulphonic acid⁴¹, 2'-hydroxy acetophenoneoxime⁴², Acenaphthene quinone monoxime⁴³, 3-(o-Acetophenyl)-1-phenyltriazine-N-oxide⁴⁴, Thiosalicylidene ethylene-diimine⁴⁵, 1-(2-thiazolyazo)-2-naphthol⁴⁶.

Thiosemicarbazones of some aldehydes and ketones are also promising new photometric reagents for nickel, Di-2-pyridyl ketone thiosemicarbazone⁴⁷, Picolinaldehyde-4-phenyl-3-thiosemicarbazone⁴⁸, 4-aryl-1-benzoyl thiosemicarbazone⁴⁹, Quinoline-2-aldehyde

Table 3.1 Review of the methods for the photometric determination of Nickel(II)

Reagent	pH	λ_{max}	Sensitivity molar extinction coefficient range ppm.	Interference and remark	Ref.
	2	3	4	5	6
1-hydroxy-2-acetonaphtho-neoxime	8.5 to 9.5	396	$\epsilon = 5.75 \times 10^3$ sensitivity is 0.01 $\mu\text{g cm}^{-2}$	Fe(III), Co(II), Cu(II) V(IV) interfere	10
Nioxime(cyclohexane-1,2-dione dioxime)	alkaline pH	460	-	Complex is stable for 4 hrs.	11
Thiobenzoyl acetone(3-mercapto-1-phenyl-but-2-en-1-one)	8.8 to 9.4	500	Sensitivity is 10 $\mu\text{g cm}^{-2}$	Pb, Cu, Zn, Hg, Pd, Co CN ⁻ BDTA interfere	32
2-mercapto-4-thiochrome	5 to 10	415	Sensitivity is 3 $\mu\text{g cm}^{-2}$	W(VI), V(VI), Mo(VI), Fe(II) Cu(II), Fg(II) interfere.	33
Thiothenayl trifluoro-acetone	5.5 to 6	450	$\epsilon = 35000$	Oxalgle, citrate, EDTA interfere.	34
2-and 3-hydroxy benzo-phenone	8.5 to 9	590	-	U, Al, Fe, Th, Cu & Co masked by EDTA	35
Sodium purpurin sulphonate	8.1	520	-	Co(II) strongly interfere	36
Alizarin maroon and Eosin	5 to 5.6	585	$\epsilon = 14000$	CN ⁻ interfere seriously	37
5-chloro-2-pyridyl-azo-o-cresol	1 M NH ₃	620	$\epsilon = 26000$	Many cations do not interfere	38
1,5-bis-(2-carboxy-methoxy phenyl)-3-phenyl formazan.	pH 6	620	$\epsilon = 33000$	Cu masked with thiourea	39

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Table 3.1 contd....

1	2	3	4	5	6
2-(p-Sulphophenylazo)-1,8-dihydroxy naphthalene 3,6-Disulphonic acid	2.5 to 7	575	$\epsilon = 7.0 \times 10^3$ sensitivity is $0.05 \mu\text{g cm}^{-2}$	Zn(II), Fe(III), Cd(II), Al(III), Zr(IV), F ⁻ citrate interfere.	40
4-hydroxy-3-nitroso naphthalene-1-sulphonic acid	8.6	307	-	Not sensitive but selective	41
2'-hydroxy acetophenone oxime	7	375	$\epsilon = 4100$	-	42
Acenophthene quinone monoxime	8.5	430	Sensitivity is $0.0047 \mu\text{g cm}^{-2}$	Selective	43
3-(o-Acetophenyl)-1-phenyl-triazine-N-oxide	7.5	435	$\epsilon = 1.09 \times 10^4$	Thiosulphate strongly interfere	44
Thiosalicylidene ethylene diimine	3.0 to 3.5	505	$\epsilon = 2760$	Many cations and anions interfere.	45
1-(2-thiozolyazo)-2-naphthol	4.7 to 10	595	Sensitivity is $0.0015 \mu\text{g cm}^{-2}$	Zn, Co, Cu, Bi, V masked by P ₂ O ₄ ⁴⁻	46
Di-2-pyridyl ketone thiosemicarbazone	6 to 6.9	395	$\epsilon = 1.96 \times 10^4$	-	47
Picolinaldehyde-4-phenyl-3-thiosemicarbazone	8.0 to 9.0	390	-	Not selective due to interference from many cations.	48
4-aryl-1-benzoyl-thiosemicarbazone	8.0 to 10.0	-	-	1:2 complex	49
Quinoline-2-aldehyde	7.5	460	sensitivity is $0.0097 \mu\text{g cm}^{-2}$	Au(II), Pb(II) and SCN ⁻	50

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Table 3.1 contd....

