Asian Journal of Chemistry Vol. 21, No. 7 (2009), 5469-5474

Spectrophotometric Determination of Nickel(II) by Using *Bis*-[2,6-(2′-Hydroxy-4′-sulpho-1′-naphthylazo)]pyridine Disodium Salt

BANJIT BARMAN* and SUDARSAN BARUA
Department of Chemistry, Cotton College, Guwahati-781 001, India
E-mail: banjit_barman@rediffmail.com

Bis-[2,6-(2′-hydroxy-4′-sulpho-1′-naphthylazo)]pyridine disodium salt (HSNP), a water soluble heterocyclic azo dye has been used for the trace determination of nickel(II). HSNP on complexation with nickel(II) to form a purple coloured, water soluble 1:1 complex with molar extinction coefficient (ε) 7.86×10^4 L mol^{-1} cm^{-1} at 565 nm in the pH range 6.1-9.75. Beer's law is obeyed upto 1.65 ppm of Ni(II). The optimum concentration range for determination of Ni(II) is 0.15-0.80 ppm with Sandell's sensitivity of 0.000744 (μg Ni(II) cm^{-2}). The stability constant of the Ni(II)-HSNP complex as calculated by the Job's method in an ionic strength with respect to 0.01 M Na_2SO_4 solution is found to be 1.22×10^8.

Key Words: Spectrophotometry, *Bis*-[2,6-(2′-hydroxy-4′-sulpho-1′-naphthylazo)]pyridine disodium salt, Nickel(II).

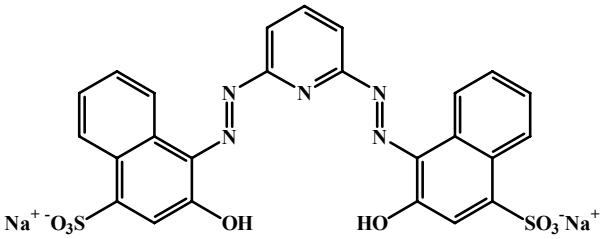
INTRODUCTION

The ultra trace element nickel is both essential and toxic for animals and humans. A Ni-poor nutrition of < 0.1 mg/kg dry matter leads to Ni deficiency symptoms. Ni is a component of the urease and it is also essential for several species of bacteria which occur in the rumen of ruminants. Ni deficiency symptoms, however, have not yet been found in animals and humans since the Ni often exceeds the Ni requirement. On the other hand, an external Ni exposure to nickel alloys induces Ni dermatitis in 8 to 14 % of nickel-sensitive women and in > 1 % of men after the filling of the Ni deposition in the body. Experiments with some animal species showed that Ni exposure leads to disturbances in the Mg and above all in the Zn metabolism. Ni excess induces Zn deficiency symptoms which are similar to *parakeratosis* in pigs. They correspond to the symptoms of nickel allergy in humans. The Ni intake of humans, therefore, leads to the gradual filling of the Ni pool in the body. This can induce nickel dermatitis in Ni-sensitive women and men. The Ni requirement of adults does not exceed 25 to 35 μg/day. The Ni balance of men and women is positive (+ 20 %) and shows that Ni incorporation even in the case of a Ni consumption may exceed by far the requirement[1]. The majority of chocolates and candies are made mainly from cocoa, milk solids, dry fruits, fruit flavours and sugar. The amount of nickel ranges from 0.041 to 8.29 μg/g with an average of 1.63 μg/g in different chocolates and candies[2].

Several reagents for the spectrophotometric determination of Ni(II) have been reported[3] of which heterocyclic azo-dyes constitute an important class of chromogenic reagents with high photometric sensitivities[4]. Nickel has been determined spectrophotometrically in hydrogenated oils[5-8], chocolates and candies[9,10]. In the present method, *bis*-[2,6-(2′-hydroxy-4′-sulpho-1′-naphthylazo)]pyridine disodium salt (HSNP), a new heterocyclic azo dye has been used for the determination of Ni(II) in hydrogenated oils, chocolates and candies.

EXPERIMENTAL

Synthesis and characterization of the reagent: 2,6-Dichloropyridine (Fluka) (0.05 mol) was refluxed with excess of 99 % hydrazine hydrate (Qualigens) for 2 h to get the corresponding hydrazide. The hydrazide of 2,6-dichloropyridine (0.025 mol) was dissolved in minimum volume of dilute hydrochloric acid and then coupled with sodium salt of 1,2-napthaquinone-4-sulphonic acid (0.05 mol) dissolved in minimum volume of water. A red precipitate appears, filtered and dried.



