CHAPTER - V

DETERMINATION OF NICKEL

5.1 INTRODUCTION

White, tough, lustrous, ductile, fairly hard, high melting (1450^o) and high boiling (2730^o), nickel is closely akin to cobalt and iron. Nickel is one of the most commonly used elements. The familiar use of nickel is as a coinage metal. Its corrosion-resistant bright alloys with copper and zinc were once popular for household utensils. Today it is an important constituent of steel, designed for toughness and is used as decorative "nickel plate" on iron and steel. Although pure nickel displays quite good electrical conductance, its alloys with Cu (constantan), with Mn and Cu (manganin) and with Cr (nichrome) are very poor electrical conductors and are very useful as electrical resistors and "heating elements." Several industrial catalysts contain variable proportions of nickel.

Although several organic reagents have been proposed for the photometric determination of nickel, each has its own limitations and relatively few of them are recommended in the standard works,[1,2] and many are not available commercially. Only a few reagents have specific applications, desired sensitivity and selectivity.

Methods involving rubeanic acid[3], 4-isopropylcyclohexane-2:2-dione dioxime,[4] nicotinamidoxime,[5] cycloheptane 1:2 - dione dioxime,[6] calcichrome[7] and chlorindazon DS[8] are all time consuming due to slow rate of formation of complex. Reagents like solochrome red ERS[9] and 1-(2-pyridylazo)-2-naphthol require elevated temperature for complex formation. 6-Nitro quinoline dithiol[11] has been recently reported as a colorimetric reagent.

The most commonly used reagents for photometric determination of nickel (II) are oximes and dioximes such as dimethylglyoxime,[12-15] furil-α-dioxime,[16-22] α-benzoin oxime,[23] azonaphthols, dithizone and dithiols. But in extraction with DMG, nioxime,[24,25] 4-isopropyl-1,2-cyclohexanedionedioxime,[26] diethyldithiocarbamate,[27] potassium dithiooxalate,[28] thiotropolone[29] and dithiosalicylic acid,[30] many cations interfere seriously. Quinoxaline-2,3-dithiol[31,32] suffer from the instability of the reagent and its insolubility in most solvents.

Thiosemicarbazones of some aldehydes and ketones are also promising new spectrophotometric reagents for nickel. Recently introduced important reagents are azonaphthols or their substituted derivatives such as PAN[33-36] or TAN,[37] isopentyl esters[38] and thenoyltrifluoroacetone.[39,40] CHDT,[41] PAT,[42] phthalaldehyde thiosemicarbazone,[43] biacetylmonoxime thiosemicarbazone[44] are being used for photometric determination of nickel.

Complex salts of Ni(II) with schiff bases derived from aminoguanidine and o-hydroxy acetophenone[45] have been prepared and characterized on the basis of analytical UV and IR data. In our laboratory the reaction between nickel and o-hydroxy acetophenone guanylhydrazone was investigated and a new spectrophotometric method for estimation of nickel is presented in this chapter.

The proposed reagent o-hydroxy acetophenone guanylhydrazone readily forms a yellow complex with nickel in aqueous medium. The method is simple and rapid. The results are reproducible. As the complex ion has high value of molar extinction coefficient, the method is suitable for determination of nickel at tracer level.

5.2 EXPERIMENTAL

All the chemicals used were of analytical grade.

5.2.1 Standard solutions :

Standard Nickel Solution :

A stock solution of nickel (1 mg/ml) was prepared by dissolving A.R. grade nickel chloride hexahydrate in distilled water containing a few mls of concentrated hydrochloric acid. It's nickel content was determined gravimetrically by dimethyl glyoxime[46] method. Further dilutions for experimental purposes were done with distilled water.

Reagent Solution :

A stock solution of the reagent o-hydroxy acetophenone guanylhydrazone (HAG) was prepared by dissolving 192 mg of it in 100 ml distilled water (1.92 mg/ml i.e. 0.01 M).

Buffer Solution :

Buffer solution of pH 11 was prepared by dissolving appropriate amount of sodium carbonate.

5.2.2 Recommended Procedure :

An aliquot of the solution containing about 10 µg of Ni(II) was taken in a 10 ml volumetric flask. To this 2.5 ml of reagent (HAG) solution of concentration 0.01 M was added. The pH of the solution was adjusted to 10.5 by adding 0.8 ml of buffer solution of pH 11 and was diluted upto to mark with distilled water. The absorbance of the complex was measured from 350 to 520 nm against reagent blank, prepared in the same manner excluding metal ion. The concentration of nickel was determined from standard calibration curve obtained under identical conditions.