1	2	3	4	5	6
2-4-Dihydroxy acetophenone thiosemicarbazone	6.2 to 6.8	385	Sensitivity is $0.016 \mu\text{g cm}^{-2}$	Co(II), Fe(III), Cr(III) Cu(II) interfere.	51
Biacetyl monoxime 4-phenyl 3-thiosemicarbazone	5.2 to 10.0	375	$\epsilon = 17000$	-	52
Phthalimide dithiosemicarbazone	9.5 to 10.0	440	$\epsilon = 1.13 \times 10^4$	Common ions do not interfere	55
Salicylaldehyde thiosemicarbazone	6.5 to 7.0	970	$\epsilon = 0.98 \times 10^4$	-	56
Thiovioluric (5-hydroxy imino-2-thiobarbituric) acid.	8.5 to 9.1	375	-	Co, Fe, Cu, Rh, Pt, EDTA PO_4^{3-} interfere	57
1-(2-naphthyl)-3-(2-pyridyl) thiourea	4.9 to 10.2	460	Sensitivity is 1.6 mg cm^{-2}	No interference from Cu, Hg, Fe(II), Al, Zn, Mn.	58
Benzyltrimethyl tetradecyl ammonium chloride	8.5 to 9.5	500	Sensitivity is $0.85 \mu\text{g cm}^{-2}$	-	59
6-carboxy-6'-hydroxy-3',5'-di methyl azobenzene-4-sulphonic acid	7.5	520	$\epsilon = 8700$	Fe(III), Zn, Mn, Cu, Co, interfere	60
5-(3,5-dibromo-2-pyridylazo)-2,4-diaminotoluene	4.8	587	$\epsilon = 1.17 \times 10^5$	-	61
2;2'-dipyridylglyoxal bis (4,4-diphenyl semicarbazone)	4.5 to 10.6	420	1-12 $\mu\text{g}/10 \text{ ml}$	Co is interfere seriously.	62
4-Amino-5-nitrosopyrimidine -2,6-diol	highly acidic medium	390	$\epsilon = 1.64 \times 10^4$	1:2 complex	62

thiosemicarbazone⁵⁰, 2-4-Dihydroxy acetophenone thiosemicarbazone⁵¹, 4-phenyl-3-thiosemicarbazone biacetyl monoxime⁵², phthalaldehyde thiosemicarbazone⁵³, biacetylmonoxime thiosemicarbazone⁵⁴, phthalimide dithiosemicarbazone⁵⁵, salicylaldehyde thiosemicarbazone⁵⁶, are being used for photometric determination of nickel.

The summary of the reported methods for photometric determinations of nickel is given in Table 3.1. The present work accounts for the spectrophotometric determination of nickel(II) by 2-chloroquinoline-3-carbaldehyde thiosemicarbazone (QAT). Nickel(II) gives yellow coloured complex with 2-chloroquinoline-3-carbaldehyde thiosemicarbazone (pH 6, λ_{\max} 420 nm). Beer's law is obeyed upto 3 ppm of nickel(II) at 420 nm. The effect of pH, reagent concentration and diverse ions have been studied. The molar absorptivity and sandell sensitivity are $1.504 \times 10^3 \text{ L mole}^{-1} \text{ cm}^{-1}$ and $0.039 \mu\text{g cm}^{-2}$ respectively. Cd(II) and Pd(II) interfere seriously while Bi(II), Mo(VI), EDTA, Fluoride tolerated upto 200 ppm. The dissociation constant of the complex is 7.704×10^{-11} .

EXPERIMENTAL

All the chemicals used were of A.R. grade.

