CHAPTER - III

DETERMINATION OF NICKEL

3.1 INTRODUCTION :

Although several organic reagents have been proposed for the spectrophotometric 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. The researches and new methods are continued to deal with specific applications, desired sensitivity and selectivity.

Nickel 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 (German silver) and coins. Nickel is extensively used in nickel plating. Several industrial catalysts contain variable proportions of nickel.

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

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

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

The proposed reagent 2-benzoyl pyridine guanylhydrazone instantaneously forms yellow complex with nickel in alkaline medium. The method is simple and rapid. The results are reproducible. As the complex has high value of molar extinction coefficient, the method is suitable for determination of nickel in tracer quantities.

3.2 EXPERIMENTAL :

3.2.1 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 few mls of concentrated hydrochloric acid. It's nickel content was determined gravimetrically, by the dimethylglyoxime[45] method. Further dilutions for experimental purposes were done with distilled water.

Reagent solution :

A stock solution of the reagent was prepared by dissolving 60 mg of it in 100 ml distilled ethanol(0.6 mg/ml).

Buffer solution :

Buffer solution of pH 12 was prepared by mixing appropriate amounts of caustic soda and glycocoll.

3.2.2 Recommended procedure :

An aliquot of the solution containing 1 to 2 μg of Ni(II) was taken in a 10 ml volumetric flask. To this, 0.6 ml of 0.06% (2.511×10^{-3}M) reagent (BPG) solution was added. The pH of the solution was adjusted to 12.0 by adding 1.0 ml of buffer (pH = 12.0) solution and was diluted upto the mark with distilled ethanol. The absorbance was measured at 405 nm against reagent blank. The concentration of nickel was determined from a calibration curve.

3.3 RESULTS AND DISCUSSION

3.3.1 Spectral characteristics :

The absorption spectrum of Nickel - BPG complex of the solution containing 1.703×10^{-5}M Ni(II), against the reagent blank was recorded at pH 12.0. The complex absorbs maximum at 405 nm. The molar extinction coefficient at 405 nm is 1.497×10^{4} l mole^{-1}cm^{-1}. The molar extinction coefficient of the reagent at 405 nm is 0.0199×10^{4} l mole^{-1}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.

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

Wavelength λ, nm	Molar extinction coefficients, ϵ	
	Ni(II)-BPG complex $\epsilon \times 10^4$ l mole^{-1}cm^{-1}	BPG $\epsilon \times 10^4$ l mole^{-1}cm^{-1}
360	0.299	0.2948
370	0.572	0.1115
380	0.901	0.0509
385	1.092	0.0422
390	1.262	0.0387
395	1.379	0.0341
400	1.467	0.0298
403	1.485	0.0229
405	1.497	0.0199
407	1.490	0.0181
410	1.482	0.0174
415	1.409	0.0124
420	1.322	0.0049
425	1.215	0.0040
430	1.077	0.0030
440	0.733	0.0010
450	0.440	0.0000
460	0.293	0.0000
470	0.205	-
480	0.146	-
490	0.123	-
500	0.095	-

