Int. J. Chem. Sci.: 8(2), 2010, 769-776

ANALYTICAL METHOD DEVELOPMENT FOR EXTRACTIVE SPECTROPHOTOMETRIC DETERMINATION OF NICKEL USING BIS [3-HYDROXYIMINO-5-METHYL-N-METHYL]-2-IMINE AS A NEW ANALYTICAL REAGENT

R. S. LOKHANDE*, V. R. PATIL, P. P. SHEVDE and S. M. LELE

Department of Chemistry, University of Mumbai, Vidyanagri, Santacruz (E),
MUMBAI – 400 098 (M.S.) INDIA

ABSTRACT

Bis [3-hydroxyimino-5-methyl-N-methyl]-2-imine (HIMMI) is proposed as a new sensitive and selective reagent for the spectrophotometric determination of nickel. The reagent reacts with nickel in the pH range 9.0 to 9.4 to form a yellow colored 1 : 1 chelate, which is very well extracted in n-butanol. Beer's law is obeyed in the concentration range 0.01-40.00 μg mL^{-1} nickel. The molar absorptivity and Sandell's sensitivity of the extracted species are 1.4297 x 10^3 Lit mol^{-1} cm^{-1} and 4.10 x 10^{-3} μg cm^{-2}, respectively at 415 nm. The proposed method is highly sensitive, selective, simple, rapid, accurate, and has been satisfactorily applied for the determination of nickel in the synthetic mixtures, vegetable oil and alloys.

Key words: HIMMI, Nickel, Spectrophotomertic determination.

INTRODUCTION

The significance of nickel as a transition metal lies in its wide spectrum of applications covering many frontier areas of study, particularly in industrial and consumer products. Even though nickel is not considered to be as toxic as most of the heavy metals, it is an equally harmful element. Hence, owing to the significance of nickel, it's determination from associated elements by extractive spectrophotometry has been of considerable importance.

A wide variety of reagent has been reported for the spectrophotometric determination of nickel.

---

*Author for correspondence; E-mail: lokhanders@yahoo.com, vrpatil@chem.mu.ac.in

However, these methods suffer from limitations such as critical pH[1-3], require-ment of masking agent[1] or other agents[4,5], requirement of heating[6], and interference from some ions[1,7] etc. A method, far superior in sensitivity and selectivity to those reported in the literature, is developed for the extractive spectrophotometric determination of nickel with bis [3-hydroxyimino-5-methyl-N-methyl]-2-imine (HIMMI). A close literature survey indicates that HIMMI has so far not been employed for either coordination or analytical studies. The proposed method is free from limitations.

EXPERIMENTAL

The stock solution of nickel was prepared and standardized[8] and working solution of lower concentration was obtained by suitable dilution. The absorbance measurements were carried out on a Shimadzu UV visible 2401 spectrophotometer with 1 cm quartz cell and the pH measurements were carried out using appropriate buffer solution with ELICO LI-120 pH meter.

Recommended procedure

The extraction experiments were performed by shaking the appropriate organic and aqueous solution at O/A phase ratio of 1. The reagent HIMMI formed a yellow coloured complex with nickel (II), which was transferred in a separating funnel. It was extracted into 10 cm^3 n-butanol and then transferred to 10 mL volumetric flask by passing through some amount of sodium sulphate in order to absorb trace amount of water. The amount of nickel present in the organic phase was determined quantitatively by spectrophotometric method by taking absorbance at 415nm and that in the aqueous phase, it was determined by known method.

RESULTS AND DISCUSSION

Extraction as a function of pH

In order to obtain the optimum extraction condition for nickel, the extraction was carried out at various pH (1.0-12.0) keeping the organic to aqueous volume ratio of 1 : 1. The extraction was found to be quantitative in the pH range 9.0-9.4 and hence, pH 9.2 was seleced for further studies (Fig. 1).

Absorption spectrum

The absorption spectrum of Ni (II) : HIMMI in n-butanol, shows an intense absorption peak at 415 nm. The absorption due to the reagent in negligible at this

wavelength and hence, the absorption measurements were taken at this wavelength using a reagent blank.