Standard Nickel(II) solution

A stock solution of nickel(1 mg/ml) was prepared by dissolving A.R. grade nickel ammonium sulphate hexahydrate in distilled water. It was standardised with EDTA volumetrically⁶⁴.

Further dilution for experimental purposes were made by diluting the stock solution with distilled water.

Reagent solution :

0.26 gm of QAT was dissolved in DMF and water (1:1) and diluted to 100 ml. The molarity of the resulting solution is 1.0×10^{-2} .

Buffer solution :

Buffer solutions required were prepared as described in Chapter II.

Recommended Procedure :

To an aliquot of the solution containing upto 10 ppm of nickel(II), add 1.5 ml of 1.0×10^{-2} M reagent solution and a buffer solution of pH 6 (sodium acetate-acetic acid). Dilute this to 10 ml with DMF and water (3:2) in a volumetric flask. Measure the absorbance against reagent blank.

RESULTS AND DISCUSSION

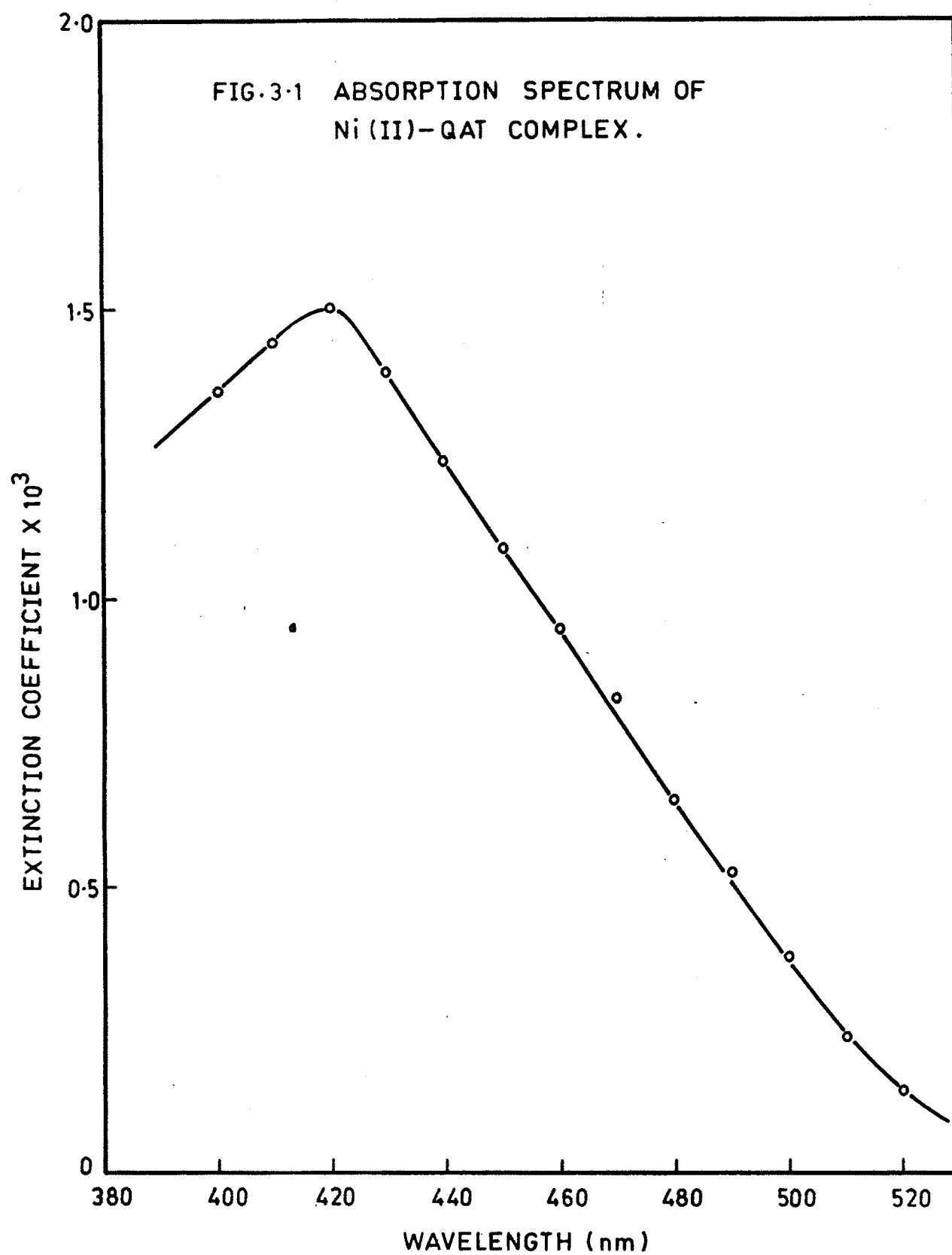
Spectral Characteristics :

