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CHAPTER-V

PHOTOMETRIC DETERMINATION OF NICKEL (II) WITH 6-METHYL, 2-CHLOROQUINOLINE 3-CARBALDEHYDE THIOSEMICARBAZONE

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INTRODUCTION :

Several years ago, the determination of a few parts per million of impurity elements in electrolytic nickel was considered more academic than practical. Today, methods such neutron activation and mass spectrometry are being applied in expectation that a few parts per billion may be determined with comparable accuracy. This situation was created largely by demands of the space age for materials of ever higher purity.

Nickel has long been one of the purest of the primary metals used as alloying elements a fact greatly to the credit of the nickel procedures. Much of the primary electrolytic nickel marketed today is better than 99.9 percent pure. Some of the poorer grades marketed, however, may be no better than 99.5 percent pure and may contain upto 20 or 30 different impurity elements.

Chemical and spectrochemical were being developed by the electronic industry as early as the 1930's help to provide the high purity required in thermonic, Cathodes for radio tubes. Despite this, the literature on nickel analysis is not extensive as compared with that of some of the more common metals. Further more, many methods published only a few years ago are inadequate for today's needs as regards limits of detection, Concentration ranges or the number or the number and variety of elements that can be determined in nickel.

The purpose of this book, therefore, is to present the bestmethods available for the analysis of the nickel being marketed today and to discuss some of the methods that may be required for analysis of tomorrow's nickel.

Spectrophotometric determination is better that is, more sensitive and accurate - than other methods for some elements. It is also useful in many cases for substantiating other more rapid methods. The methods described in this chapter include both of these catagories, for some of the elements in nickel. They include procedures developed in the literature for analysis of nickel, and procedures described for other materials but adapted for nickel.

Of the Comprehensive published methods for analysis of nickel, those of ASTM[1,2] the British Standards Institution[3], Luke[4-7] and Andrew and Gentry[8] has also published methods for the analysis of nickel. The methods published by the International Nickel Company, In.,[11] are suitable for analysis of nickel and high nickel alloys on the macro scale.

As most of the methods mentioned above were designed several years ago for the analysis of nickel and nickel alloys used in the electronic and alloy industries, reliable methods for the determination of delerious trace impurities are generally not available. Some such impurities are antimony, arsenic, Selenium, and tellurium. A review of the literature on the determination of boron, Chromium, Magnesium, titanium, and tungsten is given below.

In 1957 Chirnside, Cluley and Profitt[12] proposed a method for the determination of boron, where by the nickel was simultaneously anodically dissolved and cathodically deposited on a pool of Mercury and the resulting solution was analysed by the Curcumin method, Luke[4] dissolved the nickel in a hydrochloric acid-platinic chloride mixture, distilled the boron as methyl borate, and determined it by the curcumin method.

Luke[5] published a method for the determination of chromium in electrolytic nickel. Copper was removed with dithizone; nickel, Cobalt, iron, titanium and aluminium were removed with ammonia in the presence of the perchlorate, ion. After the chromium was oxidized it was determined spectrophotometrically with S-diphenyl-Carbazide. Andrew and Gentry[8] and the British Standards Institution[3] adopted the method of de Lippa[13] for the determination of chromium without prior separation of the elements normally found in electronic nickel. After dis solution of the sample in nitric acid, it was evaporated almost to dryness, and the chromium was oxidized in a dilute sulphuric acid solution by potassium bromate. The chromium was determined spectrophotometrically with S-diphenylcarbazide.

Table - 5.1 : Review of the methods for the Photometric Determination of Nickel (TI)

Reagent	pH	max	Sensitivity molar extinction coefficient range ppm	Interference and remark	Ref
1	2	3	4	5	6
1-hydroxy-2-acetonaphtoneoxime	8.05 to 9.5	396	ϵ =5.75 x 10^3 Sensitivity is 0.01 μg Cm^{-2}	Fe(III),Co(II),Cu(II) V(IV) interfere	14
Nioxime (Cyctohexane 1,2-dione dioxime)	alkaline pH	460	-	Complex is stable for 4 hrs.	25
Thiobenzoyl acetone (3-mercapto-1-phenyl-but-2-en-1-one	8.8 to 9.4	500	Sensitivity is 10 μg Cm^{-2}	Pb,Cu,Zn,Hg,Pd,Co CN$^-$ EDTA interfere	16
2-mercapto-4-thiochrome	5 to 10	415	Sensitivity is 3 μg Cm^{-2}	W(VI),V(VI),Mo(VI) Fe(II),Cu(II),Fg(II) interfere	17
Thiothenayl trifluoroacetone	5.5 6	450	ϵ = 35000	Oxalgle, Citrate, EDTA interfere	18
2-and 3-hydrozy benzo. phenone	8.5 to 9	590	-	U,Al,Fe,Th,Cu,and Co masked by EDTA	19
Sodium purpurin Sulphonate	8.1	520	-	Co(II)strongly interfere	20

