

C H A P T E R - III

DETERMINATION OF NICKEL

### 3.1 INTRODUCTION

About 90 % of the world's output of the nickel is from the canadian deposits. In these, the metal is associated with Cu, Fe, Co and small amounts of Ag, Au and Pt metals in arsenical ores.

Nickel melts at  $1450^{\circ}$  and boils at  $2730^{\circ}$ . It is a hard white metal which takes a high polish and is both malleable and ductile. It is magnetic, but much less than is iron. It loses its magnetic properties at  $340^{\circ}$ .

Nickel is one of the most commonly used elements. The chief use of nickel is for making nickel steel. Substantial amounts of nickel are used for the preparation of other nickel alloys, particularly those based on copper e.g. coinage cupro-nickel and constantan are both nickel-copper alloy<sup>s</sup>. Monel metal is also a cupronickel usually containing a little iron and manganese. Nichrome is a nickel-chromium-iron alloy. These alloys are very poor electrical conductors and are very useful as electrical resistors and "heating elements". Nickel is also used for nickel plating, and as a catalyst for the reduction of organic compounds by hydrogen.

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<sup>1,2</sup> and many are not available commercially. Only a few reagents have specific applications, desired sensitivity and selectivity.

The most commonly used reagents for photometric determination of nickel (II) are oximes and dioximes such as dimethylglyoxime<sup>3-6</sup>, furil- $\alpha$ -dioxime<sup>7-13</sup>,  $\alpha$ -benzoin oxime<sup>14</sup>, azonaphthols, dithizone and dithiols. But in extraction with DMG, nioxime<sup>15,16</sup>, 4-isopropyl-1,2-cyclohexanedionedioxime<sup>17</sup>, diethyldithiocarbamate<sup>18</sup>, potassium dithiooxalate<sup>19</sup>, thiotropolone<sup>20</sup> and dithicsalicylic acid<sup>21</sup>, many cations interfere seriously. Quinoxaline-2,3-dithiol<sup>22,23</sup> suffers from the instability of the reagent and its insolubility in most solvents.

Methods involving rubeanic acid<sup>24</sup>, 4-isopropylcyclohexane 2:2-dione dioxime<sup>25</sup>, nicotinamidoxime<sup>26</sup>, cycloheptane 1:2 dione-dioxime<sup>27</sup>, calcichrome<sup>28</sup> and chlorindazon DS<sup>29</sup> are all time consuming due to slow rate of formation of complex. Reagents like solochrome red ERS<sup>30</sup> and 1-(2-pyridylazo)-2-naphthol<sup>31</sup> require elevated temperature for complex formation. 6-Nitro quinoline dithiol<sup>32</sup> has been recently reported as a colorimetric reagent.

Thiosemicarbazones of some aldehydes and ketones are also promising new photometric reagents for nickel. CHDT<sup>33</sup>, PAT<sup>34</sup>, phthalaldehyde thiosemicarbazone<sup>35</sup>, biacetylmonoxime thiosemicarbazone<sup>36</sup> are being used for photometric determination of nickel. Recently introduced important reagents are azonaphthols or their substituted derivatives such as PAN<sup>37-40</sup> or TAN<sup>41</sup>, isopentyl esters<sup>42</sup> and thenoyltrifluoroacetone<sup>43,44</sup>.

Extractive spectrophotometric determination of nickel with diphenylcarbazone<sup>45</sup> in presence of pyridine have been reported recently. Other analytical reagents for nickel such as rubeanic acid in presence of quinoline,  $\alpha$ -picoline and collidine<sup>46</sup>, rubeanic acid in presence of pyridine<sup>47</sup>, 2-hydroxy-4-ethoxyacetophenone oxime (HEAO)<sup>48</sup> and 1-phenyl-3-thiobenzoyl thiocarbamide<sup>49</sup> have been reported recently.

Complex salts of Ni(II) with Schiff bases derived from aminoguanidine and o-hydroxy acetophenone<sup>50</sup> have been prepared and characterized on the basis of analytical UV and IR data.

In our laboratory, the reaction between nickel and cinnamaldehyde guanylhydrazone (CAG) was investigated and a new spectrophotometric method for estimation of nickel is

presented in this chapter. The proposed reagent, CAG 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.

### 3.2 EXPERIMENTAL

All the chemicals used were of analytical grade.

