CHAPTER - IV

DETERMINATION OF NICKEL*

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4.1 INTRODUCTION

Nickel is one of the most commonly used elements. There is tremendous development and expansion of industries with important uses of it, as its alloys and compounds. Nickel is extensively used in nickel plating. It finds many applications in industry including a variety of steels, stainless steel, resistance alloys like nichrome, constantum and manganin, alloys for heating elements, alloys for cutlery and coins. Several inudstrial catalysts contain variable proportions of nickel.

Several organic reagents have been proposed for the photometric determination of nickel, but relatively few of them are recommended in the standard works[1,2] and many are not available commercially. Only a few reagents are selective and sensitive.

Very commonly used reagents for spectrophotometric determination of nickel(II) are oximes, dioximes, azonapthols, dithizone and dithiols. Dimethylglyoxime[3], nioxime,[4,5] 4-isopropyl-1,2-cyclohexanedione dioxime,[6] diethyl dithiocarbamate,[7] potassium dithiooxalate,[8] thiotropolone,[9] dithiosalicylic acid[10] and quinoxaline-2,3-dithiol[11,12] reagents used for photometric determination of nickel(II) find many disadvantages. Some of them are unstable while some of them are insoluble in most of the solvents.

Methods involving several reagents like chlorindazon DS[13], calcichrome,[14] cycloheptane 1:2 dione dioxime,[15] nicotinamidoxime,[16] 4-isopropyl cyclohexane- 2:2 - dione dioxime[17] and rubeanic acid[18] are all time consuming due to slow rate of formation of complex. Reagents like solochrome red ERS[19] and 1-(2-pyridylazo)-2-naphthol[20] require elevated temperature for complex formation.

Recently introduced important reagents are azonaphthols such as PAN,[21-24] or TAN,[25] isopentyl esters,[26] and thenoyltrifluoroacetone.[27,28] Thiosemicarbazones of some aldehydes and ketones are also promising new photometric reagents for nickel. CHDT,[29] PAT,[30] phthalaldehyde thiosemicarbazone,[31] biacetylmonoxime thiosemicarbazone[32] are being used for photometric determination of nickel.

Complex salts of Ni(II) with schiff bases derived from aminoguanidine and salicylaldehyde[33] have been prepared and characterized on the basis of analytical, UV and IR data. In our laboratory the reaction between nickel and salicylaldehyde guanylhydrazone was investigated and a new spectrophotometric method for estimation of nickel is presented in this chapter.

The proposed reagent salicylaldehyde 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.

4.2 EXPERIMENTAL

4.2.1 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 dimethylglyoxime[34] method. Further dilutions for experimental purposes were done with distilled water.

Reagent solution :

A stock solution of the reagent was prepared by dissolving 178 mg of it in 100 ml distilled water (1.78 mg/ml i.e. 1.0×10^{-2} M).

Buffer solution :

Buffer solution of pH 12.39 was prepared by mixing appropriate amounts of borax and sodium hydroxide.

4.2.2 Recommended Procedure :

An aliquot of the solution containing about 10 µg of Ni(II) was taken in a 10 ml volumetric flask. To this, 0.6 ml of reagent (SAG) solution of concentration 1.0 x 10^{-3} M was added. The pH of the solution was adjusted to 9.52 by adding 1.0 ml of buffer solution of pH 12.39 and was diluted upto the mark with distilled water. The absorbance of the complex was measured at 370 nm against reagent blank. The concentration of nickel was determined from a calibration curve.

4.3 RESULTS AND DISCUSSION

4.3.1 Spectral Characteristics :

The absorption spectrum of Nickel(II)-SAG complex of the solution containing 10 μg Ni(II) [1.0 ml of 0.01 mg/ml i.e. 1.704 x 10^{-4} M] and 0.6 ml of 1.0 x 10^{-3} M reagent (SAG) against the reagent blank was recorded at pH 9.52. The absorption spectrum shows a peak with an absorption maximum at 370 nm. At this wavelength the colourless reagent solution has no significant absorption. The molar extinction coefficient at 370 nm is 1.0563 x 10^{4} l $mole^{-1}cm^{-1}$. The complex is stable after 15 minutes. Absorption spectra of the complex and reagent are shown in figure 4.1. The observations for the spectra are given in table 4.1.