Fig.3.1 shows the absorption spectrum of the nickel(II)-QAT complex containing 1.694×10^{-4} M of nickel(II) and 1.0×10^{-3} M of reagent at pH 6 using reagent blank. Absorption measurements were made in the spectral region 395 to 520 nm and recorded in

Table 3.2. From the graph, it was found that 420 nm will be suitable wave length for nickel determination. The molar absorptivity of the complex is $1.504 \times 10^3 \text{ L mole}^{-1} \text{ cm}^{-1}$ at 420 nm.

Table 3.2 Molar extinction coefficients of Ni(II) QAT complex
 (QAT) = $1.0 \times 10^{-3} \text{ M}$, pH = 6
 Ni(II) = $1.69 \times 10^{-4} \text{ M}$.

Wave length nm	Molar extinction coefficient of complex $\times 10^3 \text{ L mole}^{-1} \text{ cm}^{-1}$
395	1.321
400	1.357
405	1.387
410	1.445
415	1.479
420	1.504
425	1.445
430	1.387
435	1.298
440	1.180
445	1.0911
450	0.9441
460	0.8260
470	0.6491
480	0.5310
490	0.3835
500	0.2360
510	0.1489



Effect of time on absorbance :

In order to study the effect of time on the absorbance of nickel(II)-CAT complex containing 1.69×10^{-4} M nickel(II) at pH 6, the absorbance measurements were recorded at different time intervals at 420 nm. It was observed that there is instantaneous development of colour and the absorbance remains constant for 21 hours and decreases after that. Hence the complex is stable for 21 hrs.

Effect of Reagent Concentration :

Solutions containing the same amount of nickel (1.694×10^{-4} M) but different amounts of reagent varying from 0.2 to 1.5 ml of 1.0×10^{-2} M reagent solutions were prepared. The pH 6 buffer was added and the solution was made upto 10 ml with DMF: water (3:2). Absorbance measurements were recorded at 420 nm. against the simultaneously prepared reagent blank. The data given in the Table 3.3, Fig.3.2 shows that 1.694×10^{-4} M nickel(II) solution required minimum 0.8 ml of 1.0×10^{-2} M reagent solution for maximum complexation. At higher concentration of the reagent, there was insignificant increase in the absorbance. However, 1.5 ml of 1.0×10^{-2} M reagent solution was employed for further studies to ensure maximum colour intensity of the nickel complex.

Table 3.3 Effect of reagent concentration on the absorbance of Ni-QAT complex

$$(\text{Ni}) = 1.69 \times 10^{-4} \text{ M}$$

$$(\text{QAT}) = 1.0 \times 10^{-2} \text{ M}$$

Reagent ml	Absorbance at 420 nm
0.2	0.060
0.3	0.095
0.4	0.125
0.5	0.150
0.6	0.175
0.7	0.225
0.8	0.250
0.9	0.255
1.0	0.255
1.2	0.250
1.5	0.255

Effect of pH :

A series of solutions containing 1.69×10^{-4} M nickel(II) and 1.0×10^{-3} M of the reagent but varying in the pH from 3 to 9 were prepared and the absorption measurements were recorded at 420 nm. The results are summarised in Table 3.4. It was observed that maximum absorbance was obtained at the