1	2	3	4	5	6
Alizarin maroon and Fosin	5 to 5.6	585	$\epsilon = 1400$	CN^- interfere seriously	21
5-Chloro-2-pyridyl-azo-O.Cresol	1M NH_3	620	$\epsilon = 26000$	Many cations do not interfere	22
1,5-bis-(2-carboxy methoxy phenyl)-3-phenyl formazin	pH_6	620	$\epsilon = 33000$	Cumasked with thiourea	23
2-(P-Sulphophenylazo) -1, 8-dihydroxy naphthalena 3,6- Disolphonic acid	2.5 to 7	575	$\epsilon = 7.0 \times 10^3$ Sensitivity is 0.05 $\mu g\ Cm^{-2}$	Zn(II),Fe(III), CD(II), Al(III), Zr(IV), F^- citrate interfere	24
4-hydroxy-3-nitraso naphthalene-1-sulphonic acid	8.6	307	-	Not sensitivite but selective	25
2'-hydroxy acetophenone oxime	7	375	$\epsilon = 4100$	-	26
Acetophthene quinone monoxime	8.5	430	Sensitivity is 0.0047 $\mu g\ Cm^{-2}$	Selective	27

1	2	3	4	5	6
3-(O-Acetopheny)-1 Phenyl-triazine-N-oxide	7.5	435	$\epsilon = 1.09 \times 10^{4}$	Thiosulphate strongly interfere	28
Thiosalicylidene ethylene diimine	3.0 to 3.5	505	$\epsilon = 2760$	Many cations and anions interfere	29
1-(2-thiozolylazo) 2-naphthol	4.7 10	595	Sensitivity is 0.0015 μg Cm^{-2}	Zn,Co,Cu,Bi,V masked by by $P_2 O_4^{-4}$	30
Di-2-pyridyl ketone thiosemicarbazone	6 to 6.9	395	$\epsilon = 1.96 \times 10^{4}$	-	31
Picolinaldehyde-4-phenyl-3-thiosemicarbazone	8.0 to 9.0	390	-	Not selective due to interference from many cations	32
4-aryl-1-benzoyl-thiosemicarbazone	8.0 to 10.0	-	-	1:2 complex	33
Quinoline-2-aldehyde	7.5	460	Sensitivity is 0.0097 μg Cm^{-2}	Au(II),Pb(II) and SCN^{-}	34
2-4-Dihydroxy acetoph-enone thiosemicarbazone	6.2 6.8	385	Sensitivity is 0.016 μg Cm^{-2}	Ca(II),Fe(II),Cr(III), Cu(II) interfere	35

1	2	3	4	5	6
Biacetyl monoxime-4-Phenyl -3-thiosemicarbazone	5.2 to 10.0	375	ϵ = 17000	-	36
Phthalimide dithiosemicarbazone	9.5 to 10.0	440	ϵ = 1.13 x 10^{-4}	Common ions do not interfere	37
Salicylaldehyde thiosemicarbazone	6.5 to 7.0	970	- 0.98 x 10^{4}	-	38
Thiovioluric (5-hydroxy imino-2-thiobarbituric) acid	8.5 to 9.1	375	-	Co,Fe,Cu,Rh,Pt, EDTA, PO_4^{-3}	39
1-(2-naphtyl)-3-(2-pyridyl thiourea	4.9 10.2	460	Sensitivity is 1.6 μg Cm^{-2}	No interference from Cu,Hg,Fe(II)Al,Zn,Mn	40
Benzyltrimethyl tetradedyl ammonium chloride	8.5 9.5	500	Sensitivity is 0.85 μg Cm^{-2}	-	41
6-Carboxy-6'-hydroxy -3', 5'-dimethyl azo benzene-4-sulphanic acid	7.5	520	ϵ = 8700	Fe(III) Zh,Mn,Cu,Co, interfere	42

1	2	3	4	5	6
5-(3,5-dibromo-2-pyridylazo) -2 4-diaminotoluene	4.8	587	ϵ = 1.17 x 10^5	-	43
2,2'-dipyridylglyoxalbis (4,4-diphenyl semicarbazone)	4.5 to 10.6	420	1-12 µg/10 ml	Co is interfere Seriously	44
4-Amino-5-nitrosopyrimidine-2,6 diol	highly acidic medium	390	ϵ = 1.64 x 10^4	1:2 complex	45