#### 3.2.1 Standard solutions :

##### Standard Nickel Solution :

A stock solution of nickel (1 mg/ml) was prepared by dissolving 0.4495 g of A.R. grade nickel nitrate hexahydrate in distilled water containing a few mls of concentrated hydrochloric acid and was diluted to 100 ml with distilled water. Its nickel content was determined gravimetrically by dimethyl glyoxime<sup>51</sup> method. Further dilutions for experimental purposes were done with distilled water.

##### Reagent Solution

A stock solution of the reagent cinnamaldehyde guanylhydrazone (CAG) was prepared by dissolving 188 mg of

it in 100 ml ethanol (1.88 mg/ml i.e. 0.01 M).

#### Buffer solution

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

#### 3.2.2 Recommended Procedure :

An aliquot of the solution containing about 10  $\mu\text{g}$  of Ni(II) was taken in a 10 ml volumetric flask. To this, 3.5 ml of reagent (CAG) solution of concentration 0.01 M was added. The pH of the solution was adjusted to 10.0 by adding of 1.0 ml of buffer solution of pH 11.0 and was diluted upto the mark with ethyl alcohol. The absorbance of the complex was measured from 360 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.

### 3.3 RESULTS AND DISCUSSION

#### 3.3.1 Spectral characteristics :

The absorption spectrum of Nickel(II)-CAG complex of the solution containing 10  $\mu\text{g}$  of Ni(II) [1 ml of 0.01 mg/ml i.e.  $1.703 \times 10^{-4}\text{M}$ ] and 3.5 ml of 0.01 M reagent (CAG) against reagent blank was recorded at pH 10. The absorption

spectrum shows a peak with an absorption maximum at 390 nm. At this wavelength the colourless reagent solution has no significant absorption. The molar extinction coefficient at 390 nm is  $0.7647 \times 10^4 \text{ l mole}^{-1} \text{ cm}^{-1}$ . Absorption spectra of the complex and reagent are shown in figure 3.1. The observations for the spectra are given in table 3.1.

### 3.3.2 Effect of pH :

The effect of variation in pH on the absorbance of Ni(II)-CAG complex was studied over the pH range 2.0 to 12.0. The complex has maximum and constant absorbance over the pH range 9.0 to 11.0. Therefore, pH 10.0 was selected as the optimum pH for further studies. The observations are given in table 3.2 (Fig 3.2).



Table 3.1 : Molar extinction coefficients of Ni(II)-CAG complex and reagent CAG.

Wavelength $\lambda$ , nm	Molar extinction coefficients, $\epsilon$	
	Ni(II)-CAG complex $\epsilon \times 10^4 \text{ l mole}^{-1} \text{ cm}^{-1}$	Reagent, CAG $\epsilon \times 10^4 \text{ l mole}^{-1} \text{ cm}^{-1}$
365	0.360	0.0205
370	0.471	0.015
380	0.695	0.010
385	0.750	0.0075
390	0.765	0.006
395	0.706	0.004
400	0.640	0.003
410	0.441	0.002
420	0.329	0.001
430	0.253	-
440	0.200	-
450	0.171	-
460	0.148	-
470	0.124	-
480	0.100	-
490	0.082	-
500	0.071	-
510	0.053	-
520	0.047	-



Table 3.2 : Effect of pH

pH	Absorbance at 390 nm
2.0	0.08
4.0	0.22
5.0	0.27
6.0	0.37
7.0	0.48
8.0	0.86
9.0	1.30
10.0	1.30
11.0	1.30
11.5	1.15
12.0	1.00

### 3.3.3 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 4.5 ml in which concentration of nickel was kept constant at 10 ppm. The complex is developed as per recommended procedure. The results in table 3.3 show that four times the molar excess of the reagent is sufficient for full colour development.