Bis-[2,6-(2′-hydroxy-4′-sulpho-1′-naphthylazo)]pyridine disodium salt

The compound is a dark red powder and is highly soluble in water. The purity of the compound was checked by thin layer chromatography and IR spectra. The IR spectra of HSNP in KBr were recorded in FTIR-8400S Fourier transform infrared spectrophotometer (Shimadzu).

The IR-spectra of the ligand showed the following results: ν(-OH) 3510 cm^{-1}; ν(-N=N-) 1600 cm^{-1}; ν(C-O) at 1130 cm^{-1}.

Stock solution of nickel was prepared by dissolving appropriate amount of nickel(II) chloride (BDH) and was standardized by the standard method[10]. A 1×10^{-4} M solution was prepared in double distilled water by diluting the stock solution. A 1×10^{-3} M aqueous solution of HSNP was prepared in double distilled water. The solution is stable for more than 1 month. But, solutions more than 6 d old are not used for analysis. Dilute solutions of hydrochloric acid and sodium hydroxide were used for pH adjustment. A borate buffer of pH 8.0 was prepared.

The absorbance was measured by UV-1700 pharmaspec UV-visible spectrophotometer (Shimadzu) and UV-visible spetrophotometer 108 (Systronics) with 10 mm quartz cells. The pH measurements were carried out with an Elico LI 120 digital pH meter.

RESULTS AND DISCUSSION

Spectral characteristics of the complex and effect of pH: A series of solutions containing known amounts of nickel(II) and a solution of HSNP (1.0 mL of 1.0×10^{-3} M) were prepared and pHs were adjusted at different levels in a total volume of 10 mL. The spectra of the solutions were recorded against the corresponding reagent blanks. It has been observed that only one complex is formed at all pH values (Fig. 1). Plot of pH *versus* absorbance at λ_{max} (565 nm) shows that constant and maximum absorbance is exhibited in the pH range 6.1 to 9.75.

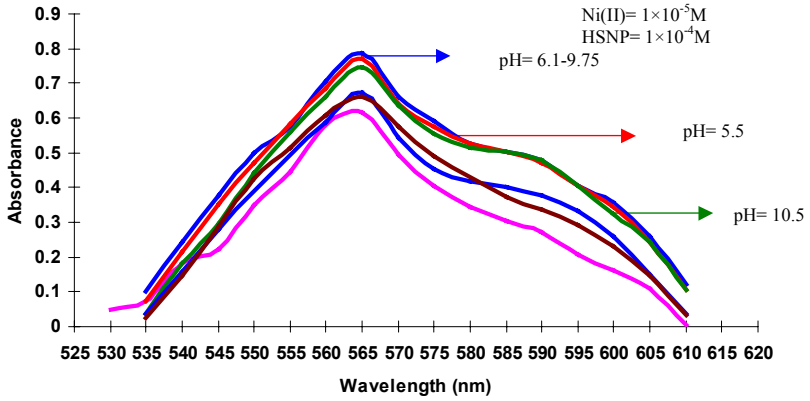


Fig. 1. Absorption Spectra for Ni(II)-HSNP complex at different pH

Beer's law validity and optimum concentration range: Linearity between the absorbance of the complex and Ni(II) concentration was examined by varying the concentration of Ni(II) in the solutions containing a fixed amount of the ligand solution at pH 8.0 and measuring the absorbance at 565 nm against the corresponding reagent blank. Beer's law is obeyed from 0-1.65 ppm of Ni(II). The result obtained for the validity of the Beer's law optimum range of concentration for accurate determination as calculated from Ringbom's plot is 0.15-0.8 ppm of Ni(II).

Effect of reagent concentration: Study of the effect of reagent concentration on complexation reaction showed that for maximum complexation six times of the reagent is required. In subsequent studies, however, 10 times molar excess of the reagent was used.

Molar composition and stability of the complex: The stoichiometry of the complex was ascertained by making use of Job's method of continous variations. The curve obtained by plotting absorbance *versus* mole fraction of the metal ions at 565 nm and pH 8.0 shows that the metal to ligand ratio in the complex is 1:1. The stability constant of the Ni(II)-HSNP complex as calculated by the Job's method in an ionic strength with respect to 0.01 M Na_2SO_4 solution is found to be 1.22×10^8. The physico-chemical characteristics of the Ni(II)-HSNP complex is summarized in the Table-1.