The summary of the reported methods for Photometric determinations of nickel is given in Table 5.1. The present work accounts for the spectrophotometric determination of nickel (II) by 6-Methyl-2-Chrloroquinoline 3- Carbaldehyde thiosemicarbazone (6-Me-QAT). Ni(II) gives yellow coloured complex with 6-Methyl-2-Chloroquinoline 3-Carbaldehyde thiosemicarbazone (pH 8 λmax- 408 nm). Beer's law is obeyed upto 6 ppm of nickel (II) at 408 nm. The effect of pH, reagent concentration and diverse ions have been studied. The molar absorptivity and Sandell sensitivity are 3.120×10^4 L $Mole^{-1}$ Cm^{-1} and 0.039 μg Cm^{-2}. The dissociation constant of the complex is 7.704×10^{-11}

EXPERIMENTAL

Standard Nickel(II) Solutions :

A stock solution of nickel (1mg/ml) was prepared by dissolving Nickel sulphate hexahydrate in distilled water. It was standardised with EDTA volumetrically[46]. Further dilution for experimental purposes were made by diluting the stock solution with distilled water.

Reagent Solution :

0.055 gm. 6-Me-QAT was dissolved in DMF and water (1:1) and diluted to 100 ml. The molarity of the solution is 2.676×10^{-4} M. The solution is found to be stable for more than a week.

Recommended Procedure :

To an aliquot of solution containing upto 2.5 ppm Nickel, add 1.2 ml of 2.676×10^{-4} M reagent solution and a buffer solution of pH 8. Dilute to this to 10 ml with DMF and water (3:2) in a volumetric flask. Measure the absorbance against reagent blank.

RESULTS AND DISCUSSION

Special Characteristics :

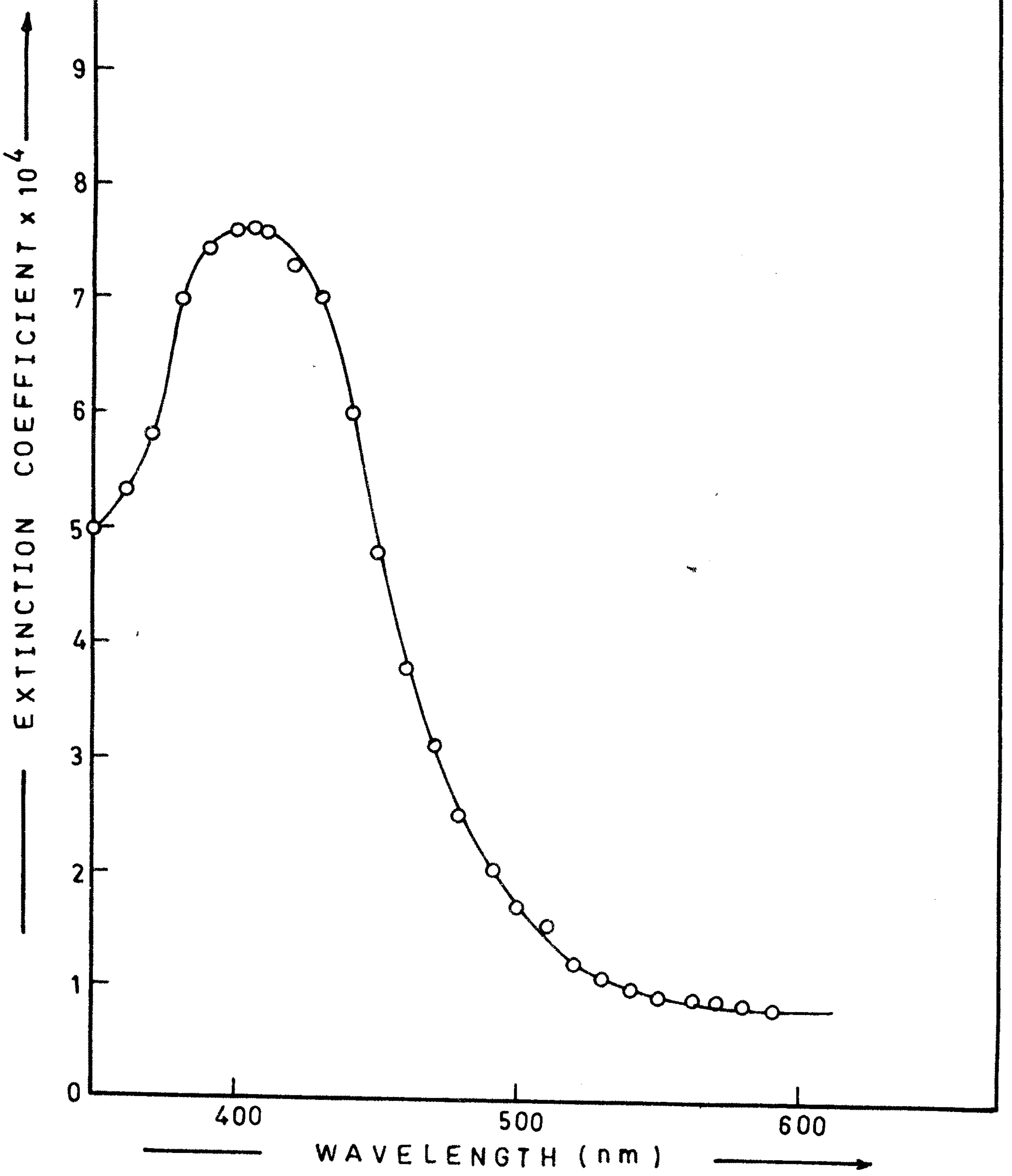
Figure 5.1 shows the absorption Spectrum of the Nickel (II) 6-Me-QAT complex containing 1.690×10^{-3} M of Nickel and 2.676×10^{-4} M reagent at pH 8 using reagent blank. Absorption measurements were made in the spectral region 350 nm to 600 nm and recorded in table 5.2. From the group it was found that 408 nm will be suitable wavelength for the Nickel determination. The molar absorptivity of the complex is 7.680×10^{2} L Mol^{-1} Cm^{-1} at 408 nm.