5.3 RESULTS AND DISCUSSION

5.3.1 Spectral Characteristics :

The absorption spectrum of Nickel(II)-HAG complex of the solution containing 10 µg of Ni(II) [1 ml of 0.01 mg/ml i.e. 1.703×10^{-4} M] and 2.5 ml of 0.01 M reagent (HAG) against the reagent blank was recorded at pH 10.5. The absorption spectrum shows a peak with an absorption maximum at 380 nm. At this wavelength the colourless reagent solution has no significant absorption. The molar extinction coefficient at 380 nm is 0.882×10^{4} l mole^{-1} cm^{-1}. The complex is stable for 60 minutes. Absorption spectra of the complex and reagent are shown in figure 5.1. The observations for the spectra are given in table 5.1

Table 5.1 : Molar extinction coefficients of the Ni(II)-HAG complex and the reagent HAG

Wavelength λ, nm	Molar extinction coefficients, ϵ	
	Ni(II)-HAG Complex $\epsilon \times 10^4$ l mole^{-1} cm^{-1}	Reagent, HAG $\epsilon \times 10^4$ l mole^{-1} cm^{-1}
350	0.411	0.0300
360	0.647	0.0176
370	0.823	0.0100
375	0.863	0.0078
380	0.882	0.0058
390	0.705	0.0041
400	0.689	0.0036
410	0.423	0.0033
420	0.108	0.0030
430	0.055	0.0026
440	0.032	0.0023
450	0.020	0.0020
460	0.017	0.0016
470	0.011	0.0015
480	0.011	0.0011
490	0.008	0.0010
500	0.0058	0.0008
510	0.0058	0.0005
520	0.0058	0.0005

5.3.2 Effect of pH :

The effect of variation in pH on the absorbance of Ni(II)-HAG complex was studied over the pH range 2.0 to 13.0. The complex has maximum and constant absorbance over the pH range 10.0 to 11.0. Therefore, pH 10.5 was selected as the optimum pH for further studies. The observations are given in table 5.2 (Fig. 5.2).

Table 5.2 : Effect of pH

pH	Absorbance at 380 nm
2.0	0.005
3.0	0.006
4.0	0.006
5.0	0.006
6.0	0.007
8.0	0.28
9.0	0.60
10.0	1.30
10.5	1.30
11.0	1.30
12.0	1.10
13.0	1.08