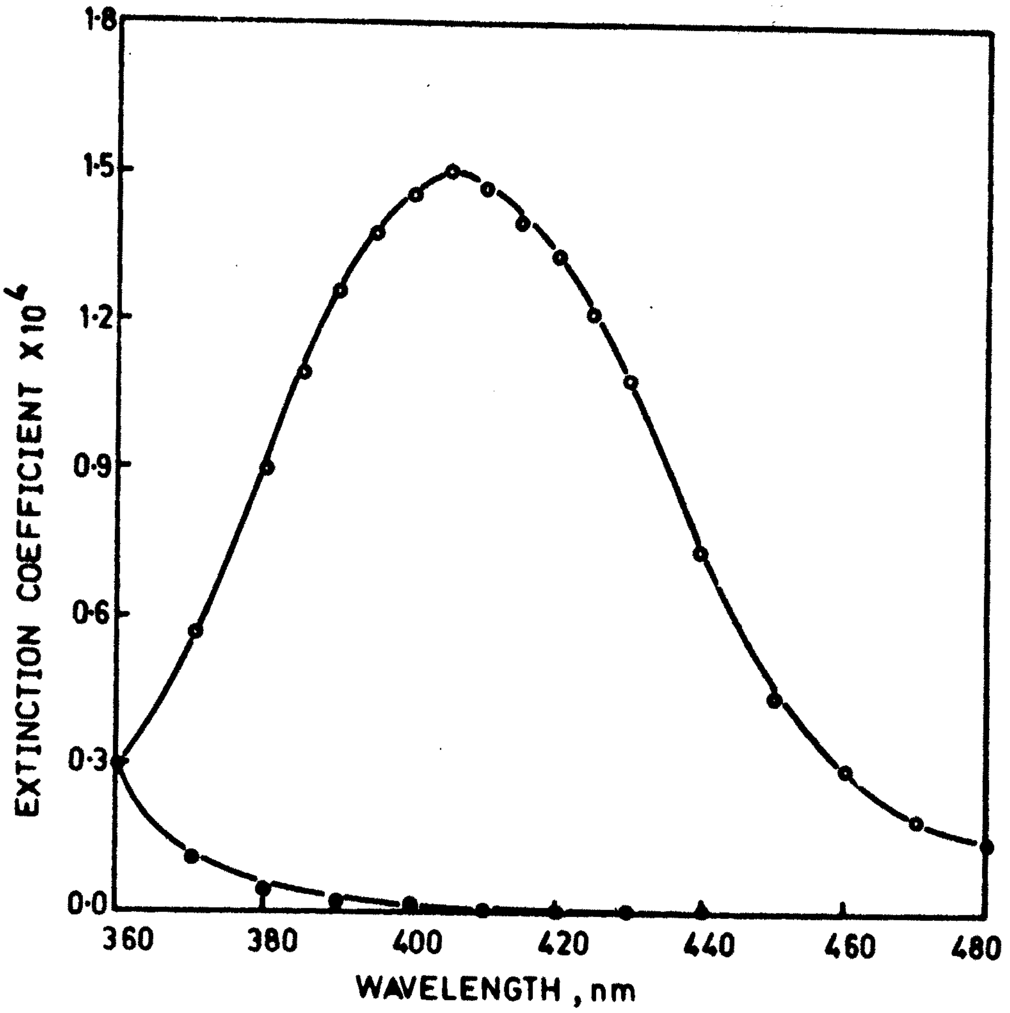

FIG.3·1 ○—○ ABSORPTION SPECTRUM OF NICKEL-BPG COMPLEX
●—● ABSORPTION SPECTRUM OF REAGENT (BPG)