Table 4.1 : Molar extinction coefficients of the Ni(II)-SAG complex and the reagent (SAG).

Wavelength λ, nm	Molar extinction coefficients, ϵ	
	Ni(II)-SAG complex $\epsilon \times 10^4$ l mole^{-1}cm^{-1}	Reagent, SAG $\epsilon \times 10^4$ l mole^{-1}cm^{-1}
320	0.1761	0.085
330	0.3228	0.090
340	0.6162	0.055
350	0.8216	0.024
360	0.9683	0.008
365	0.9977	0.006
370	1.0563	0.002
375	0.9390	0.002
380	0.8803	0.001
390	0.6455	0.000
400	0.4695	-
410	0.3521	-
420	0.2347	-
430	0.1761	-
440	0.1174	-
450	0.0735	-
460	0.0686	-
470	0.0680	-
480	0.0587	-
500	0.0587	-
520	0.0587	-
540	0.0587	-
560	0.0587	-

4.3.2 Effect of pH :

The effect of variation in pH on the absorbance of Ni(II)-SAG complex was studied over the pH range 2.0 to 13.0. The complex has maximum and constant absorbance over the pH range 8.5 to 10.5. Therefore, pH 9.52 was selected as the optimum pH for further studies. The observations are given in table 4.2 (Fig. 4.2).

Table 4.2 : Effect of pH

pH	Absorbance at 370 nm
3.0	0.02
4.0	0.03
6.0	0.06
7.0	0.08
8.0	0.09
8.5	0.13
9.0	0.13
10.0	0.13
10.5	0.13
11.0	0.06
12.0	0.03
13.0	0.03