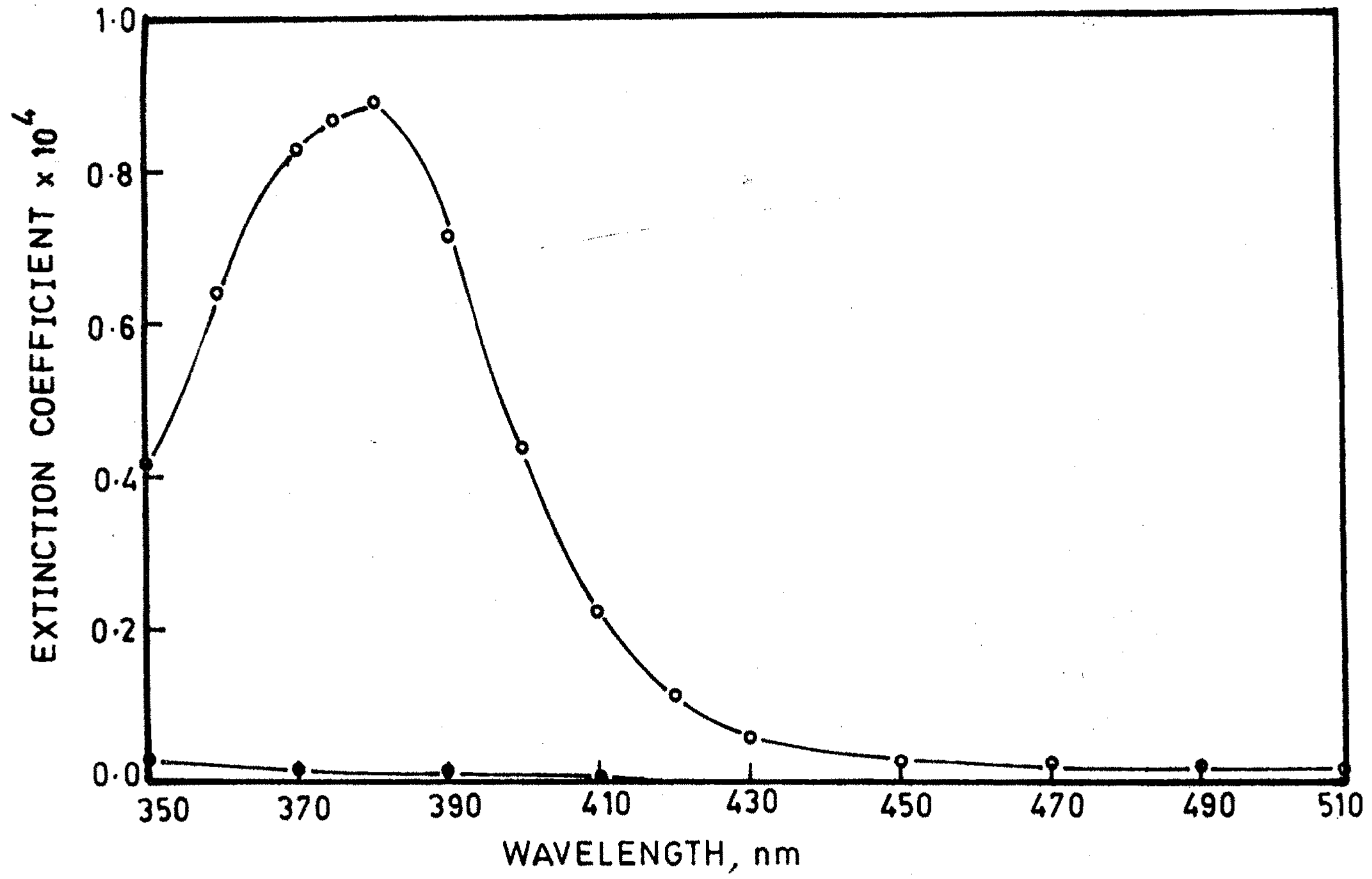


FIG.5·1- ○—○ ABSORPTION SPECTRUM OF NICKEL-HAG COMPLEX.
●—● ABSORPTION SPECTRUM OF REAGENT (HAG).

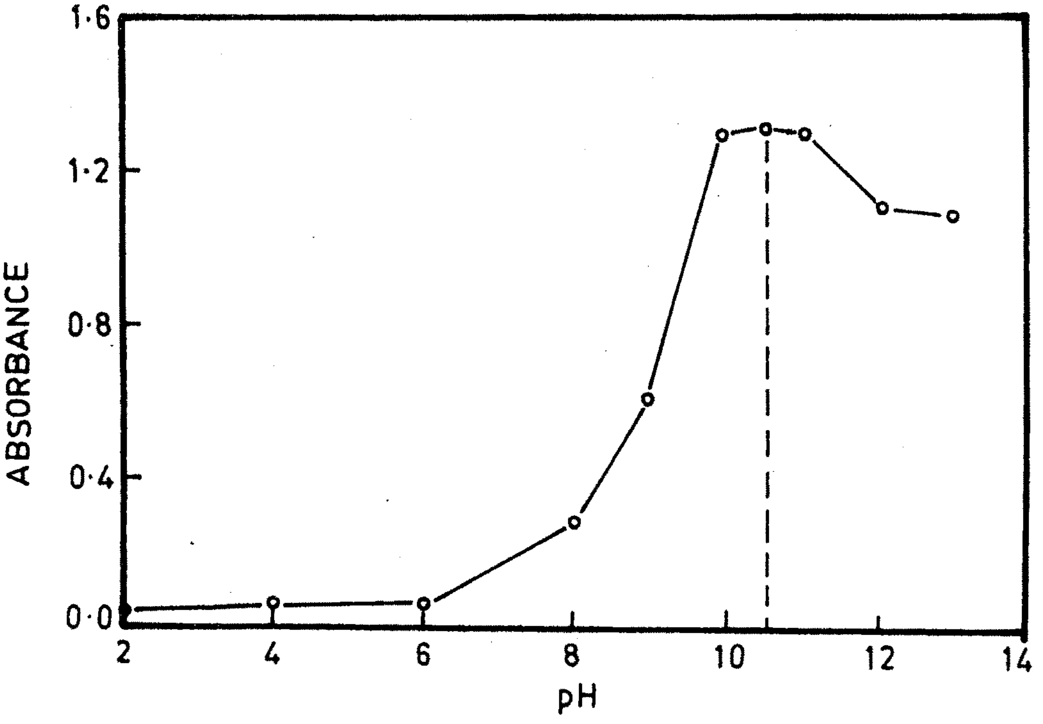


FIG. 5·2- EFFECT OF pH.