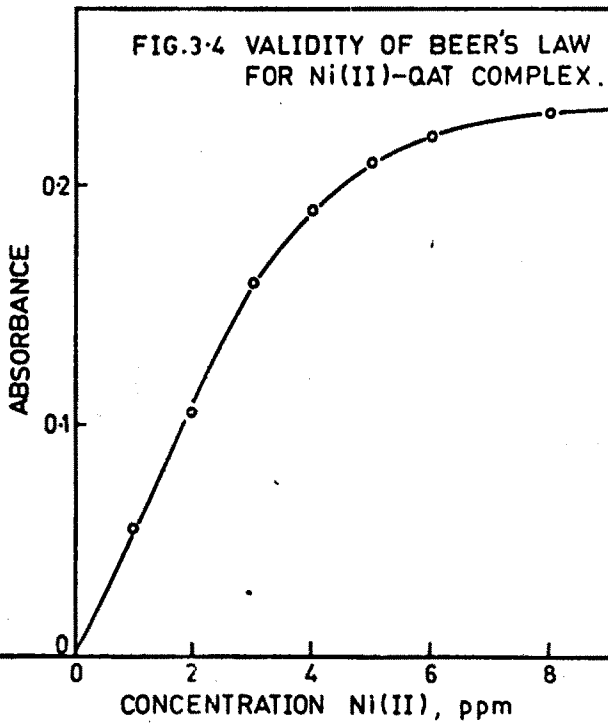
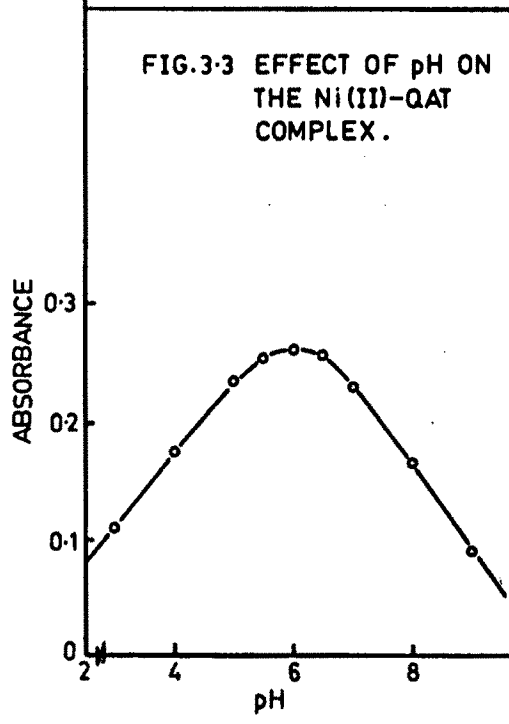
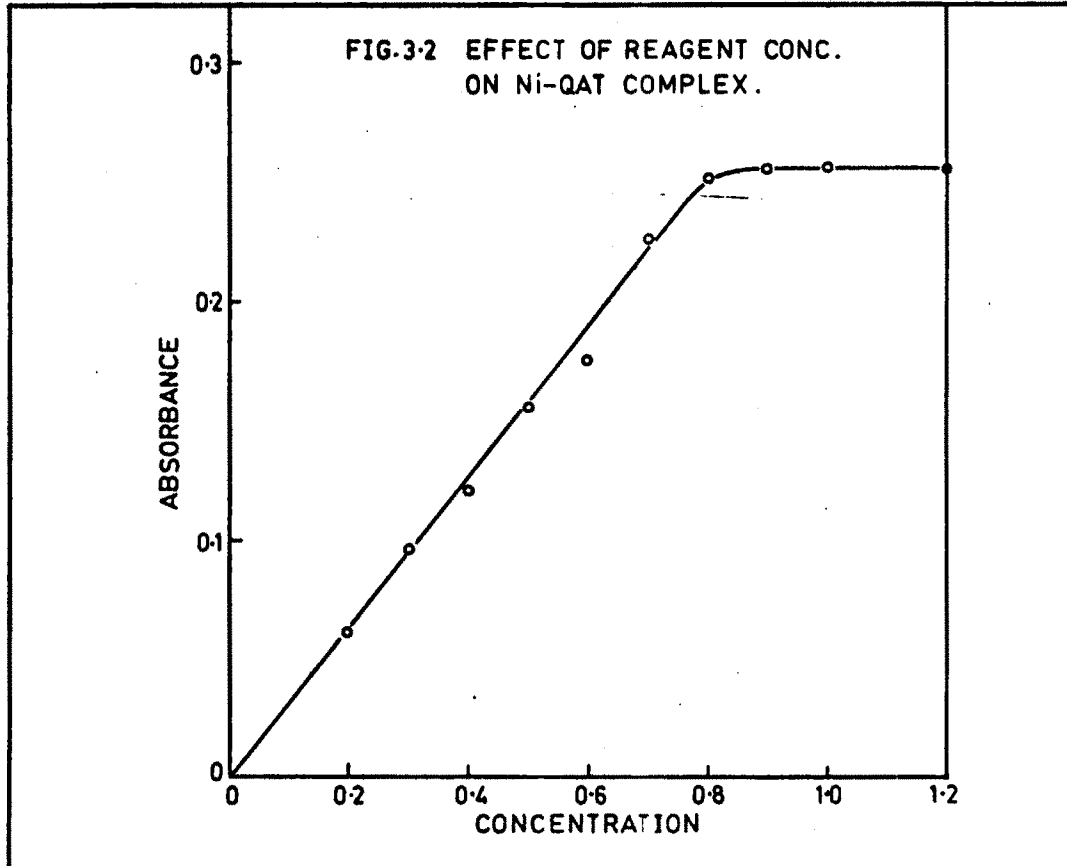
pH 6. The absorbance of the solutions decreases at higher or lower pH values than this which is shown in Fig.3.3. Hence the pH 6 was maintained in further studies.