Table 5.2

Molar Extinction Coefficient of Ni(II) -6-Me-QAT Complex

λ nm	Molar Ext.Coefficient of complex 10^4 L $Mole^{-1}$ Cm^{-1}
350	4.911
360	5.331
370	5.810
380	6.994
390	7.408
390	7.408
400	7.662
408	7.680
410	7.680
420	7.366
430	6.698
440	5.828
450	4.804
460	3.869
470	3.983
480	2.57
490	2.088
500	1.704
510	1.449
520	1.254
530	1.124
540	1.035
550	0.9704
560	0.9349
570	0.8994
580	0.8757
590	0.8579
600	0.8284

FIG. 5·1 — ABSORPTION SPECTRUM OF Ni(II) - 6Me - QAT COMPLEX.



Effect of Time on Absorbance :

In order to study effect of time on the absorbance of Nickel (II) 6-Me-QAT complex containing 1.690×10^{-3} M Ni(II) at pH 8, the absorbance measurements were recorded at different time intervals at 408 nm. It was observed that there is instantaneous development of colour and the absorbance remains constant for 24 hours and decreases after that. Hence the complex is stable for atleast 24 hours.

Effect of Reagent Concentration :

Solutions containing the same amount of Nickel (1.690×10^{-3} M) but different amounts of reagent varing from 0.2 to 1.2 ml of 2.676×10^{-4} M reagent solution were prepared. The pH 8 buffer was added and the solution was made upto 10 ml with DMF Water (3:2). Absorbance measurements were recorded at 408 nm against the simultaneously prepared reagent blank. The data given in Table (5.3 fig. 5.2) shows that 1.690×10^{-3} M Nickel solution required minimum 1 ml of 2.676×10^{-4} M reagent solution for maximum complexation. At higher concentration of the reagent there was insignificant increase in absorbance. However, 1.2 ml of 2.676×10^{-4} M reagent solution was employed for further studies to ensure, maximum colour intensity of the Nickel complex.

Table 5.3

Effect of Reagent Concentration on the Absorbance of Ni(II) 6-Me-QAT Complex.

(Ni) = 1.690 x 10^{-3} (6-Me-QAT) = 2.676 x 10^{-4} M

pH = 8

Reagent ml	Absorbance at 408 nm
0.2	0.060
0.3	0.095
0.4	0.125
0.6	0.150
0.7	0.175
0.8	0.225
0.9	0.250
1.0	0.255
1.2	0.255

Effect of pH :

A series of Solutions Containing 1.690 x 10^{-3}M. Ni(II and 2.676 x 10^{-4} M of the reagent but varying in pH from 9 to 10 were prepared and the absorption measurements were recorded at 408 nm. The results are summarised in Table 5.4. It was observed that maximum absorbance was obtained at the pH 8. The absorbance of the solutions decrease at higher or lower pH values than this which is shown in figure 5.3. Hence the pH 8 was maintained in further studies.

Table 5.4

Effect of pH on the Absorbance of Ni(II) 6-Me-QAT Complex
(Ni) = 1.690 x 10^{-3}; 6-Me-QAT = 2.676 x 10^{-4} M

pH	Absorbance at 408 nm
1	0.073
2	0.085
3	0.134
4	0.183
5	0.246
6	0.300
7	0.255
8	0.230
10	0.165

Validity of Beer's Law and Sensitivity :

The solution (final volume 10 ml) containing different amounts Nickel and the same amounts of reagnet with the pH maintained at pH 8 were used for the study. The absorption measurements were recorded against reagent blank at 408 nm. (Table 5.5 fig. 5.4) Beer's law is obeyed upto a concentration of 8 ppm of Nickel (II). The sandell snesitivity of the reaction is 0.039μgcm^{-2} of Ni(II). The Ringbom's plot (fig 5.5) indicates that the optimum range is 2 to 3 ppm of Nickel (II).