5.3.3 Effect of reagent concentration :

A series of solutions was prepared in which the volume of 0.01 M reagent was varied from 0.5 to 4.0 ml in which concentration of nickel was kept constant at 10 ppm. The complex is developed as per recommended procedure. The results in table 5.3 show that four times the molar excess of the reagent is sufficient for full colour development.

Table 5.3 : Effect of reagent concentration

[Ni(II)] = 10 ppm; (HAG) = 0.01 M

ml of reagent [HAG]	Absorbance at 380 nm
0.5	0.7
1.0	1.1
1.5	1.3
2.0	1.4
2.5	1.5
3.0	1.5
3.5	1.5
4.0	1.5

5.3.4 Stability and reaction rate :

Nickel(II)-HAG complex is stable for several hours and complex formation is instantaneous.

5.3.5 Validity of Beer's Law :

The measurement of the absorbance at 380 nm from the solution containing various amounts of nickel showed that Beer's law is valid upto 22 ppm of Ni(II) (Table 5.4, Fig. 5.3).

The optimum concentration range of nickel was determined from the Ringbom plot[47] (Fig. 5.4) and found to be 3.75 to 11.75 ppm.

Table 5.4 : Validity of Beer's Law
$[Ni(II)] = 1.7 \times 10^{-4}M$; $[HAG] = 10 \times 10^{-2}M$.

Amount of Nickel(II) ppm	Absorbance at 380 nm
5	0.30
10	0.62
15	0.88
20	1.15
25	1.35
30	1.45

5.3.6 Composition of the Complex :

The composition of Ni(II)-HAG complex was determined by Job's method of continuous variation[48] (Table 5.5), molar ratio method[49] (Table 5.6) and slope ratio method.[50] For these methods, equimolar solutions of the concentration 1.703×10^{-3} M were used. Job's curves at 375 nm, 380 nm, 390 nm and 400 nm are shown in fig. 5.5 which show the formation of 1:2 complex of Ni(II)-HAG. This composition is confirmed by mole ratio study (Fig. 5.6) and slope ratio study.