Table 3.4 Effect of pH on the absorbance of Ni(II) - QAT complex
(Ni) = 1.69×10^{-4} M (QAT) = 1.0×10^{-3} M

pH	Absorbance at 420 nm
3.0	0.110
4.0	0.175
5.0	0.235
5.5	0.255
6.0	0.260
6.5	0.255
7.0	0.230
8.0	0.165
9.0	0.090

Validity of Beer's law and sensitivity

The solutions (final volume 10 ml) containing different amounts of nickel (II) (range of final concentration 1.7032×10^{-5} M to 1.3626×10^{-4} M) and the same amounts of reagents (Final concentration 1.0×10^{-2} M) with the pH maintained at 6 were used for the study. The absorption



measurements were recorded against the reagent blank at 420 nm. (Table 3.5, Fig.3.4) Beer's law is obeyed upto a concentration of 3 ppm of nickel(II). The Sandell sensitivity⁶⁵ of the reaction is $0.039 \mu\text{g cm}^{-2}$ of Ni(II) at 420 nm for $\log \frac{I_0}{I} = 0.001$

Table 3.5 Varification of validity of Beer's law for
Ni - QAT complex
(QAT) = 1.0×10^{-2} M

Nickel taken in ppm	Absorbance at 420 nm
1	0.055
2	0.105
3	0.160
4	0.190
5	0.210
6	0.220
8	0.230
10	0.265

Composition of the complex :

The combining ratio of metal to ligand (reagent) was ascertained by Job's method of continuous variations⁶⁶ and Mole ratio method⁶⁷. For Job's method of continuous variation, a series of solutions were prepared by mixing equimolar solutions of nickel(II) and the reagent (6.83×10^{-3} M). The pH of the solution was adjusted to 6. The absorbances

of the solutions \times after diluting to 10 ml in volumetric flask were recorded at 420 nm against simultaneously prepared reagent blank (Fig.3.5, Table 3.6). The plot indicates the existence of 1:2 complex with respect to metal and reagent represented as ML_2 .

Table 3.6 Determination of the formula of the Ni-QAT complex by Job's method of continuous variation.
(Ni) = (QAT) = 6.83×10^{-3} M

Metal ion ml	Reagent ml	Mole fraction of metal	Absorbance at 420 nm
0.1	0.9	0.1	0.110
0.2	0.8	0.2	0.135
0.3	0.7	0.3	0.155
0.4	0.6	0.4	0.145
0.5	0.5	0.5	0.120
0.6	0.4	0.6	0.090
0.7	0.3	0.7	0.065
0.8	0.2	0.8	0.04
0.9	0.1	0.9	0.03