TABLE-1
PHYSICO-CHEMICAL CHARACTERISTICS OF THE Ni(II)-HSNP COMPLEX

λ_{max} (nm)	565
pH range	6.1-9.75
Beer's law validity (ppm)	0.00-1.65
Optimum concentration range (ppm)	0.15-0.8
Sandell's sensitivity (µg Ni(II) cm^{-2})	0.000744
Molar extinction coefficient (€) (L mol^{-1} cm^{-1})	7.86×10^4
Stability constant	1.22×10^8

Recommended procedure for determination of nickel: To a suitable aliquot containing 1.5-8.0 mg Ni(II), add 1 mL of 1×10^{-3} M HSNP solution, followed by 1 mL borate buffer of pH = 8.0. Dilute to 10 mL and measure the absorbance at 565 nm against the corresponding reagent blank. Determine the concentration of Ni(II) from the calibration curve recorded under the identical conditions.

Effect of diverse ions and their tolerance limits: Effect of diverse ions has been studied by preparing synthetic solutions containing 1.17 ppm of nickel(II) and varying amounts of diverse ions. Nickel(II) contents in these solutions was determined by following the recommended procedure. It was found that fluoride, chloride, bromide, iodide, nitrate, nitrite (2000 fold each), magnesium(II), calcium(II), barium(II), strontium(II), aluminium(III), manganese(II), molybdenum(VI), antimony(III) (1000 ppm each) did not interfere. It was found that phosphate (250 ppm), SCN^- (500 ppm), tartarate (200 ppm), oxalate (200 ppm), citrate (200 ppm), thiosulphate (200 ppm), thiosemicarbazone (50 ppm), Cu (5 ppm masked by TU), silver (50 ppm masked by I^-), mercury (10 ppm masked by I^-), iron (25 ppm masked by F^-), cobalt (20 ppm masked by SCN^-). However, sulphide, cyanide, zinc, cadmium and EDTA interfered seriously.

Determination of nickel in hydrogenated oils: To enhance the utility of the method, nickel has been determined in some commonly available hydrogenated vegetable oils.

Recommended procedure: Take 20 g of the sample in an Erlenmeyer flask and subject to wet oxidation[11] with concentrated nitric acid. After digestion with concentrated nitric acid several times (in small lots of 5 mL each), cool the whole mass in ice and filter through glass wool. Evaporate the filtrate in a fume cupboard to a small volume. Raise the total volume to 100 mL in a measuring flask. Take 2 mL of the dilute solution and neutralize with sodium hydroxide to bring the pH around 7.0 and determine the amount of nickel with HSNP, following the recommended procedure. The standard addition procedure was also used to ascertain the accuracy of the method. For this, a fixed amount of nickel was added to the supernatant liquid and the nickel content was determined.

In Table-2, the recovery data of nickel is given. It has been found that the recovery of nickel by the standard addition method is not < 2 %.

TABLE-2
RECOVERY DATA OF NICKEL IN HYDROGENATED OILS

Sample No.	Ni(II) present in 2.0 mL of the sample solution in ppm (average of 5 readings)	Nickel added (ppm)	Nickel present (ppm)	Nickel found (ppm)	Recovery of nickel (%)	Nickel present (µg) per g of the sample
Sample-1	0.331	0.2925	0.6235	0.6200	99.43	0.8275
Sample-2	0.412	0.2925	0.7045	0.6931	98.36	1.0300
Sample-3	0.362	0.2925	0.6621	0.6300	101.14	0.9050

Determination of nickel in chocolates and candies: Dry ash method[12,13] is used in determination of the nickel contents of chocolates and candies. Heat 5 g of the sample in a silica crucible in a low Bunsen flame to burn. Now, heat the content strongly to 450-500 ºC. Cool and add 2.0 mL of concentrated nitric acid. Evaporate to dryness and ignite again at 450-500 ºC for ≈ 1 h. Dissolve the resulting white ash in the minimum volume of dilute nitric acid. Neutralize the acid by adding NH_3 solution and remove the excess ammonia by heating. Make up the volume to 25.0 mL in a standard flask. Pipette out 1.0-5.0 mL of the solution and determine nickel by the recommended procedure.