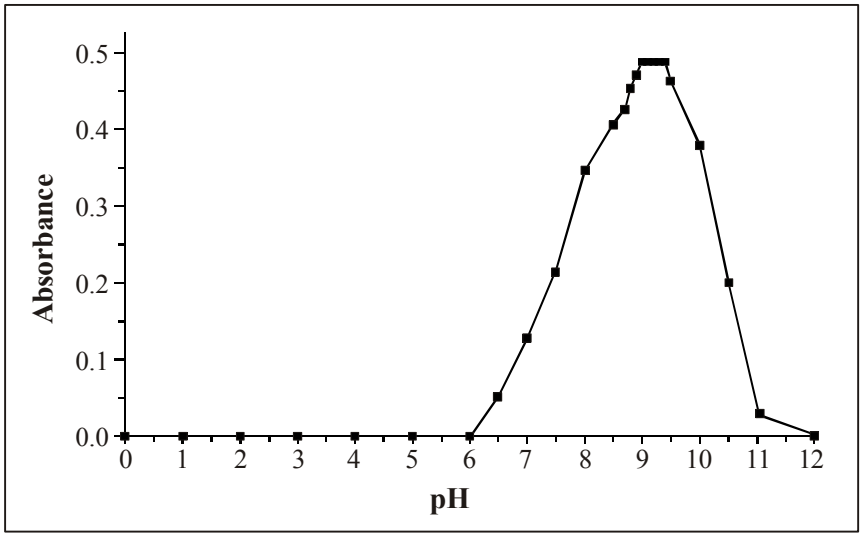

Fig. 1: The effect of pH on the extraction of nickel with HIMMI in n-butanol

Effect of solvent

The suitability of various solvents was investigated using organic solvents such as n-butanol, chloroform, carbon tetrachloride, ethyl acetate, benzene, xylene, toluene, iso-amyl alcohol, ether, pet ether etc. The extraction of nickel with HIMMI was found to be quantitative, when both were dissolved in aqueous solution containing n-butanol as a solvent. Therefore, n-butanol was used as a solvent as it gave better and quick phase separation.

Effect of salting out agents

The presence of salts of alkali and alkaline earth metals do not show any improvement in the percentage extraction of nickel between n-butanol and aqueous phase. Hence, these salts have not been added in the aqueous phase before extraction for subsequent studies.

Effect of reagent

The effect of variation in concentration of HIMMI shows that 1 mL of 0.1% ethanolic solution of HIMMI is sufficient for colour development and extraction of 20 μg/ cm^3 of nickel solution (Fig. 2).

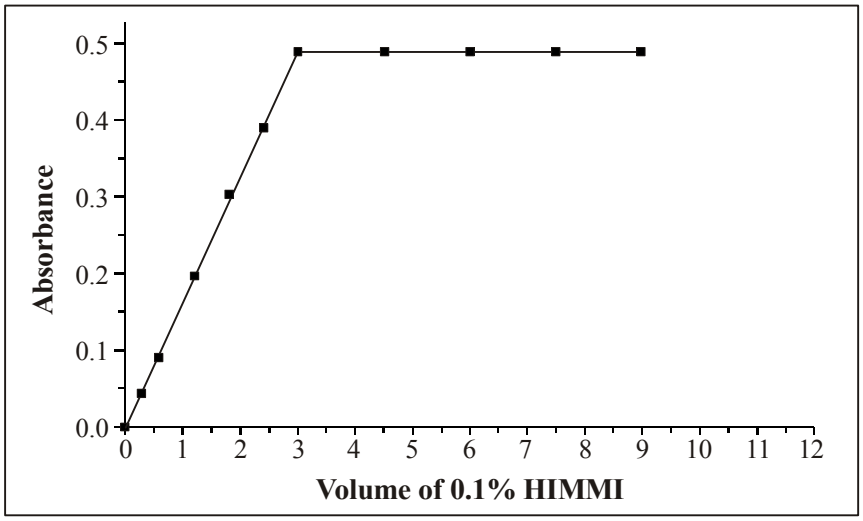

Fig. 2: Effect of reagent concentration

Effect of equilibration time

The study of change in absorbance with variation in equilibration time for the extraction of nickel shows that equilibration time of 2 minutes is sufficient for the quantitative extraction of Ni (II).