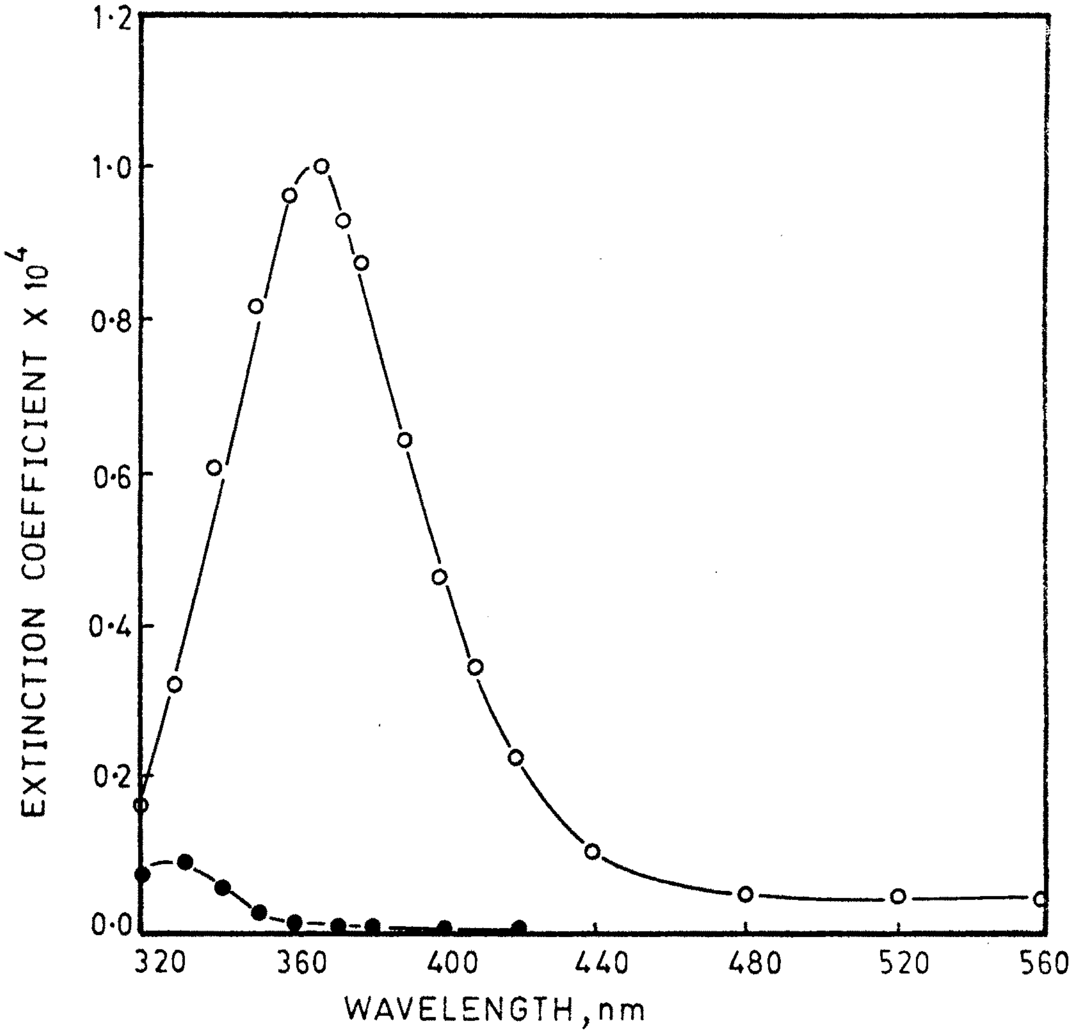


FIG.4·1 ○—○ ABSORPTION SPECTRUM OF NICKEL–SAG COMPLEX.
●—● ABSORPTION SPECTRUM OF REAGENT (SAG).

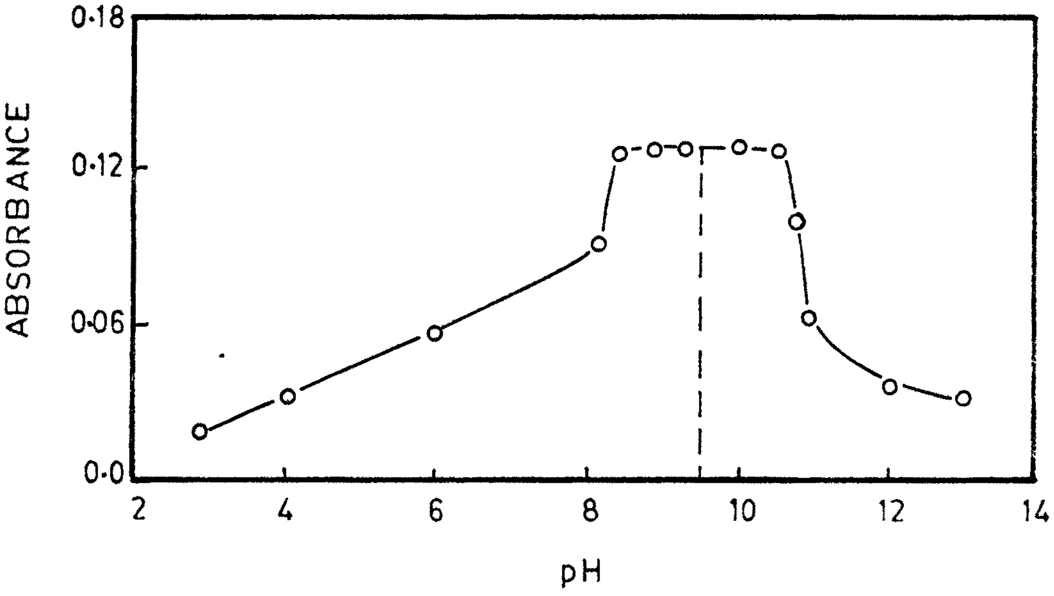


FIG. 4·2 EFFECT OF pH

4.3.3 Effect of reagent concentration :

A series of solutions was prepared in which the volume of 1.0 x 10^{-3} M reagent was varied from 0.2 to 1.0 ml in which concentration of nickel was kept constant at 1.0 ppm. The complex is developed as per recommended procedure. The results in table 4.3 show that four times the molar excess of the reagent is sufficient for full colour development.