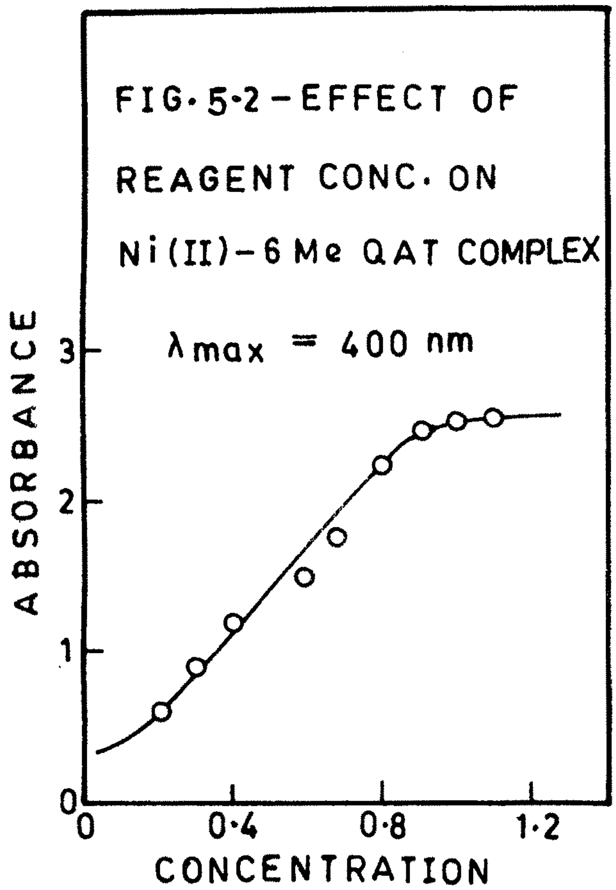


FIG. 5.2 – EFFECT OF REAGENT CONC. ON Ni(II)-6 Me QAT COMPLEX

λ_{max} = 400 nm

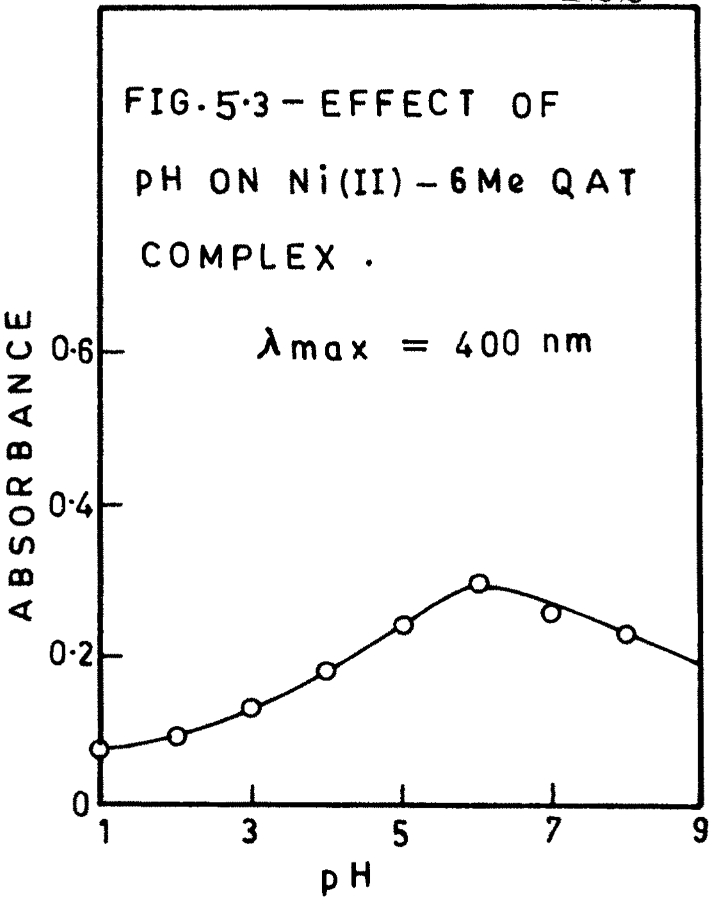


FIG. 5.3 – EFFECT OF pH ON Ni(II) – 6Me QAT COMPLEX.