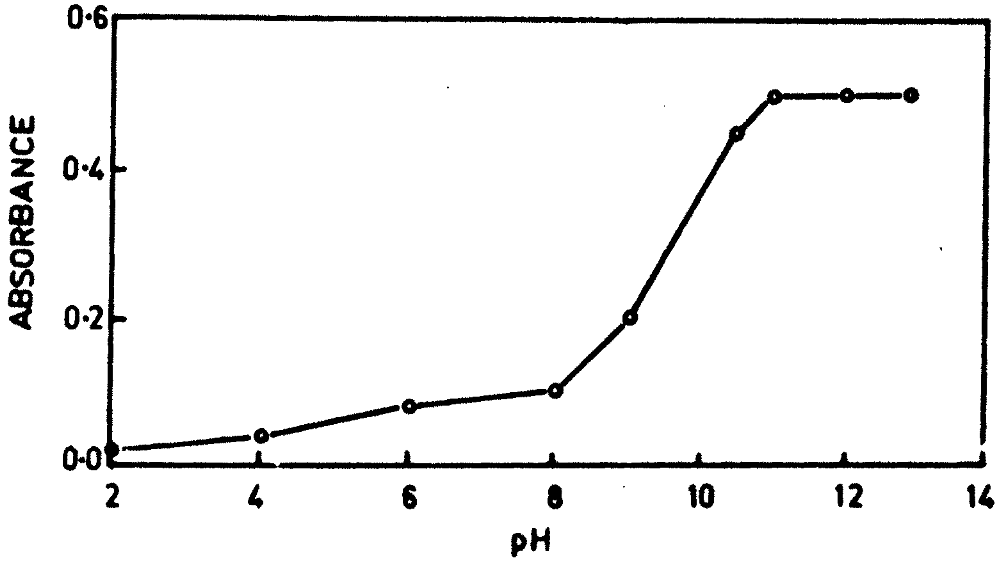

FIG.3·2 EFFECT OF pH

3.3.2 Effect of pH :

The effect of variation in pH on the absorbance of Ni(II)-BPG 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 13.0. Therefore pH 12.0 was selected as the optimum pH for further studies. The plot of observations is shown in fig. 3.2.

3.3.3 Effect of reagent concentration :

A series of solutions was prepared in which the volume of 2.511×10^{-3}M reagent was varied from 0.2 to 1.4 ml in which concentration of nickel was kept constant at 2.0 ppm. The complex is developed as per recommended procedure. The results in table 3.2 show that four times the molar excess of the reagent is sufficient for full colour development.

Table 3.2 : Effect of reagent :

$[Ni(II)] = 2.0$ ppm; $[BPG] = 2.511 \times 10^{-3}$M.

ml of reagent	Absorbance at 405 nm
0.2	0.29
0.4	0.44
0.6	0.51
0.8	0.54
1.0	0.54
1.2	0.54
1.4	0.54

3.3.4 Stability and reaction rate :

Nickel-BPG 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 405 nm from the solution containing various amounts of nickel showed that Beer's law is valid upto 11 ppm of Ni (II) (Fig.3.3).

The optimum concentration range of nickel was determined from the Ringbom plot[46] (Fig 3.4) and found to be 0.625 ppm to 2.75 ppm of nickel at 405 nm.

3.3.6 Composition of the complex :

The composition of Ni-BPG complex was determined by Job's method of continuous variation[47], molar ratio method[48] and slope ratio method.[49] For these methods, equimolar solutions of 1.703×10^{-5}M were used. Job's curve at 405 nm is shown in fig.3.5, which shows the formation of 1:2 complex, of Ni : BPG. This composition is confirmed by mole ratio study (Fig. 3.3) and slope ratio study.

3.3.7 Sensitivity :

The nickel complex of BPG does not show sensitivity towards light. The photometric sensitivity of the method was calculated by the method of Sandell[50] and found to be 0.03572 $\mu g/cm^2$ at 405 nm.

3.3.8 Degree of dissociation and instability constant :

The degree of dissociation was obtained by the method of Harvey and Manning.[49] The value of α, degree of dissociation was found to be 0.1096.

The apparent instability constant[51] was found to be 1.715×10^{-12} for Ni-BPG complex. The change in free energy[52] of the system is - 16.15 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 3.3 show that the method is reproducible. The standard deviation of the method calculated for 10 readings with different amounts of nickel are given in table 3.3.

