*Asian Journal of Chemistry* Vol. 16, No. 1 (2004), 299–303

# Spectrophotometric Determination of Nickel(II) with Phenanthrenequinone Monosemicarbazone

H.C. RAI*, ASHWINI KUMAR, K.B. SINGH† and RAMAN KUMAR‡
*Department of Chemistry, L.S. College, Muzaffarpur-842 001, India*
*E-mail: hcrai_chem@yahoo.co.in*

In the present study, spectrophotometric estimation of nickel(II) with phenanthrenequinone monosemicarbazone (PQSC) have been carried out. Nickel(II) instantaneously gives orange coloured complex on the addition of phenanthrenequinone monosemicarbazone solution. The pH, the concentration range of nickel for adherence to Beer's law and the ratio of nickel to PQSC present in the complex have been determined. Effect of foreign ions on the determination of nickel has also been investigated.

**Key Words: Spectrophotometric determination, Ni(II), Phenanthrenequinone monosemicarbazone.**

## INTRODUCTION

Colorimetric method of analysis is gaining importance these days due to simplicity and speed[1, 2]. Most of the methods used for spectrophotometric determination of nickel involve extraction of the metal from its aqueous solution after complexing it with some chelating agent. In the case of dimethylglyoxime, used in conjunction with an oxidising agent, two complexes (1 : 2 and 1 : 4) are formed. The 1 : 4 complex is more stable which is derived from 1 : 2 complex by oxidation above pH 11.0. The exact nature of the reaction is not known and a closely standardised procedure must be used. Colour development (due to 1 : 4 complex) is slow and the reaction mixture must be heated at 60–70°C for 5 min. In order to eliminate interfering ions, nickel complex (1 : 2) is extracted into chloroform. Nickel is again returned to the aqueous phase by shaking with dilute hydrochloric acid and is then converted into 1 : 4 complex. Beer's law applies up to 5 ppm of nickel. Dimethylglyoxime, if used alone, gives 1 : 2 complex, which can be extracted into chloroform. The method suffers from certain drawbacks. Sensitivity is poor (0.01 μg) and the maximum absorption is obtained in the UV region, which does not allow the use of filter photometers.

Diethylamino-3-(1-methyl-2-piperidyl-2-pyridylazo) phenol has also been used and a large number of foreign ions are tolerated. Many of the ions which cause interference can be masked by the use of suitable masking agents. Diethyl

---

[+] Kumar Balwant Singh, Department of Physics, B.R.A. Bihar University, Muzaffarpur, India.
‡Department of Chemistry, Rajendra College, Chapra, India.

dithiocarbonate method is not at all selective and separation of nickel from interfering ions is necessary. The absorbance is measured at 385 nm. 5-Dimethylamino-2-(2-thiozolylazo) phenol has been used for the determination of nickel and the method is highly selective.

In continuation of our studies on use of PQSC as spectrophotometric reagent for estimation of platinum metals[3], we have evaluated the reagent with respect to nickel(II).

## EXPERIMENTAL

Nickel solution was prepared by dissolving nickel nitrate (B.D.H., AnalaR) in double distilled water and standardised gravimetrically with dimethylglyoxime.

### Absorption spectra and effect of pH

A series of solutions were prepared containing a known amount of nickel (1 mL of $5 \times 10^{-4}$ M) and an excess of reagent (1 mL $5 \times 10^{-3}$ M). The pH's were adjusted to different levels with acetate buffer. For higher pH's, sodium hydroxide was added. The contents were diluted to 10 mL with water and extracted in 10 mL of chloroform. The absorption spectra of the complex against a reagent blank (Fig. 1) show maximum absorbance at 460 nm. A plot of absorbance *vs.* pH (Fig. 2) shows that the absorbance remains constant between 7.8 and 7.5. Subsequent studies have been carried out at pH 8.5.

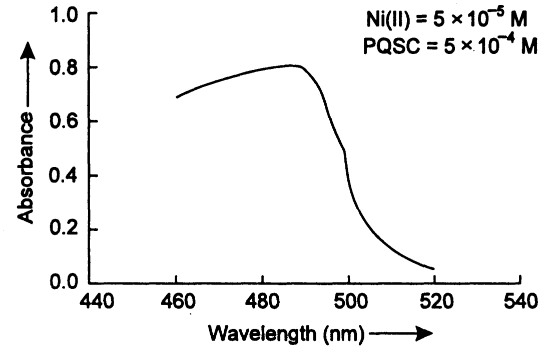

Fig. 1. Absorption spectrum of Ni-PQSC complex at pH 8.5.

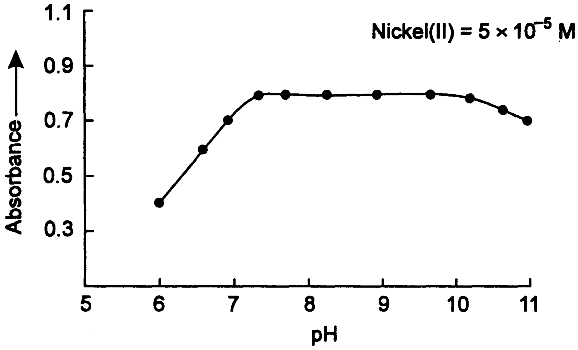

Fig. 2. Effect of pH on Ni-PQSC complex.