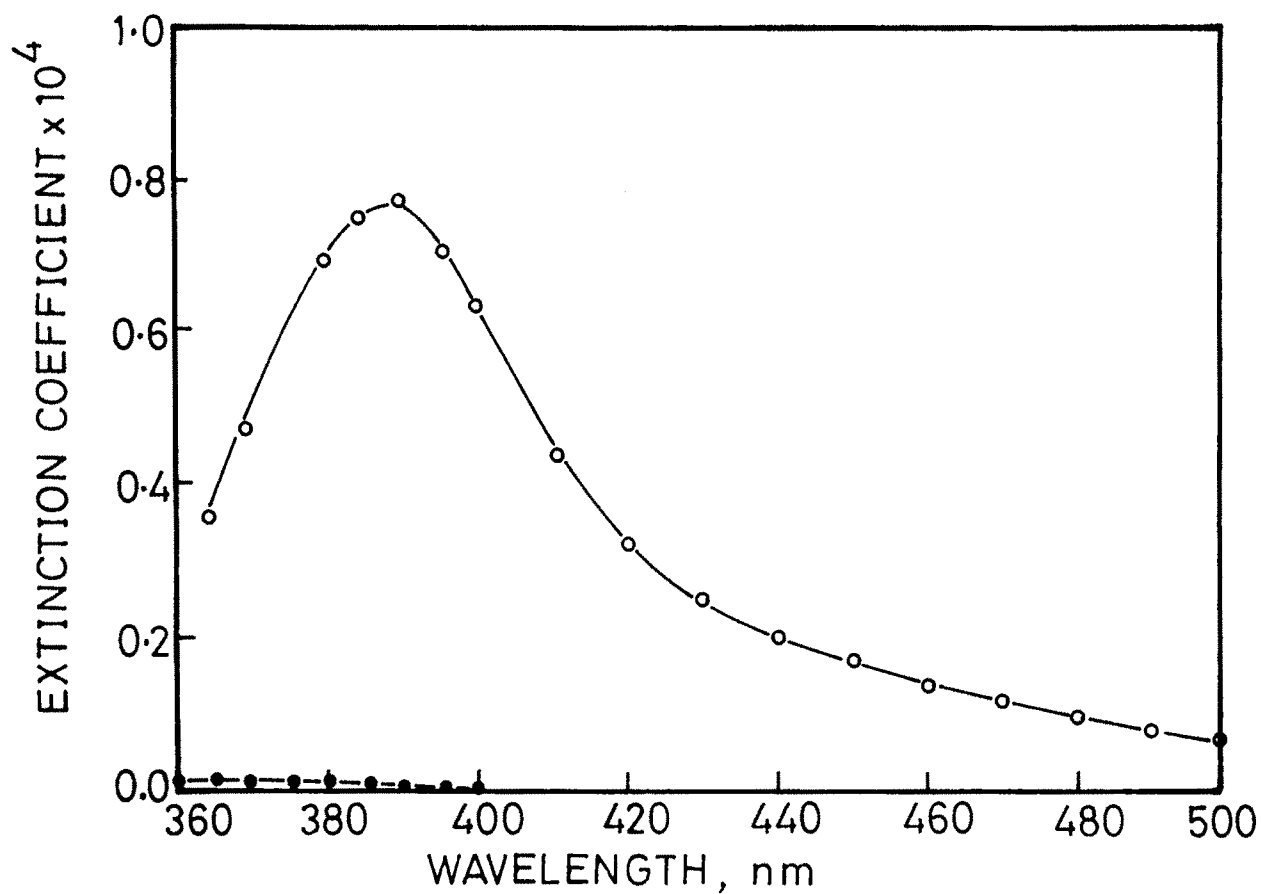


FIG. 3.1 — (○—○) ABSORPTION SPECTRUM OF NICKEL-CAG COMPLEX.  
 (●—●) ABSORPTION SPECTRUM OF REAGENT (CAG).