Table 3.3 : Reproducibility of the method :

Nickel(II) ppm	Mean of 10 observations	Standard deviation	Coefficient of variation, %
1	0.05	0.001	2.00
2	0.10	0.0025	2.50
3	0.15	0.004	2.67

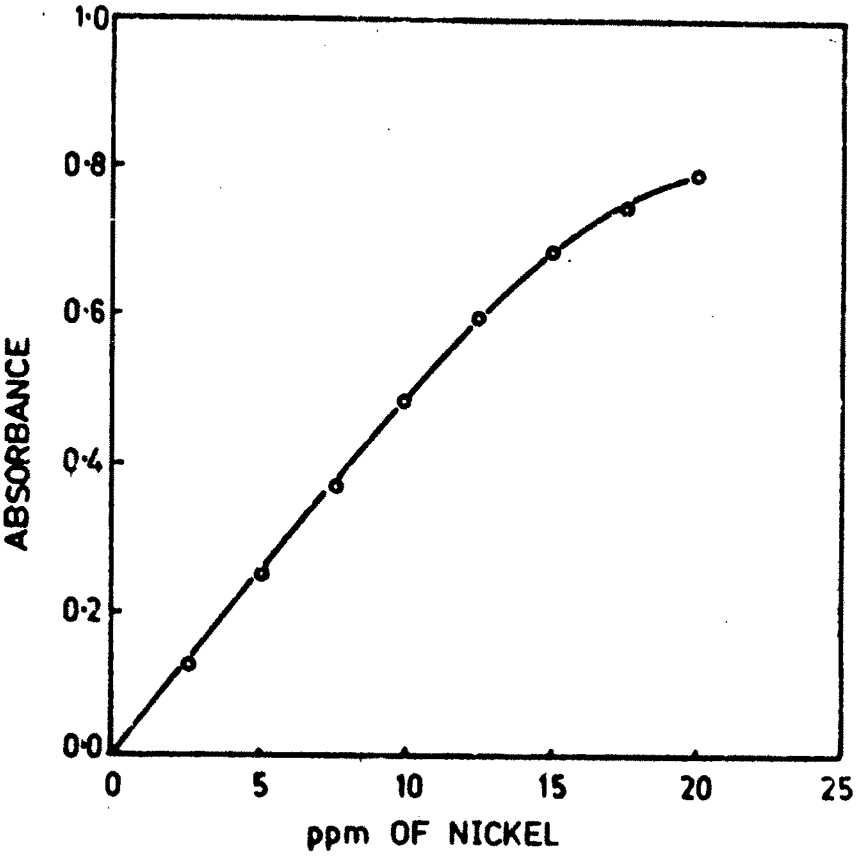

FIG.3·3 VALIDITY OF BEER'S LAW.

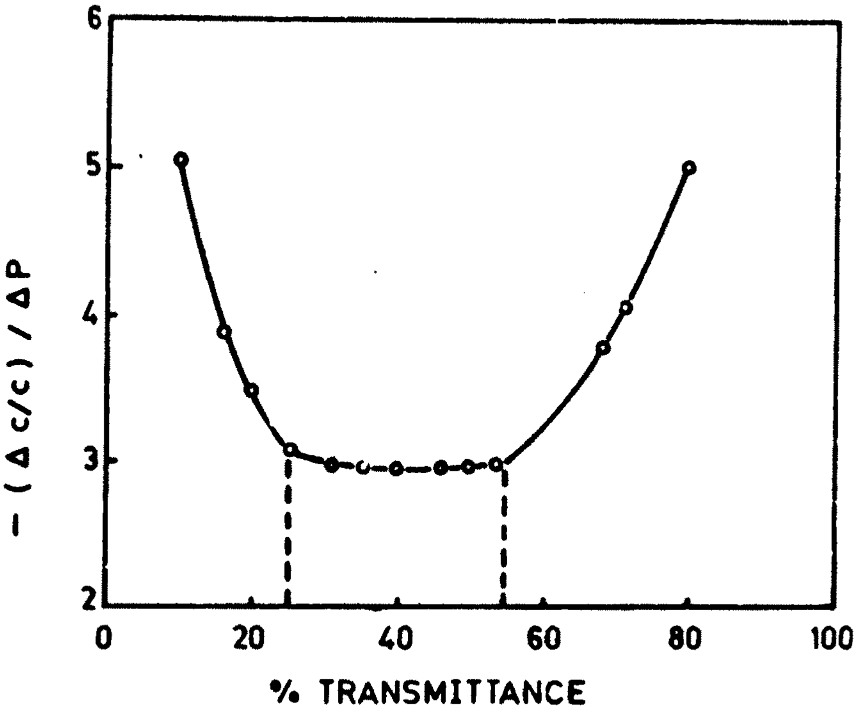

FIG. 3·4 RINGBOM PLOT.