Table 4.3 : Effect of reagent concentration

[Ni(II)] = 1.0 ppm; [SAG] = 1.0 x 10^{-3}M

ml of reagent (SAG)	Absorbance at 370 nm
0.2	0.10
0.4	0.15
0.5	0.17
0.6	0.18
0.7	0.18
0.8	0.18
1.0	0.18

4.3.4 Stability and reaction rate :

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

4.3.5 Validity of Beer's Law :

The measurement of the absorbance at 370 nm from the solution containing various amounts of nickel showed that Beer's law is valid upto 5 ppm of Ni(II) (Fig. 4.3).

The optimum concentration range of nickel was determined from the Ringbom plot[35] (Fig. 4.4) and found to be 3.15 to 4.75 ppm.

4.3.6 Composition of the complex :

The composition of Ni(II)-SAG complex was determined by Job's method of continuous variation[36] (Table 4.4), molar ratio method[37] (Table 4.5) and slope ratio method.[38] For these methods, equimolar solutions of the concentration 1.704×10^{-4} M were used. Job's curves at 370 nm, 380 nm, 390 nm are shown in fig. 4.5, which show the formation of 1:2 complex of Ni(II)-SAG. This composition is confirmed by mole ratio study (Fig. 4.6) and slope ratio study.

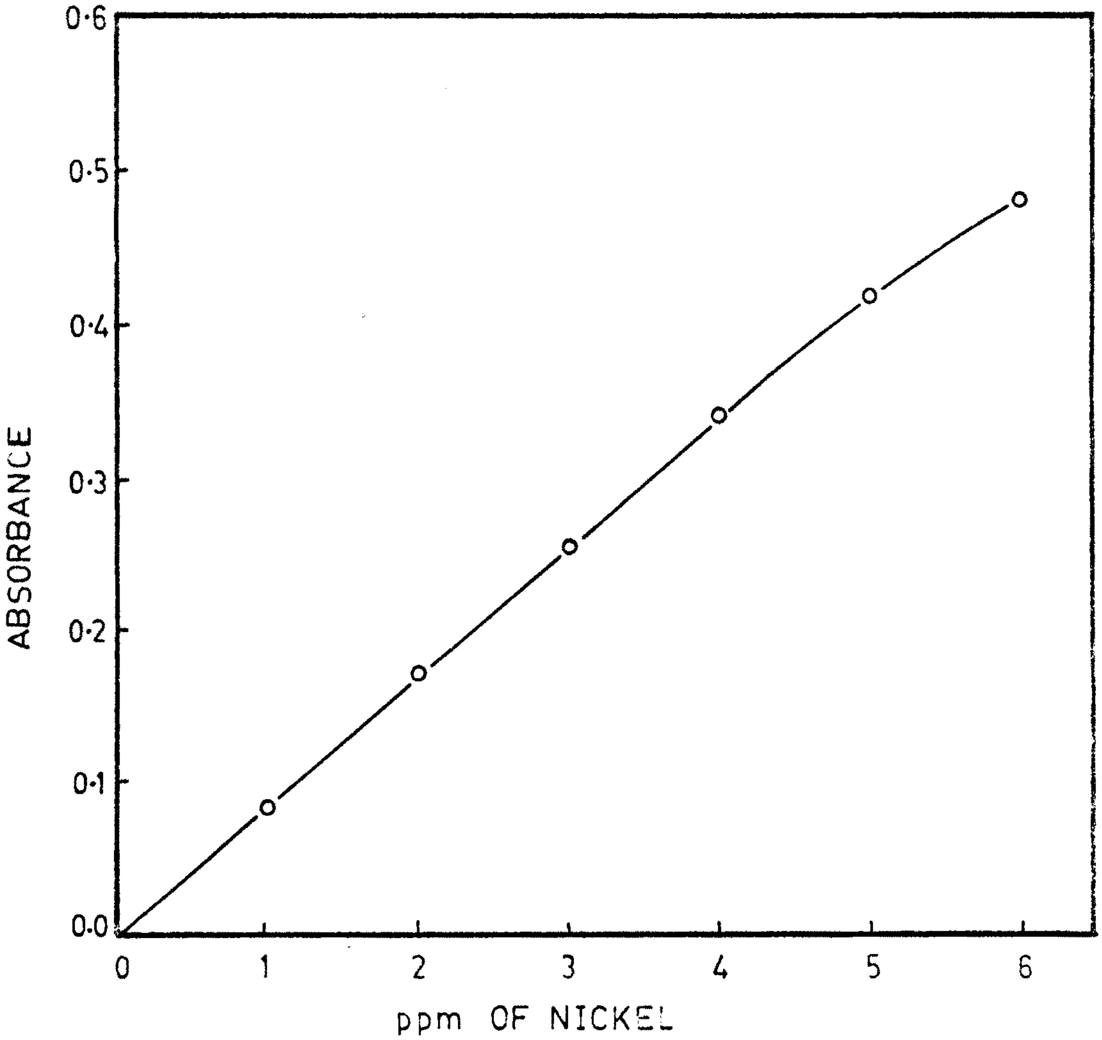


FIG. 4·3 VALIDITY OF BEER'S LAW

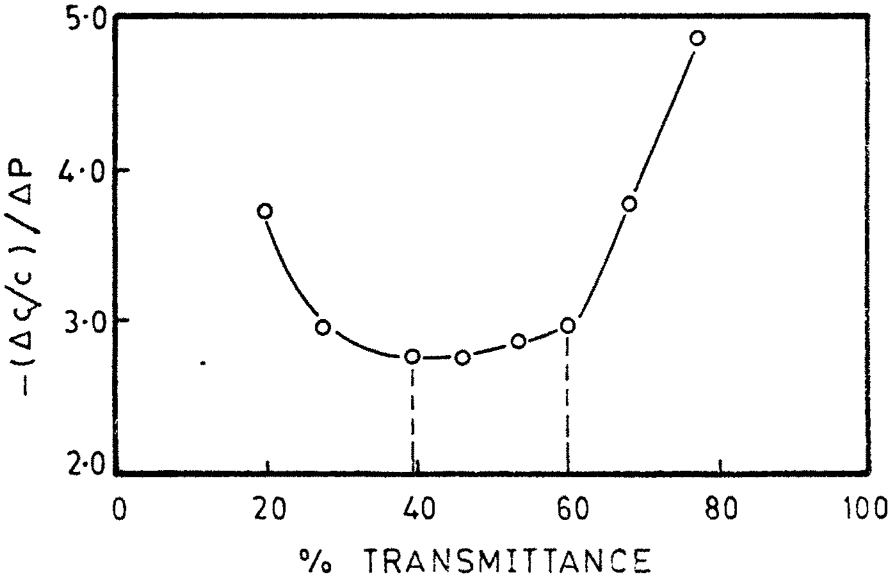


FIG. 4·4 RINGBOM PLOT

Table 4.4 : Job's continuous variation method

$[\mathrm{Ni(II)}] = [\mathrm{SAG}] = 1.704 \times 10^{-4}$ M

Nickel (II) ml	Reagent (SAG) ml	Molar Ratio M : L	Absorbances at λ,		
			370 nm	380 nm	390 nm
0.0	1.8	-	-	-	-
0.2	1.6	1 : 8	0.050	0.036	0.026
0.4	1.4	2 : 7	0.080	0.065	0.048
0.6	1.2	1 : 2	0.100	0.080	0.060
0.8	1.0	4 : 5	0.073	0.060	0.045
1.0	0.8	5 : 4	0.045	0.034	0.023
1.2	0.6	2 : 1	0.020	0.014	0.008
1.4	0.4	7 : 2	0.007	0.004	0.002
1.6	0.2	8 : 1	0.004	0.002	0.001
1.8	0.0	-	-	-	-