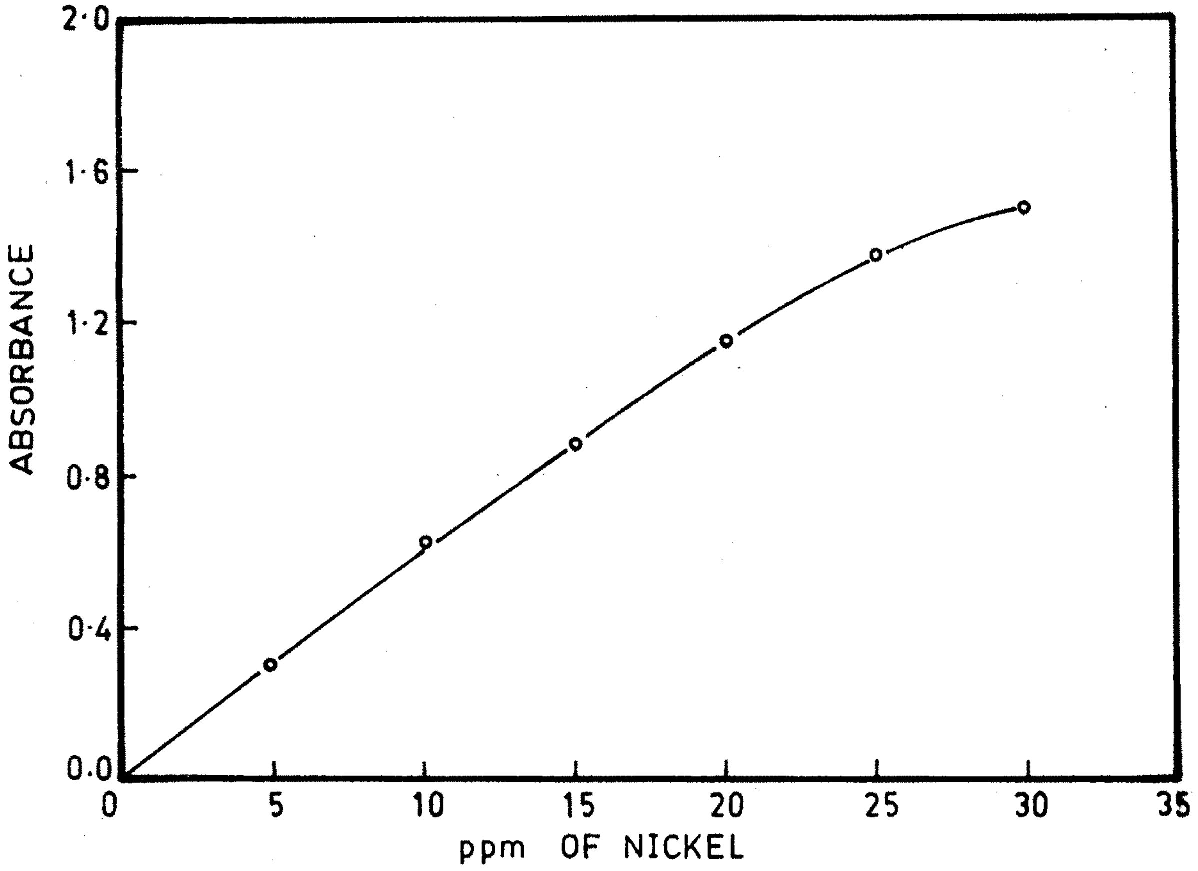


FIG. 5·3 — VALIDITY OF BEER'S LAW.

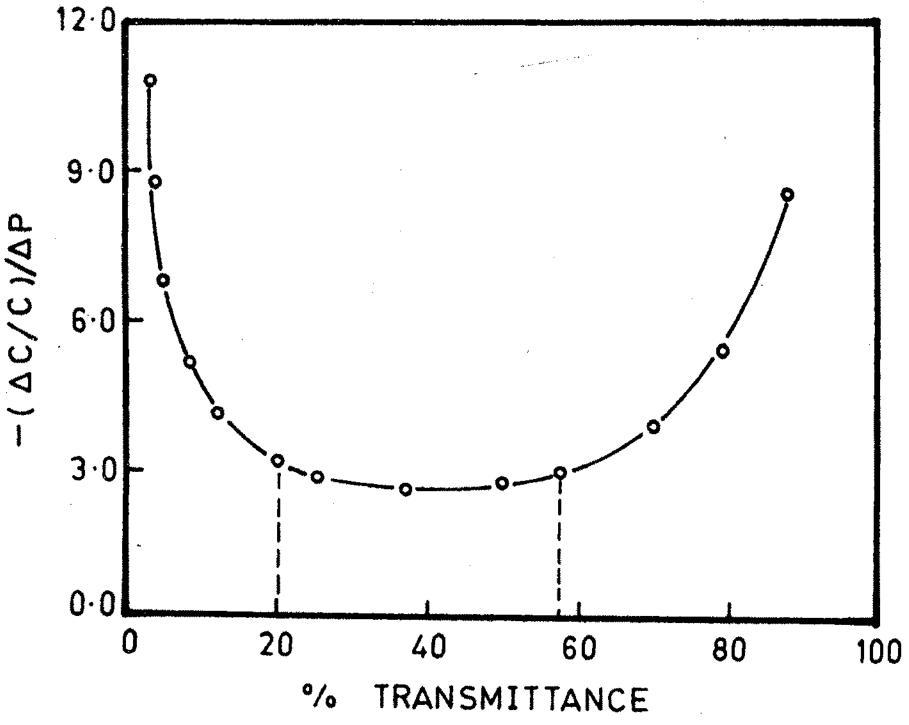


FIG. 5·4 — RINGBOM PLOT.