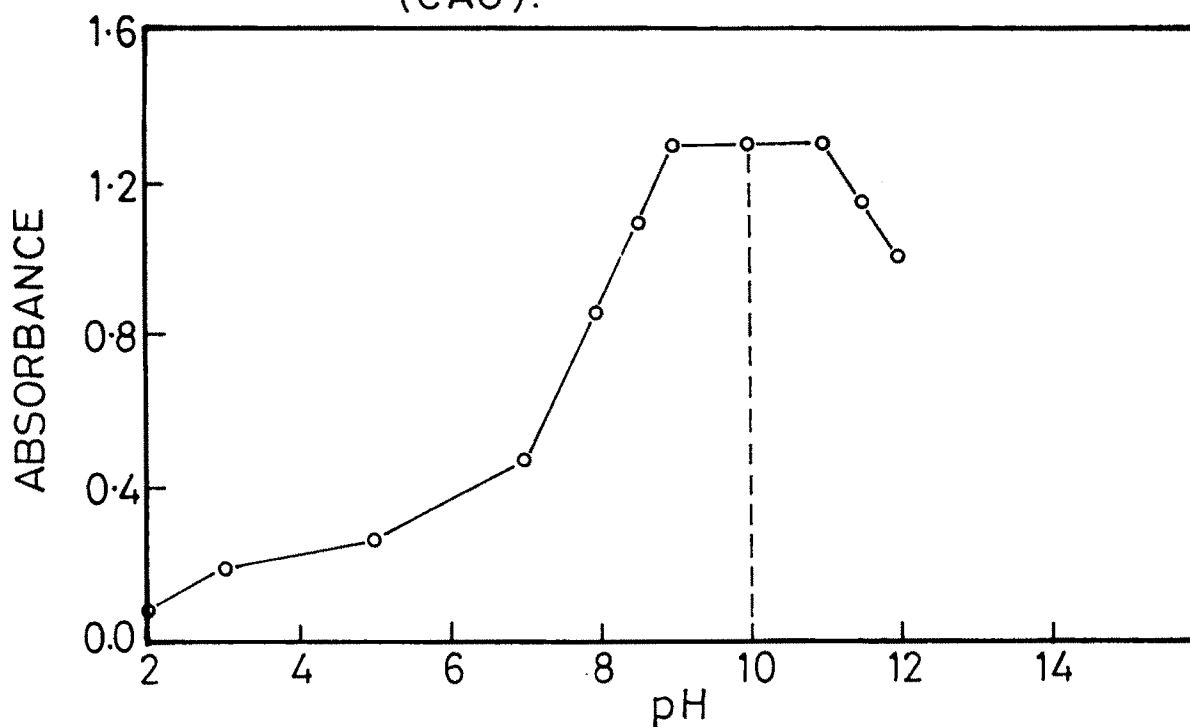


FIG. 3.2 — EFFECT OF pH .

Table 3.3 : Effect of reagent concentration

[Ni] = 10.0 ppm; [CAG] = 0.01 M

ml of reagent (CAG)	Absorbance at 390 nm
0.5	0.42
1.0	0.78
2.0	1.00
2.5	1.10
3.0	1.20
3.5	1.30
4.0	1.30
4.5	1.30

#### 3.3.4 Stability and Reaction Rate

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

#### 3.3.5 Validity of Beer's Law

The measurement of the absorbance at 390 nm from the solution containing various amounts of nickel showed that Beer's law is valid upto 10 ppm of Ni (II) (Table 3.4, Fig 3.3).

The optimum concentration range of nickel was determined from the Ringbom plot<sup>52</sup> (Fig 3.4) and was found to be from 2.1 ppm to 5.3 ppm.

Table 3.4 : Validity of Beer's law

$$[\text{Ni(II)}] = 1.703 \times 10^{-4} \text{ M}; [\text{CAG}] = 0.01 \text{ M}$$

Amount of Nickel (II) ppm	Absorbance at 390 nm
1.5	0.19
3.0	0.40
4.5	0.60
6.0	0.81
7.5	1.10
9.0	1.20
10.5	1.40
12.0	1.50
13.5	1.50
15.0	1.50