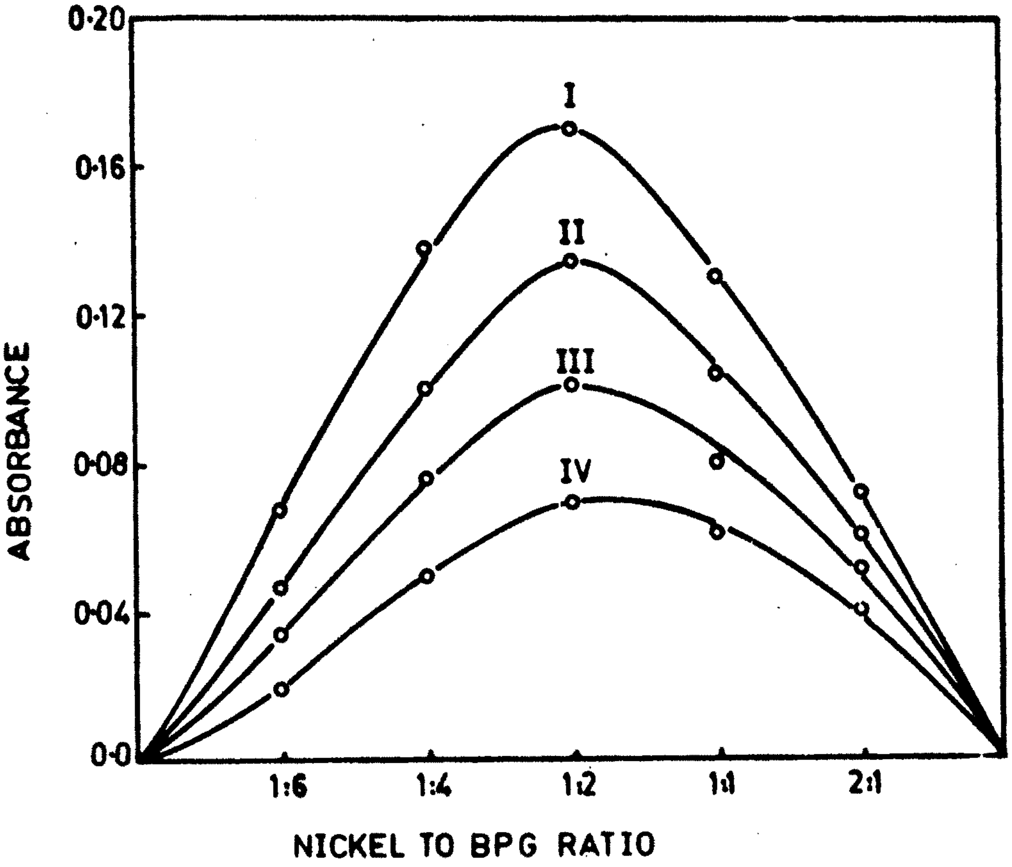

FIG. 3·5 JOB'S CONTINUOUS VARIATION METHOD.
I – 405 nm, II – 420 nm, III – 430 nm, IV – 440 nm.