TABLE-3
RECOVERY DATA OF NICKEL IN CHOCOLATES AND CANDIES

Sample No.	Ni(II) present in 2.0 mL of the sample solution in ppm (average of 5 readings)	Nickel added (ppm)	Nickel present (ppm)	Nickel found (ppm)	Recovery of nickel (%)	Nickel present (µg) per g of the sample
Sample-1	0.6125	0.14625	0.75875	0.756	99.63	6.125
Sample-2	0.5850	0.14625	0.73125	0.741	101.33	5.85
Sample-3	0.5925	0.14625	0.73875	0.737	99.76	5.925

TABLE-4
SENSITIVITIES OF DIFFERENT REAGENTS FOR NICKEL

Reagent	Sandell's sensitivity (µg Ni(II) cm^{-2})	Wavelength (nm)	Reference
Dimethylglyoxime + oxidizing agent	0.00420	445	14
Dimethylglyoxime / $CHCl_3$	0.01700	375	14
Dimethylglyoxime / $CHCl_3$	0.01200	325	14
1-(2-Pyridylazo)-2-naphthol	0.00120	570	15
Furil-α-dioxime / $CHCl_3$	0.00400	435	16
Dithio-oxamide	0.00460	640	17
4-(2-Quinolylazo)phenol	0.00230	570	18
Ammonium(2'-Amino-3'-hydroxypyridyl-4'-azo)benzene-4-arsonate	0.00210	540	19
HSNP	0.000744	565	Present method

Conclusion

The present method has been found to be simple, rapid, sensitive and can be applied for the determination of Ni(II) in hydrogenated vegetable oils, chocolates and candies. The sensitivity of the present method is promising and compares well with other known reagents (Table-4). The amount of Ni(II) in hydrogenated vegetable oils and chocolates have been found to 0.8275-1.0300 µg/g and 5.85-6.125 µg/g, respectively and is found to be within permissible limits as reported[2].

REFERENCES

1. M. Anke, L. Angelow, M. Glei, M. Muller and H. Illing, *Fresenius J. Anal. Chem.*, **352**, 92 (1995).
2. S. Dahiya, R. Karpe, A.G. Hegde and R.M. Sharma, *J. Food Compos. Anal.*, **18**, 517 (2005).
3. Z. Marczenko, Spectrophotometric Determination of Elements (Trans. Ed. : Ramsay, C.G.), John Wiley & Sons Inc., N.Y., London, Toronto (1976).
4. E.B. Sandell and H. Onishi, Photometric Determination of Traces of Metals, General Aspects, John Wiley & Sons, N.Y., Toronto, Brisbane, edn. 4 (1978).
5. A. Wasey, B.K. Bansal, M. Satake and B.K. Puri, *Bunseki Kagaku*, **32**, E211 (1983).
6. Z. Li, J. Pan and J. Tang, *Anal. Lett.*, **35**, 167 (2002).
7. A.E. Ali, T. Khayamian and B. Hemmateenejad, *Anal. Lett.*, **35**, 111 (1999).
8. A.K. Makik, K.N. Kaul, B.S. Lark, W. Faubel and A.L.J. Rao, *Turk. J. Chem.*, **25**, 99 (2001).
9. M. Ghaedi, *Spectrochim. Acta*, **65**, 295 (2007).
10. A. Duran, M. Tuzan and M. Soylak, *Environ. Monit. Assess.*, **149**, 283 (2009).
11. A.I. Vogel, A Text Book of Quantitative Inorganic Analysis, Longman Green, London (1961).
12. L.L. Reitz, W.H. Smith and M.P. Plumlee, *Anal. Chem.*, **32**, 1728 (1960).
13. A.A. Schilt and P.J. Taylor, *Anal. Chem.*, **42**, 220 (1970).
14. G.L. Traister and A.A. Schilt, *Anal. Chem.*, **48**, 1216 (1976).
15. E.B. Sandell and H. Onishi, Colorimetric Determination of Traces of Metals, John Wiley & Sons, Inc., New York, p. 3 (1978),
16. T. Dono, G. Nagakawa and H. Wada, *Nippon Kagaku Zasshi*, **85**, 590 (1961).
17. C.G. Taylor, *Analyst*, **81**, 369 (1956).
18. W.D. Jacobs and J.H. Yoe, *Anal. Chim. Acta*, **20**, 332 (1959).
19. S. Barua, B. Barman and B.S. Garg, Proceedings of the 52nd Annual Technical Session, Assam Science Society (2007).

(*Received*: 24 September 2008; *Accepted*: 30 April 2009) AJC-7493