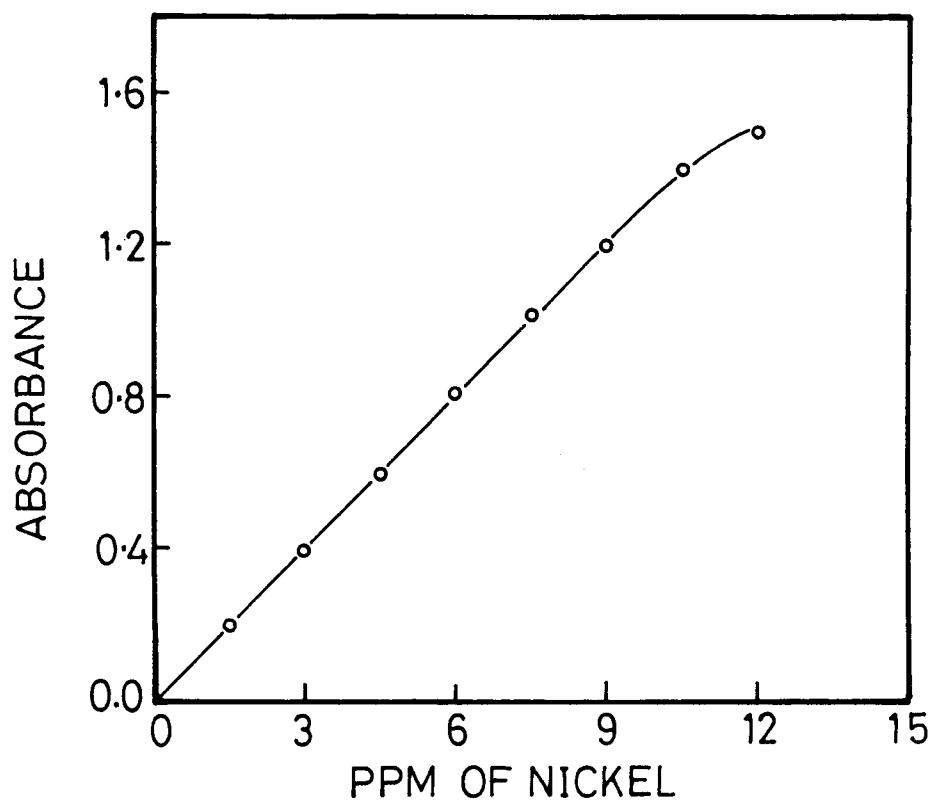


FIG. 3-3 — VALIDITY OF BEER'S LAW.

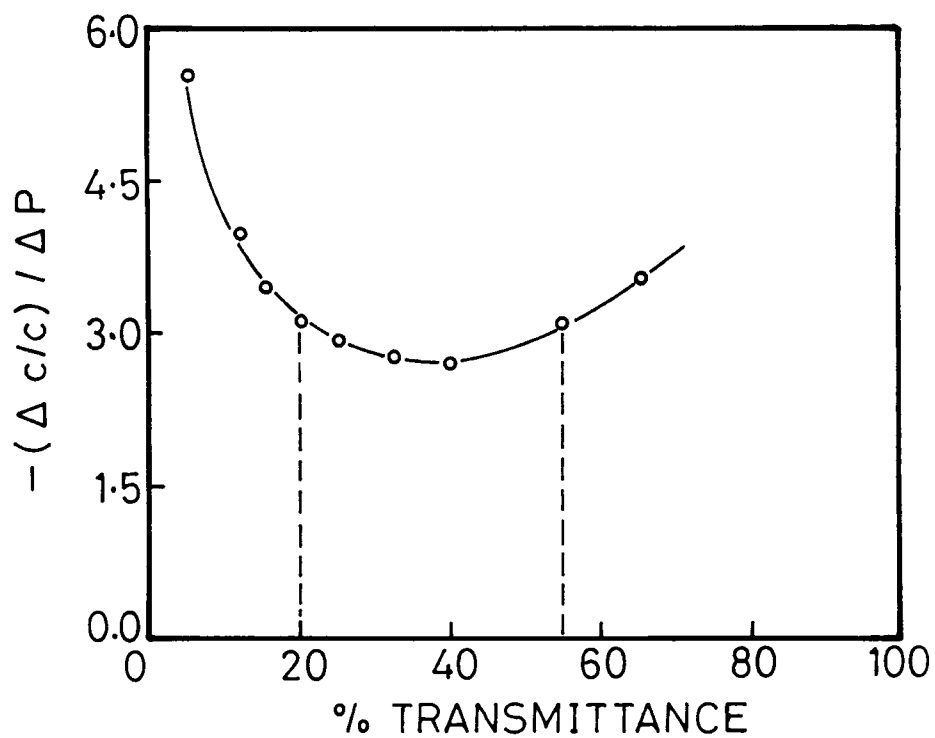


FIG. 3-4 — RINGBOM PLOT.

### 3.3.6 Composition of the complex :

The composition of Ni(II)-CAG complex was determined by Job's method of continuous variation<sup>53</sup> (Table 3.5), molar ratio method<sup>54</sup> (Table 3.6) and slope ratio method<sup>55</sup>. For these methods, equimolar solutions of the concentration  $1.703 \times 10^{-3}$  M were used. Job's curves at 390 nm, 400 nm and 410 nm are shown in figure 3.5, which show the formation of 1:2 complex of Ni(II)-CAG. This composition is confirmed by mole ratio study (Fig 3.6) and slope ratio study.