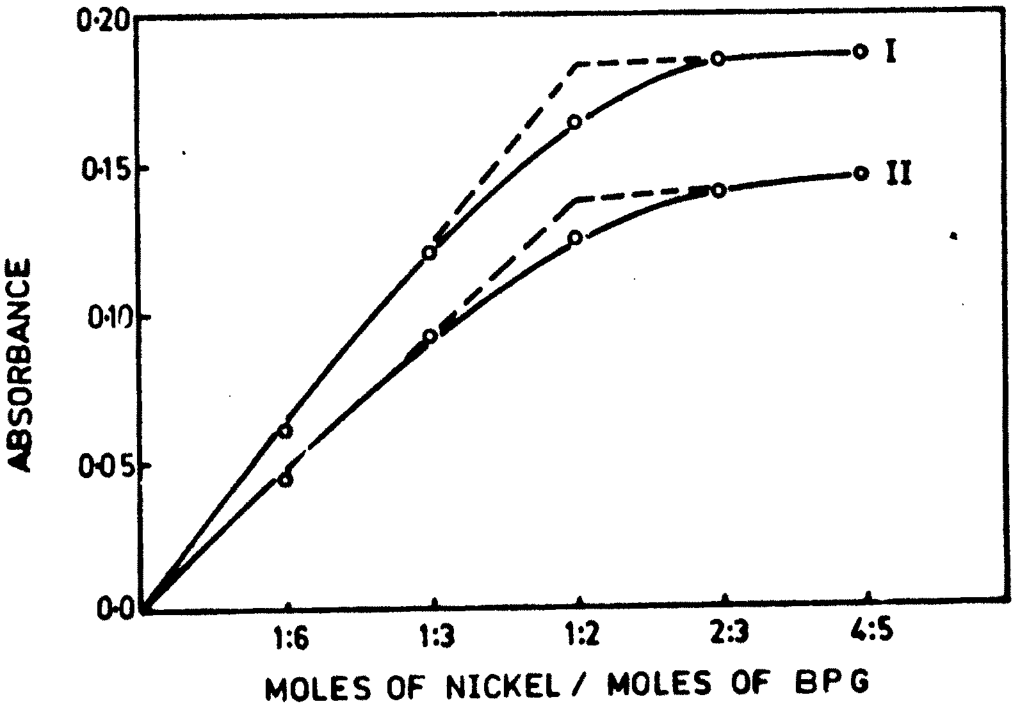

FIG. 3·6 MOLE RATIO METHOD.
I – 405 nm, II – 420 nm.

3.3.10 Effect of diverse ions :

Various ions were added to a sample containing a fixed amount of nickel (2 ppm) and the colour was developed and measured as per recommended procedure. The tolerance limit was assumed to be the amount of nickel needed to cause an error less than 2% in absorbance values. Copper in small amounts can be masked by using sodium thiosulphate. Mercury was masked with thiourea. It is found that Tl(I), Al(III), Cu(II), citrate ion, $EDTA^{-4}$ and fluoride ion interfere seriously, while Cd(II) is tolerated upto 150 ppm. The tolerance limits for th e ions are listed in table 3.4

Table 3.4 : Effect of diverse ions

$[Ni(II)] = 2$ ppm

$[BPG] = 2.008 \times 10^{-4} M$

Foreign ions	Added as	Tolerance limit, ppm
Cations		
Zn(II)	$ZnSO_4 \cdot 7H_2O$	2
Hg(II)	$HgCl_2$	0.5
Ba(II)	$BaCl_2$	1
V(V)	V_2O_5	2
Co(II)	$CoCl_2 \cdot 6H_2O$	0.1
Fe(III)	$FeCl_3$	0.1
W(VI)	$Na_2WO_4 \cdot 2H_2O$	400
Tl(I)	TlCl	none
Al(III)	$AlCl_3 \cdot 6H_2O$	none
U(VI)	$UO_2(NO_3)_2$	10
Fe(II)	$FeSO_4 \cdot 7H_2O$	1
Mg(II)	$MgSO_4 \cdot 7H_2O$	4