Stability of the complex with time

The stability of the colour of the extracted species with time shows that the absorbance of the extracted species is stable upto 5.0 hrs. Throughout the experiment, for the reason of practical convenience, the absorbance measurements have been carried out within one hour of the extraction of nickel.

Beer's law and sensitivity

Calibration graph for nickel was constructed under optimum conditions. The graph obeys Beer's law in the range of 1 to 40 µg for nickel. The molar absorptivity and Sandell's sensitivity of the system were found to be 1.4297×10^3 Lit mol^{-1} cm^{-1} and 4.10×10^{-3}µg cm^{-2}, respectively.

Composition of the extracted species

The composition of the extracted species was determined by using the Job's continuous variation method and verified by mole ratio method and slope ratio method. These methods show that the composition of Ni : HIMMI complex is 1 : 1 (Fig. 3).

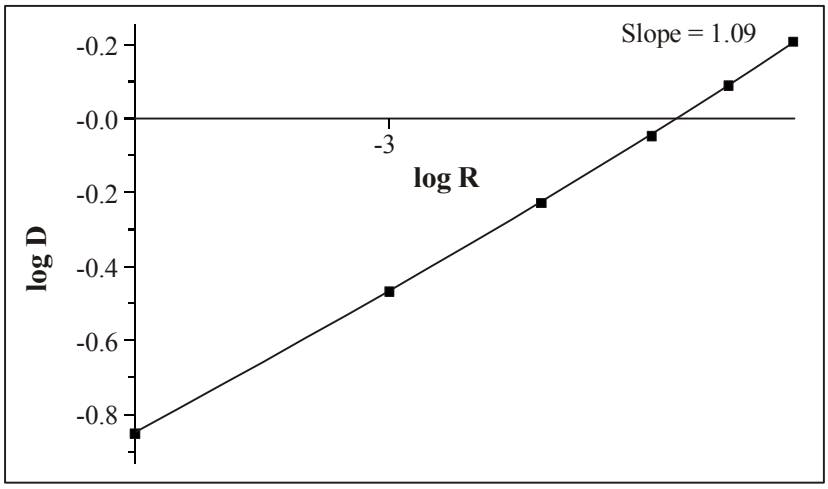

Fig. 3: Logarithmic plot of the distribution of nickel vs. concentration of HIMMI

Effect of foreign ions

The effect of foreign ions like Cl^-, Br^-, F^-, BrO_3^-, IO_3^-, SO_3, I^-, ClO_3^-, Cd (II), Mn (II), Al (III), Ca (II), Ba (II), Rh (II), Tl (I), Zn (II) and many others present in various amounts do not interfere in the spectrophotometric determination of 20 µg of nickel.

Precision and accuracy

The precision and accuracy of the method were studied by analyzing a series of solutions containing known amounts of nickel (II). The results presented in table 1, show that the R. S. D. for pure nickel solution is about 0.5%.

Table 1: Precision and accuracy in the determination of nickel

Concentration nickel (µg)		S.D.	R.S.D.(%)
Taken	Found[a]		
0.50	0.501	0.0028	0.56
0.75	0.750	0.0033	0.44
1.00	0.998	0.0050	0.51
1.25	1.250	0.0047	0.38
1.50	1.502	0.0052	0.35

[a] Average of five determinations

Application to the determination of nickel in synthetic mixtures

The present method was applied to the determination of nickel (20 μg) in various synthetic mixtures. The results are shown in Table 2.

Table 2: Analysis of synthetic mixtures

	Synthetic mixture composition[a]	Amount found[b]
1	Ni (10) + Zn (10)	9.98
2	Ni (10) + Mo (10)	9.98
3	Ni (10) + Mg(10)	9.98
4	Ni (10) + Pb (10)	9.97
5	Ni (10) + U (10)	9.91

[a]Values given are in microgram amount of the metals.