Table 5.5 : Job's continuous variation method

$[Ni(II)] = [HAG] = 1.703 \times 10^{-3} M$

Nickel(II) ml	Reagent (HAG) ml	Molar Ratio M:L	Absorbances at λ			
			375 nm	380 nm	390 nm	400 nm
0.0	1.8	-	-	-	-	-
0.2	1.6	1:8	0.06	0.08	0.04	0.02
0.4	1.4	2:7	0.22	0.28	0.15	0.08
0.6	1.2	1:2	0.33	0.40	0.22	0.13
0.8	1.0	4:5	0.30	0.34	0.20	0.11
1.0	0.8	5:4	0.23	0.28	0.16	0.09
1.2	0.6	2:1	0.18	0.22	0.13	0.06
1.4	0.4	7:2	0.12	0.15	0.09	0.04
1.6	0.2	8:1	0.06	0.07	0.04	0.02
1.8	0.0	-	-	-	-	-

Table 5.6 : Molar ratio method

$[Ni(II)] = [HAG] = 1.703 \times 10^{-3}$ M

Nickel(II) ml	Reagent (HAG) ml	Molar Ratio M:L	Absorbances at λ	
			380 nm	400 nm
0.0	2.0	-	-	-
0.2	2.0	1:10	0.025	0.020
0.4	2.0	1:5	0.060	0.045
0.6	2.0	3:10	0.090	0.070
0.66	2.0	1:3	0.130	0.095
0.8	2.0	2:5	0.165	0.115
1.0	2.0	1:2	0.180	0.135
1.2	2.0	3:5	0.200	0.145
1.33	2.0	2:3	0.205	0.150
1.4	2.0	7:10	0.205	0.160
1.6	2.0	4:5	0.210	0.165
1.8	2.0	9:10	0.210	0.170
2.0	2.0	1:1	0.215	0.175

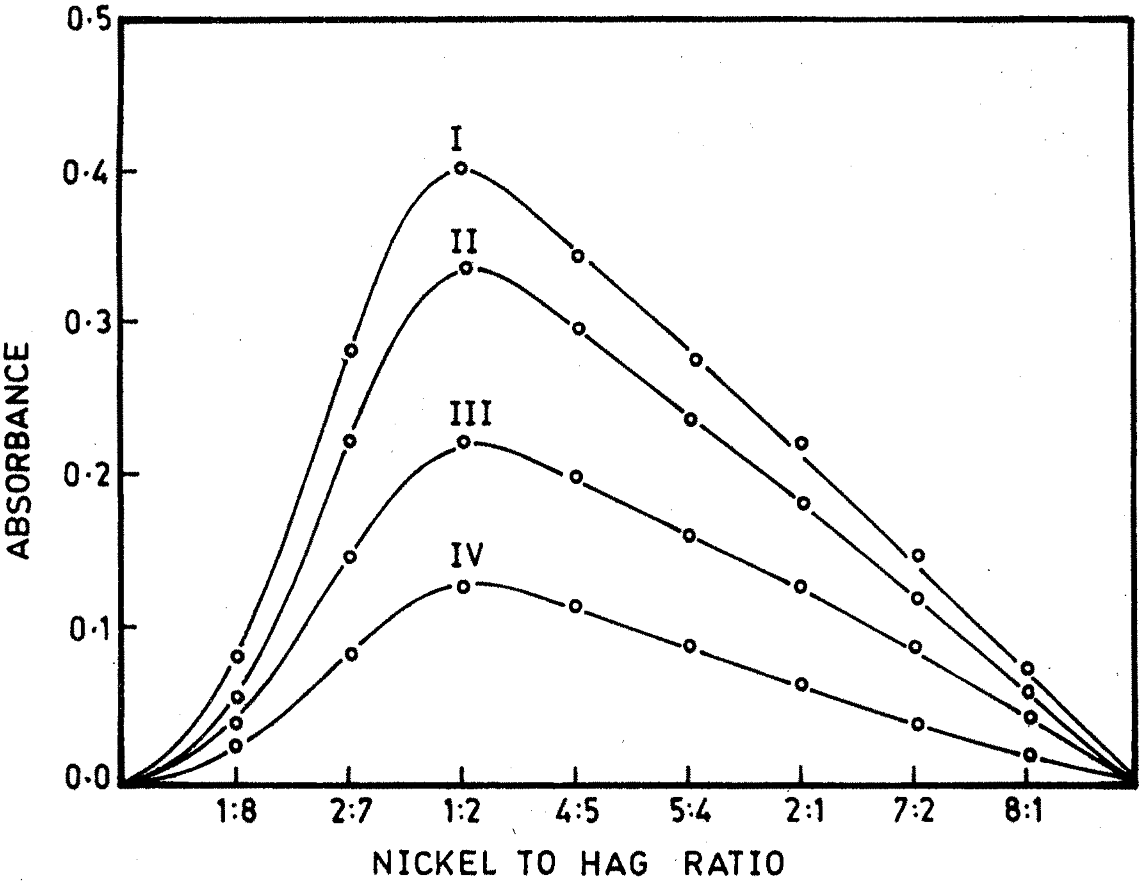


FIG. 5·5 – JOB'S CONTINUOUS VARIATION METHOD
I – 380 nm , II – 375 nm , III – 390 nm , IV – 400 nm .