Table 4.5 : Molar ratio method

$[Ni(II)] = [SAG] = 1.704 \times 10^{-4}$ M

Nickel(II) ml	Reagent(SAG) ml	Molar ratio M : L	Absorbances at λ 370 nm	Absorbances at λ 380 nm
0.0	2.0	-	-	-
0.2	2.0	1 : 10	0.020	0.015
0.4	2.0	1 : 5	0.060	0.040
0.6	2.0	3 : 10	0.080	0.060
0.66	2.0	1 : 3	0.100	0.075
0.8	2.0	2 : 5	0.125	0.090
1.0	2.0	1 : 2	0.130	0.100
1.2	2.0	3 : 5	0.140	0.110
1.33	2.0	2 : 3	0.150	0.115
1.4	2.0	7 : 10	0.152	0.117
1.6	2.0	4 : 5	0.155	0.120
1.8	2.0	9 : 10	0.157	0.125
2.0	2.0	1 : 1	0.160	0.130

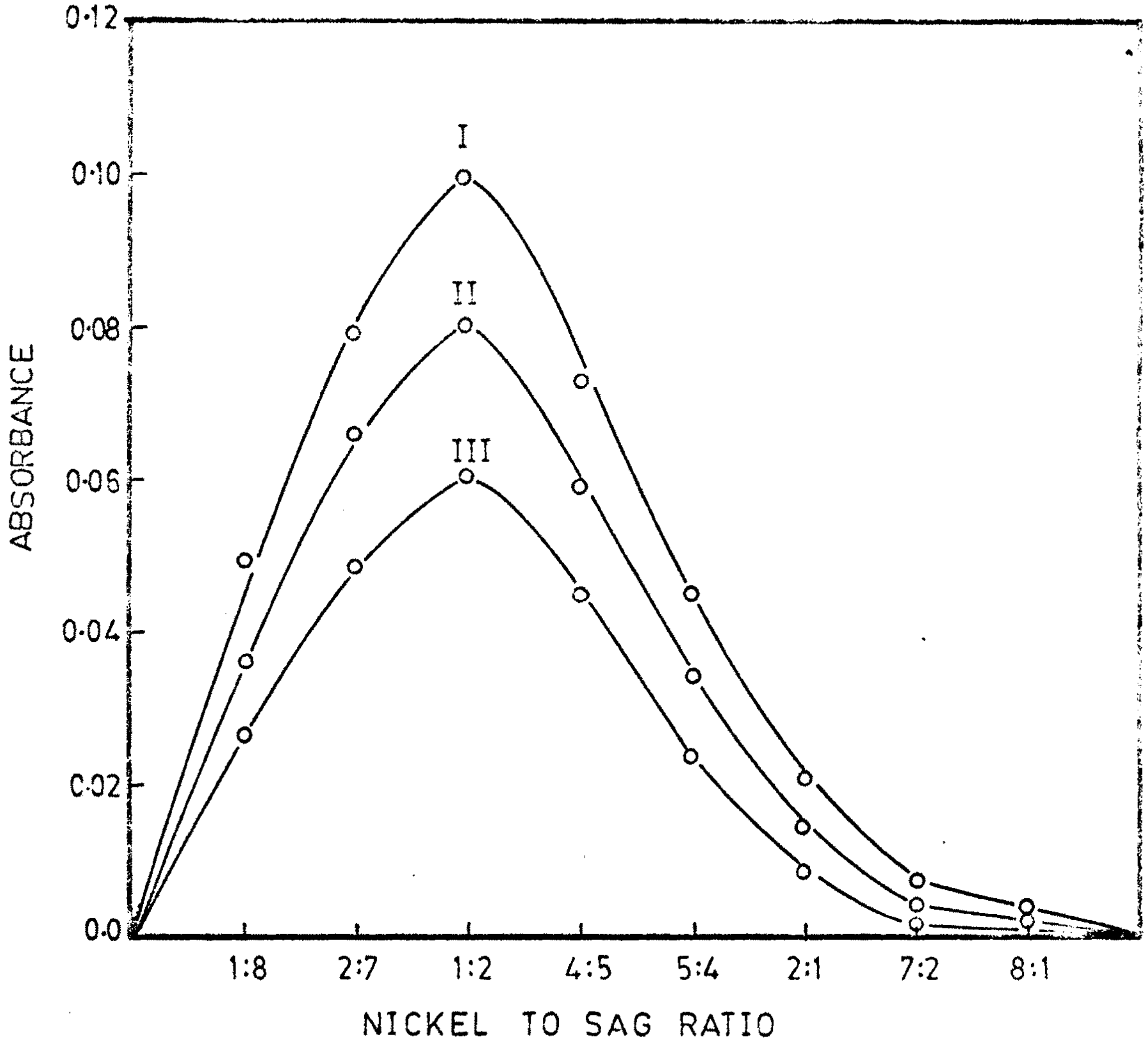


FIG. 4·5 JOB'S CONTINUOUS VARIATION METHOD.
I – 370 nm, II – 380 nm, III – 390 nm.

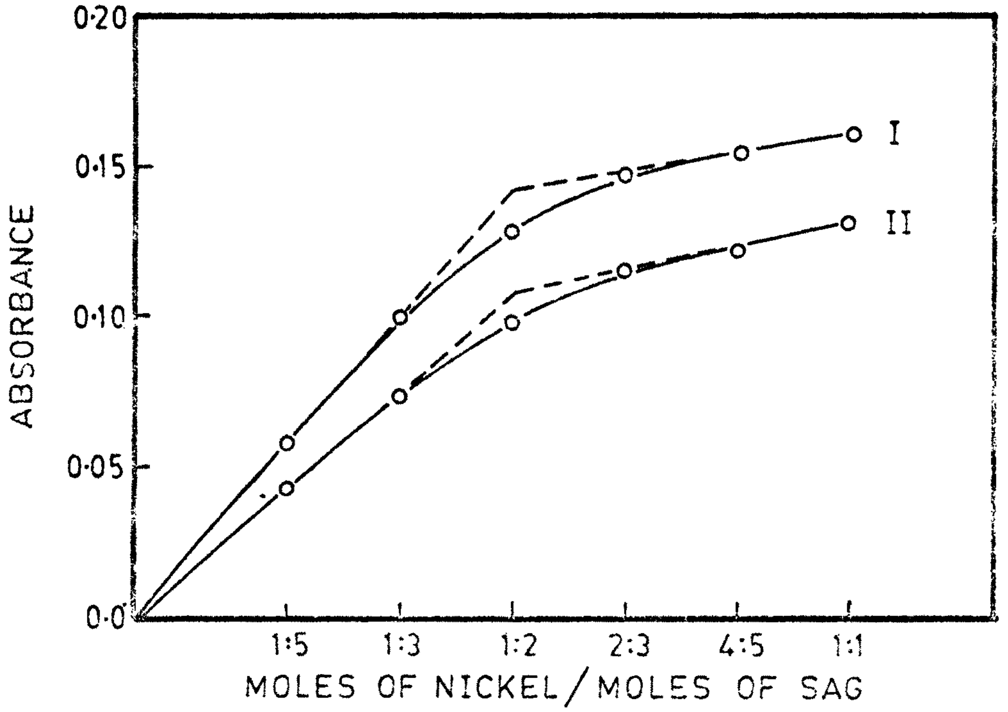
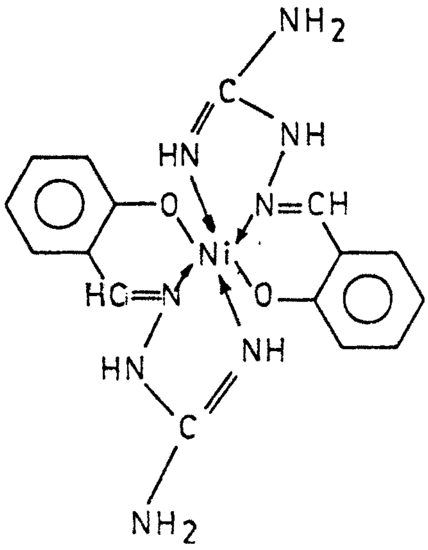


FIG. 4·6 MOLE RATIO METHOD
I – 370 nm, II – 380 nm

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



4.3.7 Sensitivity :

The nickel complex of SAG does not show sensitivity towards light. The photometric sensitivity of the method was calculated by the method of Sandell[39] and found to be 0.03907 μg/cm^2 at 370 nm.