[b]Average of five determinations

Application to the determination of nickel

Determination of nickel in alloy

About 0.3 to 0.5 g of sample (alloy) was dissolved in 15 cm^3 of aqua-regia. The solution was evaporated to dryness and the residue was treated with conc. HNO_3 and diluted to 100 cm^3. An aliquot of diluted solution was used for the extraction and spectrophotometric determination of Ni (II) by present method.

Table 3: Analysis of real samples

S. No.	Sample	Amount of Ni (II) (%)	
		Certified value	Found
1	**Nickel alloys**		
	(i) Cupronickel	54.1	54.095
	(ii) Steel	22.18	22.178
2	**Vegetable oil**	0.0014	0.0013

Determination of nickel in vegetable oil

10.0 g of fat was heated in 100 cm^3 conical flask with 10.0 cm^3 of conc. HNO_3 during which a current of air was driven through and the solution was continuously agitated. The aqueous solution was filtered and concentrated to a small volume. It was made alkaline with liquid ammonia, boiled and then filtered through a plug of paper pulp in a small filter funnel. The filtrate obtained was clear and yellowish in colour. It was diluted to known volume and further analyzed for the extractive spectrophotometric determination of Ni (II) by the present method.

CONCLUSION

The proposed method is highly sensitive and selective than the other reported methods for the extractive spectrophotometric determination of microgram amounts of nickel. It offers advantages like reliability and reproducibility in addition to its simplicity, instant colour development and suffers from less interference. It has been successfully applied to the determination of nickel at trace level in synthetic mixtures, vegetable oils and alloys.

REFERENCES

1. B. Patel, Nitin Kumar and K. K. Desai, 2, 4-Dihydroxy-5-nitropropiophenone Oxime as an Analytical Reagent : Studies on Ni (II) and Pd (II) Chealates, Asian J. Chem., **15(2)**, 751-754 (2003).

2. K. Zarei, M. Atabati and Z. Malekshabani., Simultaneous Spectrophotometric Determination of Iron, Nickel and Cobalt in Micellar Media by using Direct Orthogonal Signal Correction – Partial Least Squaqre Method, Anal. Chim. Acta. **556(1)**, 247-54 (2006).

3. A. P. Kumar, P. R. Reddy and V. K. Reddy, Simultaneous Determination of Cobalt (II) and Nickel (II) by Fourth-Order Derivative Spectrophotometric Method using 2-Hydroxy-3-methoxy-benzaldehyde Thiosemicarbazone, J. Autom. Methods. Manag. Chem., 48768 (2007).

4. M. K. Naik and N. V. Thakkar, Extractive Spectrophotometric Determination of Nickel and Palladium with 1-Phenyl-1-hydrazonyl-2-oximino-1, 2-ethanedione,. Indian J. Chem., **34A**, 410-411 (1995).

5. G. A. Shar and G. A. Soomro, Spectrophotometric Determination of Cobalt (II), Nickel (II) and Copper (II) with 1-(2 Pyridylazo)-2-naphthol1-(2 pyridylazo)-2-naphthol in Micellar Medium. The Nucleus, **41(1-4)**, 77-82 (2004).

6. X. Fan, G. Zhang and C. Zhu, Synthesis of 2-[2-(5-Methylbenzothiazolyl) azo]-5-dimethylamino benzoic Acid and its Application to the Spectrophotometric Determination of Nickel, Analyst, **123**, 109-112 (1998).

7. N. Hokoufi, F. Shemirani and F. Memarzeadeh, Fibre Optic-Linear Array Detection Spectrophotometry in Combination with Cloud Point Extraction for Simultaneous Preconcentration and Determination of Cobalt and Nickel, Anal. Chim. Acta., **601(2)**, 204-211 (2007).

8. A. I. Vogel, Textbook of Quantitative Inorganic Analysis, 3rd Ed., London (1975).

Accepted : 14.11.2009