λ_{max} = 400 nm

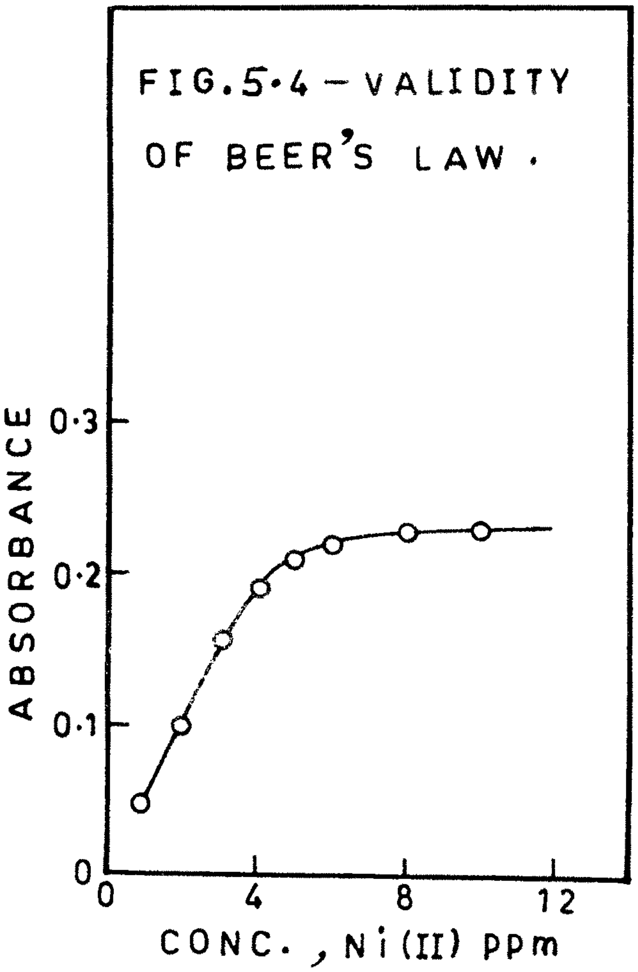


FIG. 5.4 – VALIDITY OF BEER'S LAW.

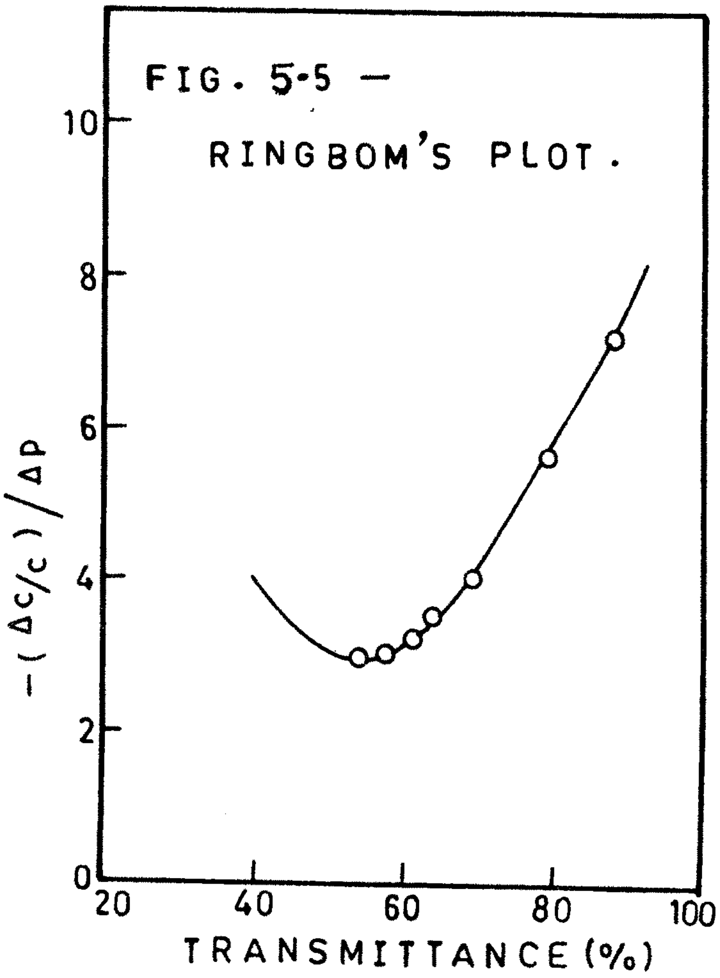


FIG. 5.5 – RINGBOM'S PLOT.

Table 5.5

Verification of Validity of Beer's Law

6-Me-QAT = 2.676×10^{-3} M, pH 8.

Ni taken ppm	Absorbance at 408 nm
1	0.055
2	0.105
3	0.160
4	0.190
5	0.210
6	0.220
8	0.230
10	0.230

Composition of the Complex :

The Comb ining ratio of metal to reagent was ascertained by Job's method of continuous variations[47] and mole ratio method[48]. For Job's method of continuous variation a series of solution were prepared by mixing equimolar solutions of Nickel (II) and the reagent (2.676×10^{-4}M). The pH of the solutions was adjusted to 8. The absorbance of the solutions after diluting to 10 ml in volumetric flask were recorded at 408 nm against simultaneously prepared reagent blank (Table 5.6 fig. 5.6.) The plot indicates the existance of 1:1 complex with respect to metal and reagent represented as ML.