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Foreign ions	Added as	Tolerance limit, ppm
Cations		
Cd(II)	$Cd(NO_3)_2$	150
Cr(VI)	K_2CrO_4	2
Ba(II)	$Ba(NO_3)_2$	4
Se(IV)	SeO_4	10
Mn(II)	$MnCl_2 . 4H_2O$	4
Pb(II)	$Pb(NO_3)_2$	4
Cu(II)	$CuSO_4 . 5H_2O$	none
Anions		
Citrate	Sodium citrate	none
Thiocyanate	Potassium thiocyanate	10
Thiosulphate	Sodium thiosulphate	10
Thiourea	Thiourea	10
Oxalate	Potassium oxalate	10
Tartrate	Antimony potassium tartrate	10
Acetate	Sodium acetate	20
Phosphate	Potassium hydrogen orthophosphate	80
$EDTA^{-4}$	Disodium salt	none
Fluoride	Ammonium fluoride.	none

3.4 APPLICATIONS

Analysis of 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 (1 ml) was added carefully. The resulting solution was evaporated to dryness. 5 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 of 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 3.5.

Table 3.5 : Analysis of alloy steel.

Alloy	Certified value of Ni, %	Experimental value of Ni, %	Relative standard deviation for 10 observations
33 d (NBS std.U.S.)	3.58	3.53	0.06

3.5: REFERENCES

1. Sandell, E.B.,"Colorimetric Determination of Traces of Metals", 3rd Ed., Interscience, New York, P.669 (1959).

2. Morrison, G.H., "Trace Analysis, physical Methods", Interscience, New York, (1965).

3. Suzuki, M. and Takenchi, T.,Japan Analyst, 9, 708 (1960).

4. Minutilli, F. and Ruggieri, P., Ran. Chim., 14, 97 (1962); A.A., 11, 577 (1964).

5. Valamizor-Calderon, R. and Trespalacios-posada, A.,Rev. Univ.Ind. Santander, Colombia, 6,7 (1964); A.A.,12, 3324 (1965).

6. Taitiro, F., Masatada, S. and Tatsuo, Y., Japan Analyst, 20, 1255 (1971).

7. Pakhomova, K. S., Volkova, L.P. and Gorshkov, V.V., Zh. Anal. Khim., 19, 1085 (1964).

8. Wilson, A.L., proceedings of SAC Conf., Nottingham (1965).

9. Bodarf, D.E., Z. Anal.Chem., 247, 32 (1969).

10. Barling, M.M. and Bank, C.V. Anal. Chem.,36,2359 (1964).

11. Peshkova, V.M., Savostina, V.M., Astakhova E.K., and Minoeva, N.R. Trudy Kom. Anal. Khim., 15, 104 (1965), A.A.., 13, 2970 (1966).

12. Savostina, V.M. Kobyukova, S.O. and peshkova, V.M., Zh. Anal. Khim., 23, 938 (1968).

13. Peshkova, V.M., Belousova, M.Ya. and Novikova, I.S., Vest Mosk, gos. Univ. Ser. Khim., 5, 57 (1968) A.A., 18,950 (1970).

14. Einaga, H. and Ishii, H., Japan Analyst., 18, 439 (1969).

15. Ferguson, R.C. and Banks, C.V., Anal. Chem, 23, 448(1951).

16. Nast, R. and Uisitals, F., Acta Chem.Scand., 8, 112(1954).

17. Hooker, D.F. and Banks, C.V.,"Preparation, properties and Application of some Substituted Alicyclic Vic-Dioximes," Ames Laboratory Iowa State University, ISC-597 (March 1955).