For mole ratio method, solutions containing the same final metal concentration (6.83×10^{-4} M) and different amounts of the reagent ranging from 1.366×10^{-4} to 9.562×10^{-4} M. concentration were prepared keeping the pH 6. Absorbances of the solutions were measured at 420 nm against the reagent

blank. The curve showed break at the metal to ligand ratio 1:2, confirming the results obtained by the application of Job's method of continuous variation (Fig.3.6, Table 3.7). The dissociation constant of the complex K is calculated by using following equation,

$$K = \frac{\alpha c(n\alpha c)^n}{c(1-\alpha)} \quad \text{and} \quad \alpha = \frac{(A_m - A_s)}{A_m}$$

The value of K comes out to be 7.704×10^{-11}

Table 3.7 Determination of the formula of Ni-QAT complex by mole ratio method.

$$(\text{Ni}) = (\text{QAT}) = 6.83 \times 10^{-3} \text{ M}$$

Reagent ml	Metal ion ml	R/M ratio	Absorbance at 420 M
0.2	0.4	0.5	0.085
0.4	0.4	1.0	0.115
0.6	0.4	1.5	0.140
0.8	0.4	2.0	0.155
1.0	0.4	2.5	0.170
1.2	0.4	3.0	0.175
1.4	0.4	3.5	0.175

Effect of diverse ions :

The effect of diverse ions was studied using 1.69×10^{-4} M of nickel and 1.0×10^{-3} M reagent in a final volume of 10 ml at

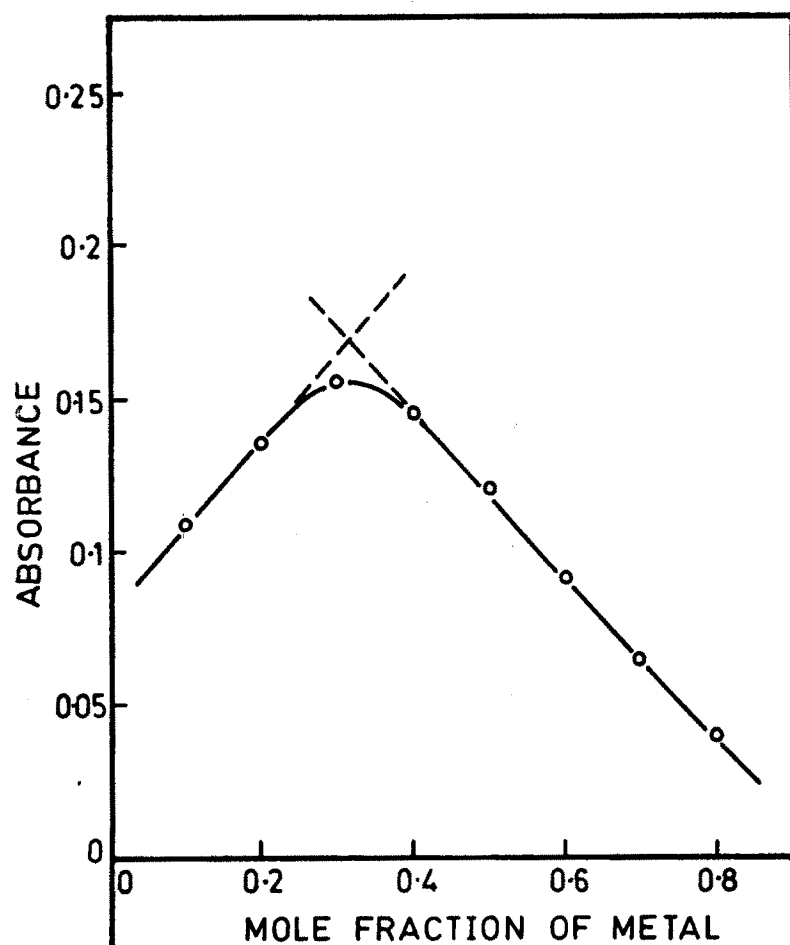
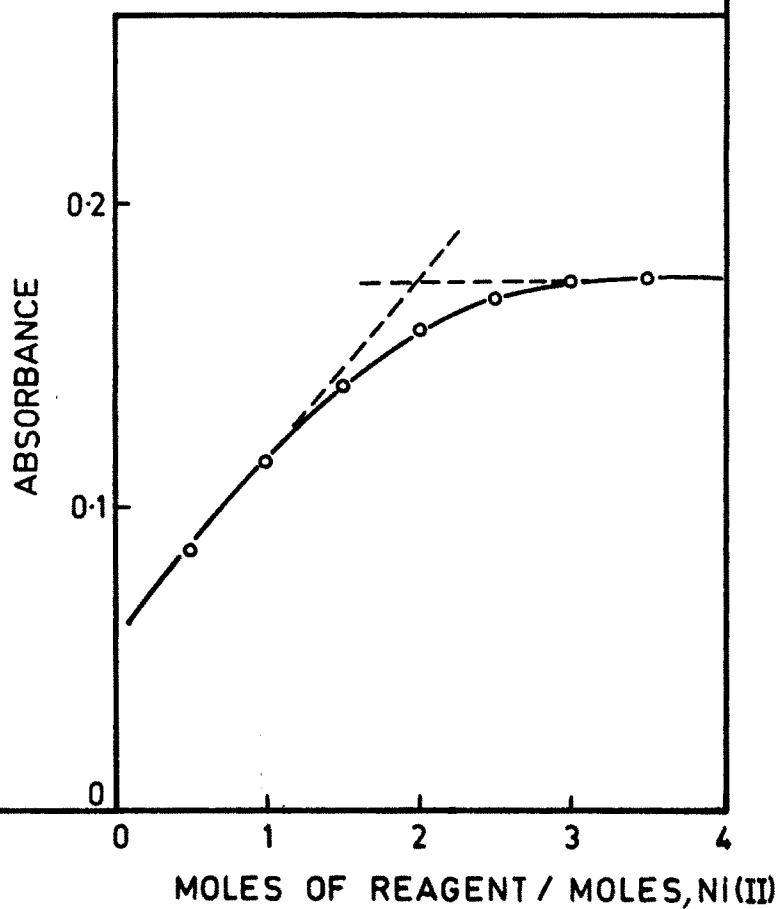