Table 3.5 : Job's continuous variation method

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

Nickel(II) ml	Reagent (CAG) ml	Molar Ratio M:L	Absorbances at $\lambda$		
			390 nm	400 nm	410 nm
0.0	1.8	-	-	-	-
0.2	1.6	1:8	0.06	0.04	0.01
0.4	1.4	2:7	0.13	0.08	0.04
0.6	1.2	1:2	0.16	0.12	0.08
0.8	1.0	4:5	0.10	0.07	0.04
1.0	0.8	5:4	0.09	0.06	0.03
1.2	0.6	2:1	0.08	0.05	0.025
1.4	0.4	7:2	0.07	0.04	0.02
1.6	0.2	8:1	0.05	0.03	0.01
1.8	0.0	-	-	-	-

Table 3.6 : Molar ratio method

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

Nickel(II) ml	Reagent (CAG) ml	Molar Ratio M:L	Absorbances at $\lambda$	
			390 nm	410 nm
0.0	2.0	-	-	-
0.2	2.0	1:10	0.11	0.08
0.4	2.0	1:5	0.13	0.10
0.6	2.0	3:10	0.18	0.14
0.66	2.0	1:3	0.22	0.16
0.8	2.0	2:5	0.26	0.19
1.0	2.0	1:2	0.29	0.22
1.2	2.0	3:5	0.315	0.235
1.33	2.0	2:3	0.33	0.25
1.4	2.0	7:10	0.34	0.26
1.6	2.0	4:5	0.35	0.265
1.8	2.0	9:10	0.35	0.270
2.0	2.0	1:1	0.355	0.275

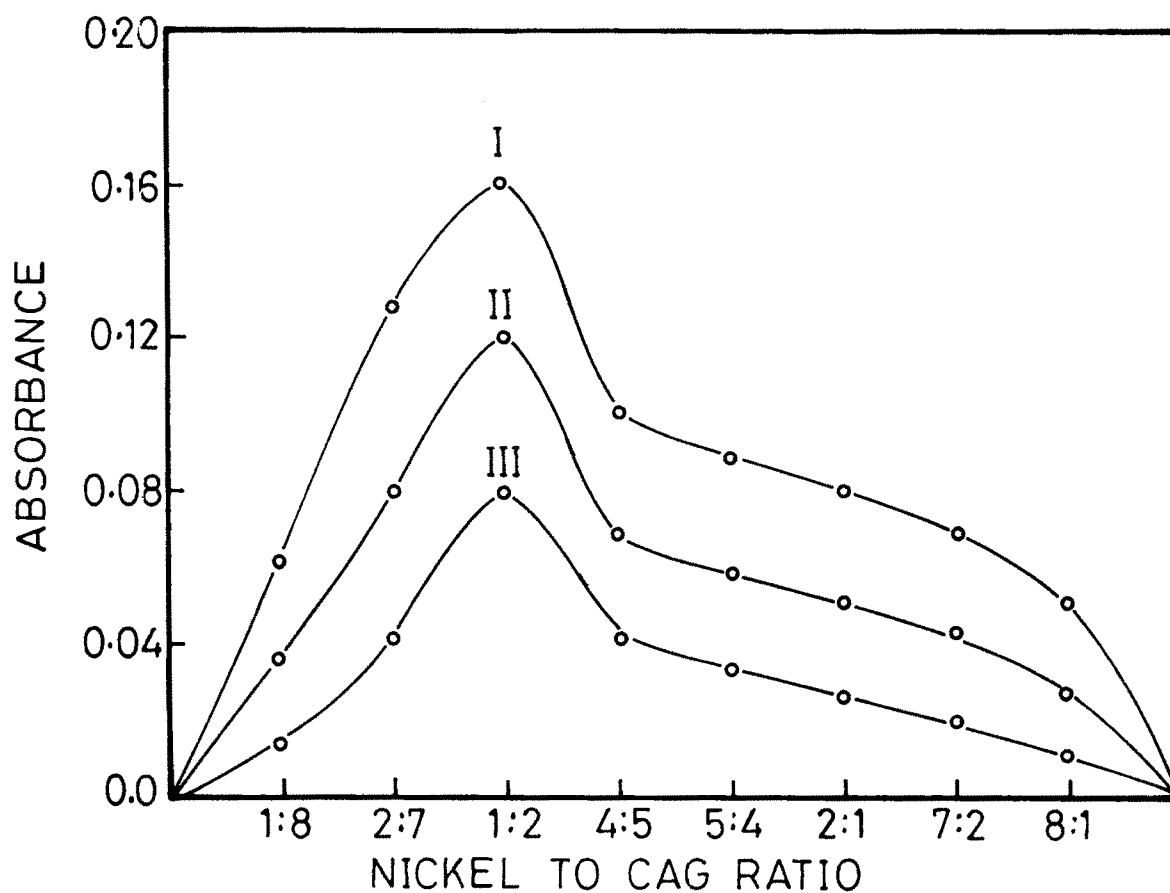


FIG. 3-5 - JOB'S CONTINUOUS VARIATION METHOD.  
I - 390 nm, II - 400 nm, III - 410 nm.