4.3.8 Degree of dissociation and instability constant

The degree of dissociation was obtained by the method of Harvey and Manning.[38] The value of α, degree of dissociation was found to be 0.0877.

The apparent instability constant[40] was found to be 8.595×10^{-13} for Ni(II)-SAG complex. The change in free energy[41] of the system is - 16.453 K cals/mole.

4.3.9 Reproducibility of the method :

In order to study the reproducibility of the present method, different amounts of nickel were determined. The results in table 4.6 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 4.6.

Table 4.6 : Reproducibility of the method

Nickel(II) ppm	Mean absorbance of six observations	Standard deviation	Coefficient of variation %
1.5	0.125	0.002	1.600
3.0	0.25	0.0045	1.800
4.5	0.38	0.007	1.842

4.3.10 Effect of diverse ions :

The effect of diverse ions was studied by using 1.0 ppm of nickel and 0.6 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 Cr(III), V(IV), Al(III), Cr(VI), Ag(I), Pd(II), Cu(II), citrate and $EDTA^{-4}$ ions interfere seriously, while the tolerance limits of W(VI), thiourea and urea are 275.0, 400.0 and 600.0 ppm respectively. For various foreign ions, the tolerance limits are given in table 4.7.

Table 4.7 : Effect of diverse ions

[Ni(II)] = 1.0 ppm [SAG] = 1.0×10^{-3} M

Foreign ions	Added as	Tolerance limit, ppm
<u>Cations</u>		
Cr(III)	$CrCl_3 \cdot 6H_2O$	none
V (IV)	$VOSO_4 \cdot H_2O$	none
Ba(II)	$BaCl_2 \cdot 2H_2O$	7.0
Al(III)	$AlCl_3 \cdot 6H_2O$	none
Bi(III)	$Bi(NO_3)_3$	1.0
Cr(VI)	$K_2Cr_2O_7$	none
Pb(II)	$Pb(NO_3)_2$	5
Zn(II)	$ZnSO_4 \cdot 7H_2O$	3
Ag(I)	$AgNO_3$	none
Cd(II)	$CdSO_4$	45
W(VI)	$Na_2WO_4 \cdot 2H_2O$	275
Pd(II)	$PdCl_2$	none
Cu(II)	$CuSO_4 \cdot 5H_2O$	none
<u>Anions</u>		
Citrate	Citric acid	none
Thiourea	Thiourea	400
Oxalate	Potassium oxalate	12
$EDTA^{-4}$	Disodium salt	none
Urea	urea	600
Acetate	Sodium acetate	100
Tartrate	Tartaric acid	17

4.4 APPLICATIONS

Analysis of nickel(II) in alloy steel :

A known weight 0.4 g of the sample of alloy steel (No.33 d NBS Std. U.S.) 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 10 minutes and diluted it to 100 ml with distilled water.

A suitable aliquot of the solution is taken. As the alloy contains large amount of iron, it is removed by extraction with IBMK from 6 M HCl medium. Excess hydrochloric acid from aqueous solution was removed by evaporation. Copper was removed by extracting it with a mixture of acetyl acetone and chloroform at pH 2.5. The aqueous solution was used for determination of nickel as per the recommended procedure. Results are given in table 4.8.

Table 4.8 : Analysis of alloy steel

Alloy	Certified value of Ni %	Experimental value of Ni, %	Relative standard deviation for 8 observations
33d NBS Std. U.S.	3.58	3.55	0.05

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