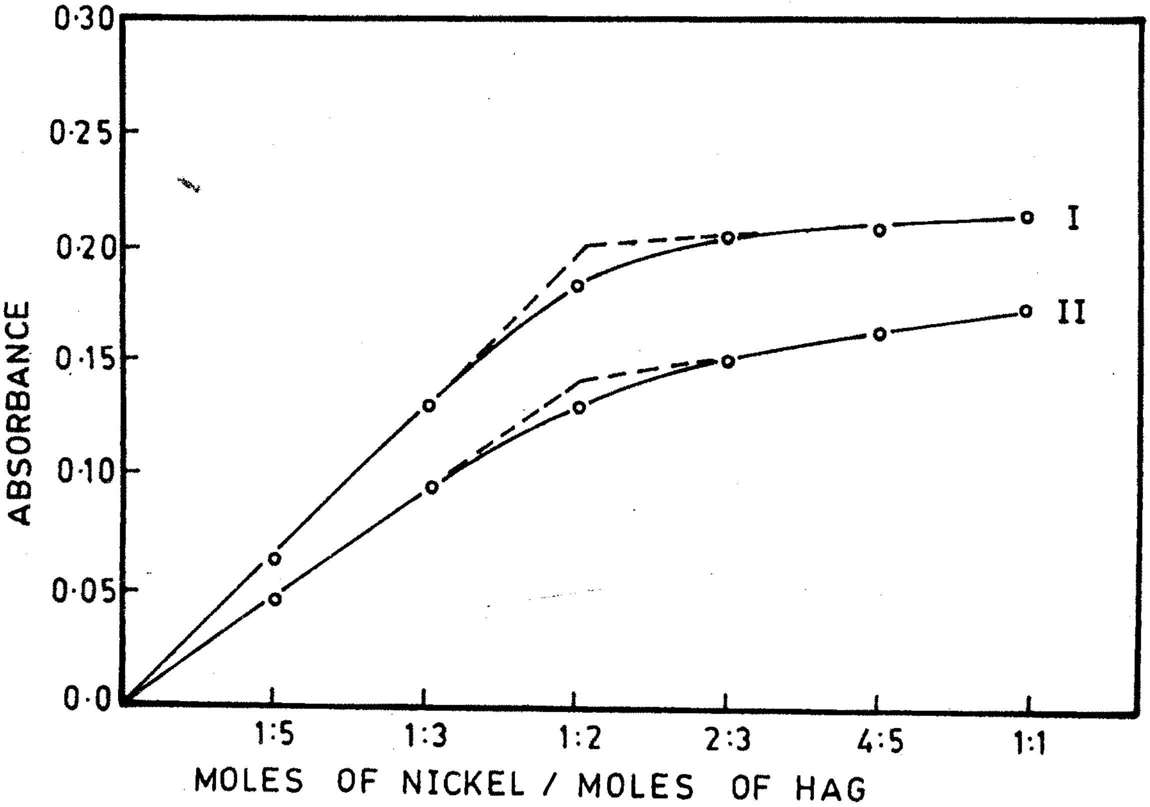
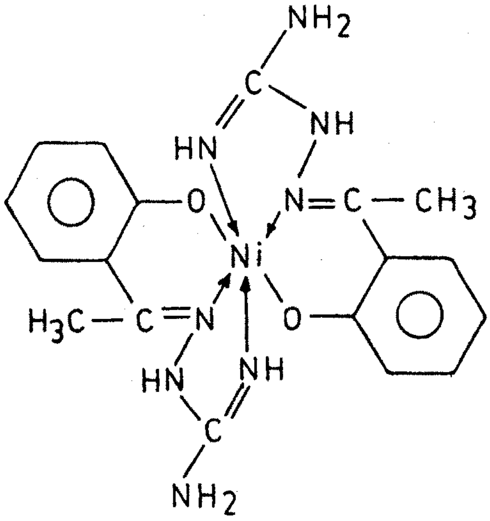


FIG. 5·6 – MOLE RATIO METHOD.
I – 380 nm , II – 400 nm .