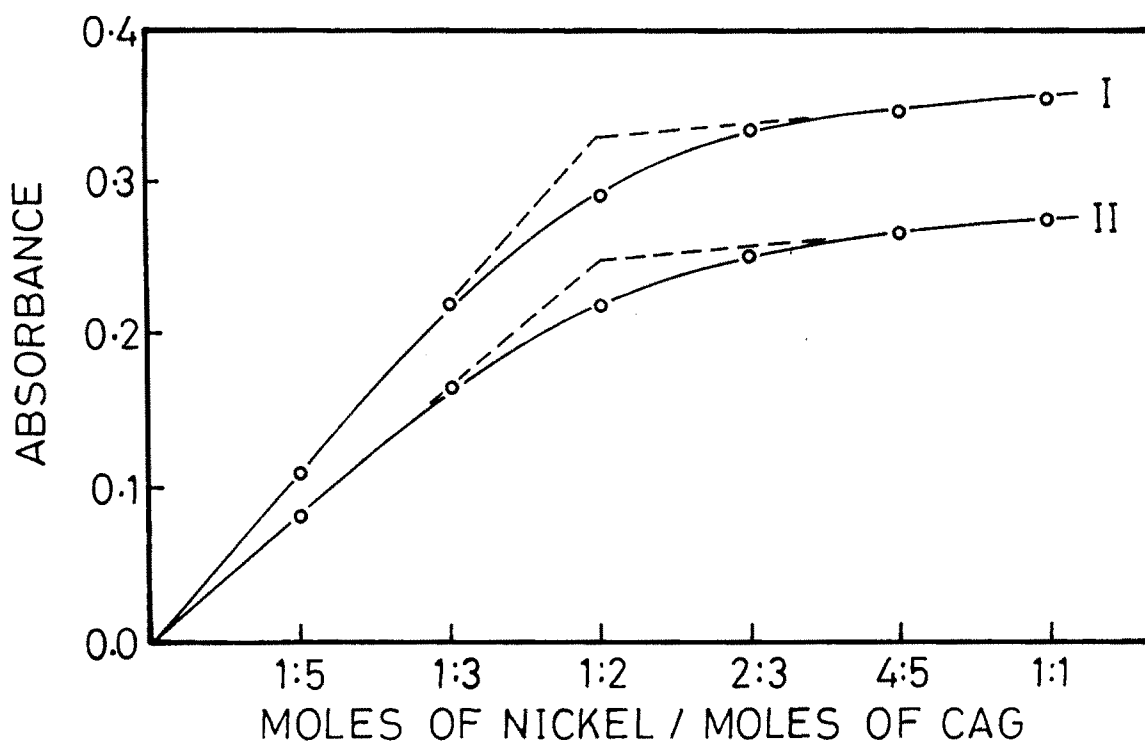
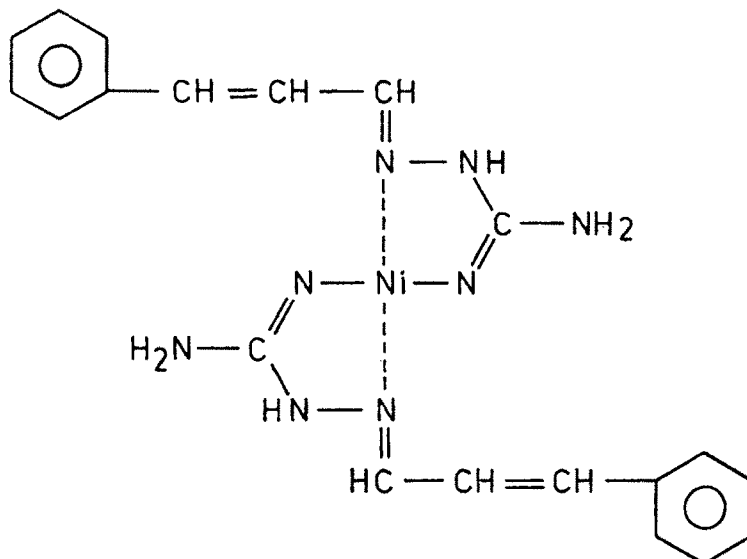


FIG. 3-6 - MOLE RATIO METHOD.  
I - 390 nm, II - 410 nm.



The probable structure for Ni(II)-CAG complex may be presented as :



### 3.3.7 Sensitivity :

The nickel complex of CAG does not show sensitivity towards light. The photometric sensitivity of the system was calculated by the method of Sandell<sup>56</sup> and was found to be  $0.05685 \mu\text{g}/\text{cm}^2$  at 390 nm.