Table 5.6

Determination of the formula by Job's method of Continuous Variation.

(Ni) = (6-Me-QAT) = 2.676×10^{-3}M, pH = 8

Metal ion ml	Reagent ml	Mole fraction of metal	Absorbance at 408 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

The dissociation constant of the complex K, is calculated from the mole ratio plot by using the following equation :

$$K = \frac{\alpha c \; (n\alpha c)}{c \; (1 - \alpha)}$$

Where n = 1

C = Molarity of the solution of complex and

α = degree of dissociation defined by

$$= \frac{AM - As}{AM}$$

Am is maximum absorption obtained from horizontal portion of the curve and As is the absorbance of stoichiometric molar ratio of reagent to Nickel in the complex. The value of K comes out to be 7.704×10^{-11}

Mole Ratio Method :

For mole ratio method, solutions, containing the same final metal concentration (2.676×10^{-3}M) and different amounts of reagent ranging from concentration were prepared keeping pH 8. Absorbance of the solutions were measured at 408 nm against reagent blank. The curve showed break at the metal to ligand ratio 1:1, confirming the results obtained by application of Job's method of continuous variations (Table 5.7 Fig. 5.7)

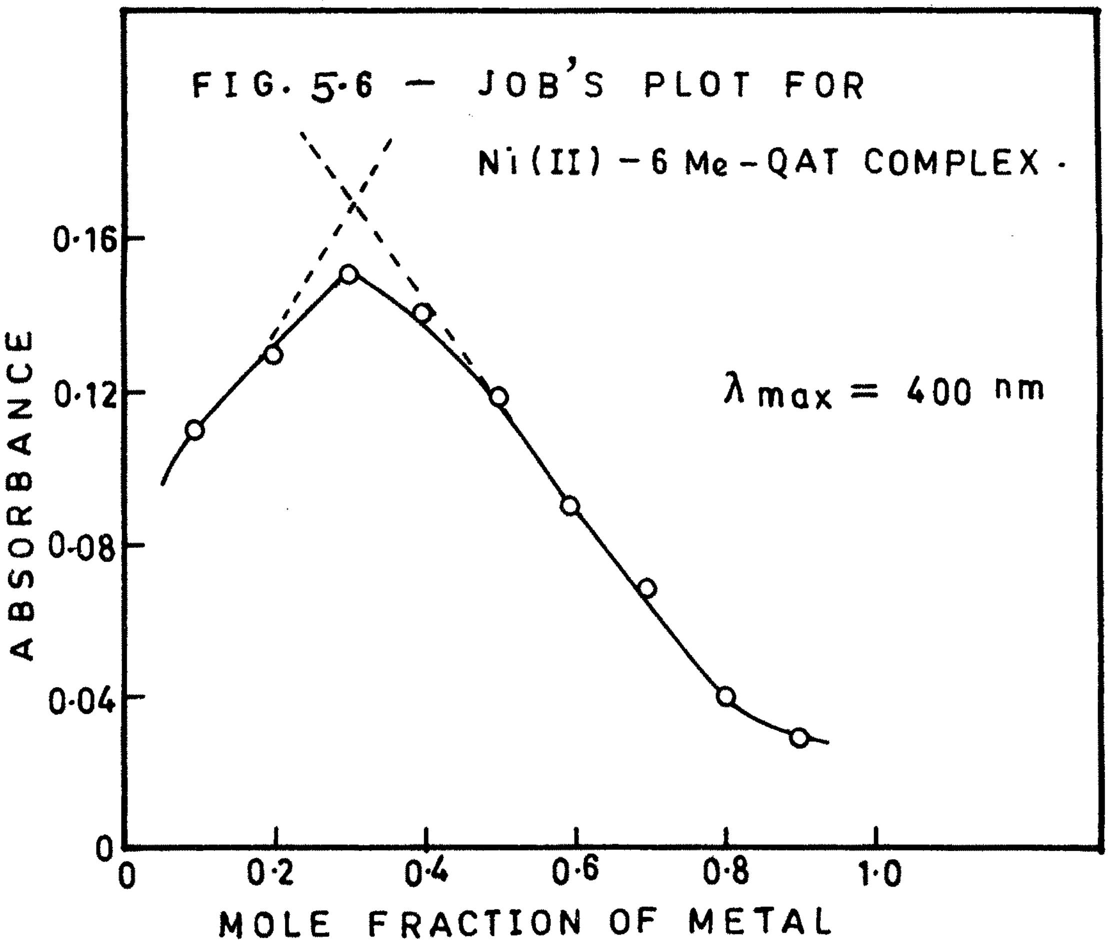


FIG. 5·6 — JOB'S PLOT FOR Ni(II) – 6 Me – QAT COMPLEX.