The probable structure for Ni(II)-HAG complex is



5.3.7 Sensitivity :

The nickel complex of HAG does not show sensitivity towards light. The photometric sensitivity of the method was calculated by the method of Sandell[51] and found to be 0.02694 μg/cm^2 at 380 nm.

5.3.8 Degree of dissociation and instability constant :

The degree of dissociation was obtained by the method of Harvey and Manning.[50] The value of α, degree of dissociation was found to be 0.075.

The apparent instability constant[52] was found to be 5.288×10^{-13} for Ni(II)-HAG complex. The change in free energy[53] of the system is -16.850 K cals/mole.

5.3.9 Reproducibility of method :

In order to study the reproducibility of the present method, different amounts of nickel were determined. The results in table 5.7 show that the method is reproducible. The standard deviation of the method calculated for six readings with different amounts of nickel are given in table 5.7.

Table 5.7 : Reproducibility of the method :

Nickel(II) ppm	Mean absorbance of six observations	Standard deviation	Coefficient of variation %
4.5	0.28	0.0025	0.8929
9.0	0.55	0.0046	0.8363
13.5	0.83	0.0078	0.9397
18.0	1.13	0.0098	0.8672

5.3.10 Effect of diverse ions :

The effect of diverse ions was studied by using 1.0 ppm of nickel and 2.5 ml of 1.0×10^{-3} M reagent. The complexes were developed as per the recommended procedure and the absorbances were measured. The results indicate that Fe(III), Co(II), Cd(II), Cr(VI), citrate and tartrate ions interfere seriously, while the tolerance limits of thiourea, urea and acetate ion are 550.0, 580.0 and 80.0 ppm respectively. For various foreign ions, the tolerance limits are given in table 5.8.

Table 5.8 : Effect of diverse ions
$[Ni(II)] = 1.0$ ppm; $[HAG] = 1.0 \times 10^{-3}M$

Foreign ions	Added as	Tolerance limit ppm
Cations		
Cr(III)	$CrCl_3 \cdot 6H_2O$	0.2
V(IV)	$VOSO_4 \cdot H_2O$	0.8
Ba(II)	$BaCl_2 \cdot 2H_2O$	1.0
Cu(II)	$CuSO_4 \cdot 5H_2O$	0.7
Ca(II)	$Ca(NO_3)_2 \cdot 4H_2O$	0.2
Zn(II)	$ZnSO_4 \cdot 7H_2O$	0.1
Mn(II)	$MnSO_4 \cdot H_2O$	0.1
Pd(II)	$PdCl_2$	0.1
Fe(III)	$FeCl_3 \cdot 6H_2O$	none
Co(II)	$Co(NO_3)_2 \cdot 6H_2O$	none
Cd(II)	$CdSO_4 \cdot 8/3\ H_2O$	none
Cr(VI)	$K_2Cr_2O_7$	none
Anions		
Citrate	Citric acid	none
Thiourea	Thiourea	550.0
Oxalate	Potassium oxalate	8.0
$EDTA^{-4}$	Disodium salt	1.00
Urea	Urea	580.0
Acetate	Sodium acetate	80.0
Tartrate	Tartaric acid	none

5.4 APPLICATIONS

Analysis of nickel(II) in nickel steel :

A known weight 0.5 g of the sample of nickel steel (No. 22 a, B.A.S. England) was dissolved in 10 ml of concentrated sulphuric acid and 50 ml water with mild heating. A few drops of concentrated nitric acid was added carefully. The resulting solution was evaporated to dryness. 5.0 ml of hydrochloric acid was added and heated for further 15 minutes and diluted it to 100 ml with distilled water.

A suitable aliquot of the solution was taken. Excess hydrochloric acid from aqueous solution was removed by evaporation. The aqueous solution was used for the determination of nickel as per the recommended procedure. Results are given in table 5.9.

Table 5.9 : Analysis of nickel steel

Alloy	Certified value of Ni %	Experimental value of Ni, %	Relative standard deviation for six observations
22 a B.A.S. England	3.0	2.88	0.04

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