### 3.3.8 Degree of Dissociation and Instability Constant :

The degree of dissociation was obtained by the method of Harvey and Manning<sup>55</sup>. The value of  $\alpha$ , degree of dissociation was found to be 0.1212.

The apparent instability constant<sup>57</sup> was found to be  $2.3509 \times 10^{-10}$  for Ni(II)-CAG complex. The change in free energy<sup>58</sup> of the system is -13.1171 K cal/mole.

### 3.3.9 Reproducibility of the method :

In order to study the reproducibility of the present method, different amounts of nickel were determined. The results in table 3.7 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 3.7.

Table 3.7 : Reproducibility of the method.

Nickel (II) ppm	Mean absorbance of six observations	standard deviation	coefficient of variation %
2.0	0.28	0.004	1.428
4.0	0.54	0.007	1.296
6.0	0.80	0.009	1.125
8.0	1.06	0.011	1.0377

### 3.3.10 Effect of Diverse Ions :

The effect of diverse ions was studied by using 2 ppm of nickel and 3.5 ml of 0.001 M reagent. The complexes were developed as per the recommended procedure and the absorbances were measured. The results indicate that Cu(II), Co(II), Pd(II) and EDTA<sup>-4</sup> interfere seriously while the tolerance limits of thiourea and urea anions are 750 ppm and 810 ppm respectively. For various foreign ions, the tolerance limits are given in table 3.8.

Table 3.8 : Effect of diverse ions

[Ni(II)] = 2 ppm; [CAG] = 0.001 M

Foreign ions	Added as	Tolerance limit, ppm
<u>Cations</u> :		
Cr(III)	CrCl <sub>3</sub> .6H <sub>2</sub> O	0.1
V(IV)	VOSO <sub>4</sub> .H <sub>2</sub> O	10.0
Ba(II)	BaCl <sub>2</sub> .2H <sub>2</sub> O	30.0
Cu(II)	CuSO <sub>4</sub> .5H <sub>2</sub> O	None
Co(II)	Co(NO <sub>3</sub> ) <sub>2</sub> .6H <sub>2</sub> O	None
Pd(II)	PdCl <sub>2</sub>	None
Zn(II)	ZnSO <sub>4</sub> .7H <sub>2</sub> O	1.0

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Foreign ions	Added as	Tolerance limit, ppm
Mn(II)	MnSO <sub>4</sub> ·H <sub>2</sub> O	0.3
Fe(III)	Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> ·(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> ·24H <sub>2</sub> O	0.4
Cd(II)	3CdSO <sub>4</sub> ·8H <sub>2</sub> O	2.0
Mo(VI)	(NH <sub>4</sub> ) <sub>6</sub> [Mo <sub>7</sub> O <sub>24</sub> ]·4H <sub>2</sub> O	10.0
Ce(IV)	Cerium(IV) ammonium sulphate	0.8
Cr(VI)	K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub>	1.0
Ag(I)	AgNO <sub>3</sub>	3.0
<u>Anions</u>		
Citrate	Citric acid	6.0
Thiourea	Thiourea	750.0
Oxalate	Sodium oxalate	20.0
EDTA <sup>-4</sup>	Disodium salt	None
Acetate	Sodium acetate	36.0
Tartrate	Tartaric acid	7.5
Urea	Urea	810.0

### 3.4 APPLICATIONS

#### Analysis of nickel(II) in cupronickel alloy :

To the known weight (0.5 g) of the sample of cupronickel alloy (No.19e, B.A.S. England), a mixture of 10 ml water, 1 ml concentrated sulphuric acid and 2 ml concentrated nitric acid was added to dissolve the alloy. When the dissolution was complete, the oxides of nitrogen was boiled off and the solution was diluted to 100 ml with 0.3 M HCl. The solution was heated and H<sub>2</sub>S was passed through it to precipitate out all the copper present in the solution. From the filtrate, H<sub>2</sub>S was boiled off and the solution was made upto 250 ml. The solution was used for the determination of nickel.

A suitable aliquot of the solution was taken. The nickel(II) is determined as per the recommended procedure. The results are given in table 3.9.

Table 3.9 : Analysis of cupronickel alloy

Alloy	certified value of Ni %	Experimental value of Ni %	Relative standard deviation for six observations
19e B.A.S England	31.2	30.5	0.07

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