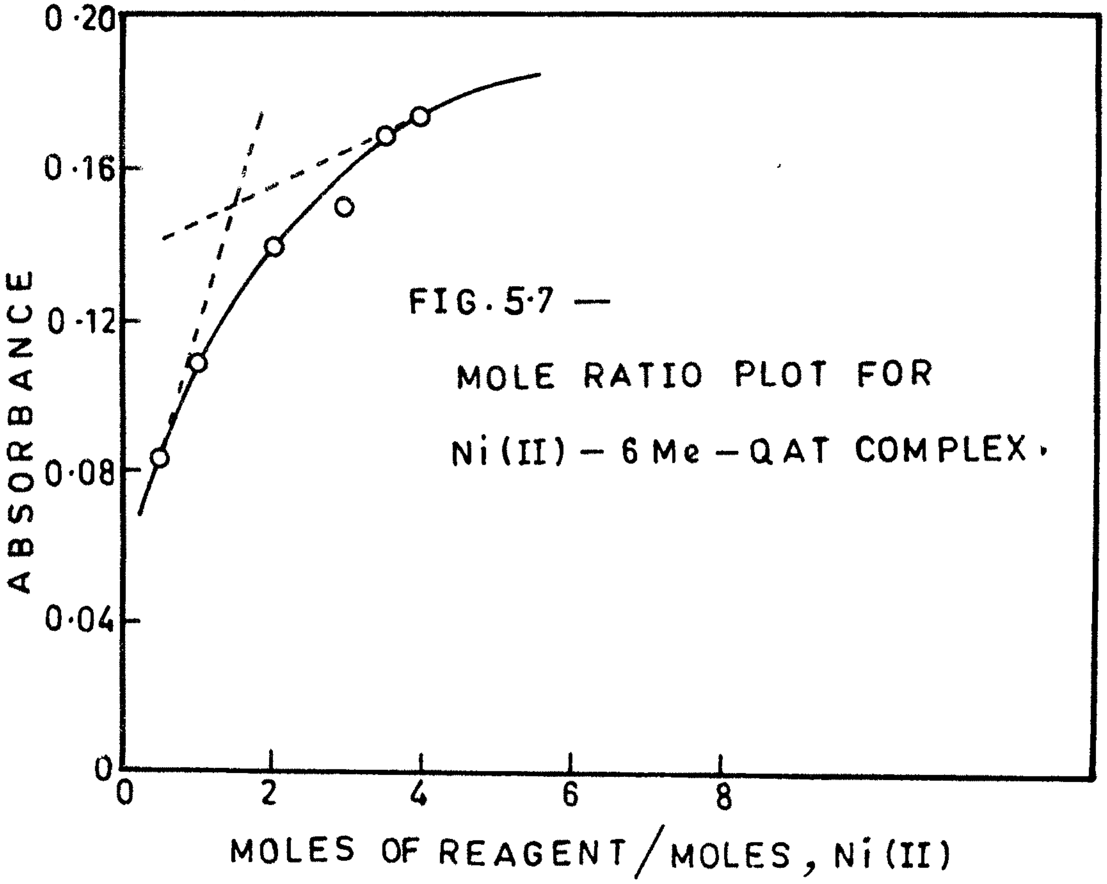


FIG. 5·7 — MOLE RATIO PLOT FOR Ni(II) – 6 Me – QAT COMPLEX.

Table 5.7

Determination of the formula of Ni(II) 6-Me-QAT complex by mole Ratio method.

(Ni) = (Q-Me-QAT) = 2.676×10^{-3} M,

pH = 8

Metal ion ml	Reagent ml	Reagent to metal ratio	Absorbance at 400 nm
0.4	0.2	0.5	0.085
0.4	0.4	1.0	0.115
0.4	0.8	2.0	0.140
0.4	1.2	3.0	0.155
0.4	1.4	3.5	0.170
0.4	1.6	4.0	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 pH 8. 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 ions

Ni(II) = 1.69×10^{-4}M

6-Me-QAT = 1.0×10^{-3} M

Metal ion	Tolerence limit PPm
Mn(II)	50
Sn(II)	10
Pb(II)	20
Pd(II)	none
Bi(III)	200
Cr(VI)	10
Mo(VI)	200
EDTA	200
Fluoride	200
Ba(II)	16
Ca	100
Cu	10
Al	50
Zn(II)	10
Mg(II)	15
Acetate	100
Citrate	150

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