18. Sandell, E.B. and perlich, R.W., Ind. Engg. Chem.Anal. Ed.,11, 309 (1939).

19. Yoe, J.H. and Wirsing, F.H., J.Am. Chem.Soc.,54, 1866(1932).

20. Shrivastava, J.N. and Singh, R.P., Talanta, 20, 1210(1973).

21. Weyers, J. and Haldky, E., Anal.Chim.Acta,28, 277 (1963).

22. Burke, R.W. and Yoe, J.H., Anal Chem.,34,1378(1962).

23. Ayres, G.H. and Annand, R.R., Anal.Chem.,35, 33 (1963).

24. Faraday, L. and Janosi, A.,Magyar Kem. Foly, 63, 19 (1957).

25. McDowell, B.L., Meyer, A.S., Feathers, R.E. and white, J.C., Anal. Chem., 31, 931 (1959).

26. Tripathi, K.K. and Banerjea, D.,Z. Anal. Chem.,176,91(1960).

27. Peshkova, V.M. and Ignateva, W. G., Zhur. Anal. Khim., 17, 1086 (1962).

28. Hajime, I. and Hisahika, E., Japan, Analyst, 16, 322(1967).

29. Dieter, M,Z. Chemie, 14, 408 (1974).

30. Janauer, G.E. and Korkish, J.,Z. Anal. Chem. 177, 407(1960).

31. Tsurumatsu, D., Genkichi, K. and Hiroko, W., J. Chem. Soc., Japan, Pure Chem. Sect., 82, 590 (1961).

32. Bhaskare, C.K. and Jagadale, U.D., Anal. Chim. Acta, 93, 335 (1977).

33. Munoz, Levya, J.A., Cano pavon, J.M. and Pino, P.F., Quim. Analit., 28, 90 (1974), A.A., 27, 3279 (1974).

34. Martinez, M.T., Bendito, D.P. and Pino, P.F., An. Quim., 69, 747 (1973).

35. Rueada, M. and Munoz Levya, J.A., Quim. Analit.,29, 122, (1975).

36. Burgos, F.S., Martinez, M.P. and pino, P.F.,inf.Quim. Analit.Pura. Apl. Ind.,23, 17 (1969).

37. Dcno, T., Nakgawa, G. and Wada, H., J. Chem. Soc., Japan, Pure Chem. Sect., 82, 590 (1961).

38. Shibata, S., Nűmi, Y. and Matsumae, T., Rep. Gov. Ind. Res. Inst. Nagoya, 11, 275 (1962), A.A., 10, 4179(1963).

39. Nakagawa, G., and Wada, H., Japan Analyst, 10, 1008 (1961).

40. Nakagawa, G. and Wada, H.,J. Chem.Soc. Japan,pure Chem. Sect., 84, 636 (1963).

41. Wada, H., and Nakagawa, G., Anal. Lett., 1, 687 (1968).

42. Busev, A.I. and Vin, D.Kh,Zh.Anal. Khim., 25, 1082 (1966).

43. De. A.K., and Rahaman, M.S.,Anal.Chim.Acta, 27, 591 (1962).

44. Akaiwa, H., Kawamoto, H., and Hara, M. Japan Analyst, 17, 183 (1968).

45. Vogel, A.I., " A Text Book of Quantitative Inorganic Analysis"., 3rd Edm., Longman-London, P.480 (1968).

46. Meitis, L., "Handbook of Analytical chemistry", 1st Ed., McGraw Hill Book Co., New York, 6-17 (1963).

47. Job, P., Compt. Rend., 180, 928 (1925). Ann. Chim. (paris), 9, 113 (1928).

48. Yoe, J.H. and Jones, A.L. Ind. Eng. Chem., Anal. Ed., 16, 111 (1944).

49. Harvey, A.E. and Manning, D.L., J. Am. Chem. Soc., 72, 4488 (1950).

50. Sandell, E.B., " Colorimetric Determination of Traces of Metals, " 3rd Ed., Interscience publishers Inc., New York, P. 688 (1965).

51. Trikha, K.C., Katyal, M. and Singh, R.P. Talanta, 14, 977 (1967).

52. Grinberg, A.A., " An Introduction to the Chemistry of Complex Compounds", 2nd Ed., 1951, Translated by Leach J.R., 1st Ed., Pergamon, London (1962), P. 275.