FIG.3-5
JOB'S PLOT FOR Ni(II)-QAT
COMPLEX.

FIG. 3-6
MOLE RATIO PLOT FOR
Ni(II)-QAT COMPLEX.



MOLES OF REAGENT / MOLES, Ni(II)

pH 6. An error less than 2 % in absorbance was considered to be tolerable. The tolerance for the various foreign ions tested has been shown in table 3.8.

Table 3.8 Effect of diverse ion

$$[\text{Ni(II)}] = 1.69 \times 10^{-4} \text{ M}$$

$$(\text{QAT}) = 1.0 \times 10^{-3} \text{ M}$$

Metal ion	Added as	Tolerance limit, ppm	Metal ion	Added as	Tolerance limit, ppm
Mn(II)	MnCl ₂ ·6H ₂ O	50	Cr(VI)	K ₂ Cr ₂ O ₇	10
Sn(II)	SnCl ₂ ·2H ₂ O	10	Mo(VI)	(NH ₄) ₆ Mo ₇ O ₂₄	200
Zn(II)	ZnSO ₄ ·7H ₂ O	10	Cd(II)	CdCl ₂ ·6H ₂ O	None
Mg(II)	MgSO ₄ ·7H ₂ O	15	Fe(III)	FeCl ₃ ·6H ₂ O	15
Al(III)	AlCl ₃ ·6H ₂ O	50	Ce(IV)	Ce(SO ₄) ₂	20
Pb(II)	Pb(NO ₃) ₂	20	Ti(IV)	Titanium oxalate	30
Pd(II)	PdCl ₂ ·2H ₂ O	none	W(vi)	Na ₂ WO ₄ ·2H ₂ O	150
Bi(III)	Bi(NO ₃) ₃ ·5H ₂ O	200	EDTA	Na-EDTA	200
Ca(II)	CaCl ₂	100	tartarate	Na-tartarate	150
Cu(II)	CuCl ₂ ·2H ₂ O	10	Citrate	citric acid	100
Co(II)	CoCl ₂ ·6H ₂ O	30	Acetate	CH ₃ COONa	100
Ba(II)	BaCl ₂ ·2H ₂ O	16	Fluoride	NaF	200
V(V)	NH ₂ VO ₃ ·H ₂ O	15	HPO ₄ ⁻²	Na ₂ HPO ₄	20
U(VI)	UO ₂ (NO ₃) ₂ ·6H ₂ O				

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