### Effect of reagent concentration

A series of solution was taken containing a fixed amount of nickel (1 mL of $5 \times 10^{-4}$ M) and increasing amounts of the ligand. The pH in each case was kept constant at 8.5 and the absorbance of chloroform extracts were measured at 490 nm against the corresponding reagent blanks, results of this study are plotted in Fig. 3 which reveals that eight times molar excess of the ligand was employed.

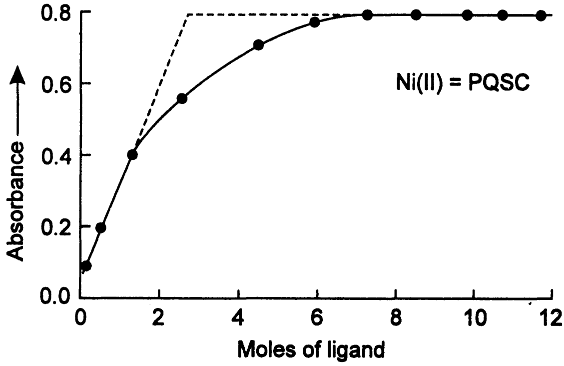

Fig. 3. Effect of reagent concentration on Ni-PQSC Complex

## RESULTS AND DISCUSSION

### Effect of time and temperature

Complex formation between Ni(II) and PQSC is instantaneous. Absorbance of chloroform extracts remains constant for at least 24 h. Small variations in temperature (25 ± 0.10°C) have no effect on absorbance.

### Physico-Chemical Constants

Adherence to Beer's law was studied by measuring absorbance of a set of solutions containing varying amounts of nickel(II) and an excess of the ligand at pH 8.5. Absorbances were measured at 490 nm against reagent blanks. The system was found to follow Beer's law (Fig. 4) up to 3.96 ppm of nickel. The optimum concentration range for accurate determination of nickel, as deduced from Ringbom plot (Fig. 5), has been found to be 1.26–3.24 ppm of nickel.

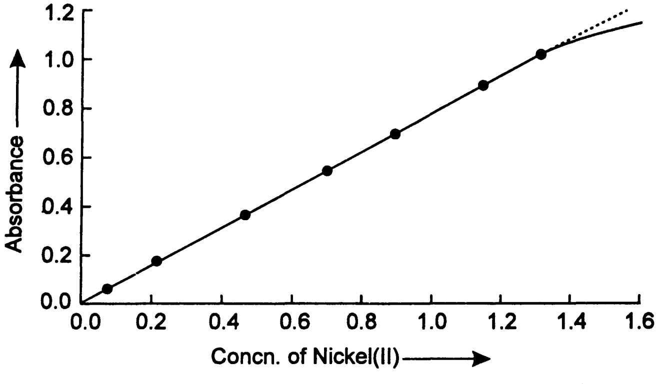

Fig. 4. Beer's law plot for Ni-PQSC complex. 1 mL = 2.95 ppm.

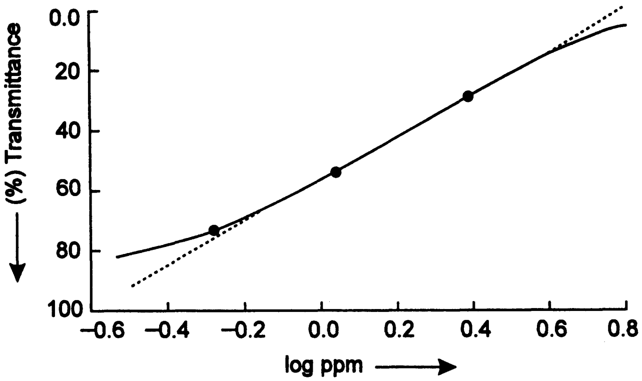

Fig. 5. Ringbom plot for Ni-PQSC complex.

Sensitivity and molar absorptivity of the complex was calculated from Beer's law data. The sensitivity expressed in terms of Sandell's definition comes out to be 0.0035 μg $Ni/cm^2$ for $\log (I_0/I) = 0.001$ and the molar absorptivity of the complex is $1.64 \times 10^4$.

## Recommended procedure for the determination

A suitable aliquot containing 12.6 and 32.4 μg of nickel(II) is taken and ten times molar excess of ethanolic solution of the reagent is added. The pH is adjusted to 8.5 with sodium acetate and sodium hydroxide in a total volume of 10 mL. To the contents, 10 mL of chloroform is added. The mixture is shaken for five minutes on an electrical shaking machine and set aside for equilibration. The organic layer is centrifuged to remove water droplets and transferred to the absorption cell for measurment of absorbance at 490 nm, against a reagent blank prepared under identical conditions. The amount of nickel is then deduced from the calibration curve.

## Precision of the method

Under experimental conditions, the absorbance of six solutions containing the same amount of nickel 2.94 ppm were measured. The average absorbance was 0.62 with standard deviation of 0.00045 and relative average deviation of ±0.402.

In the present case, PQSC has been used over the pH range 7.8–9.5. The reaction takes place at room temperature and the wavelength of maximum absorption lies in the visible region. As compared to Phenanthrenequinone monoxime (PQM), PQSC is more sensitive. A comparison of the sensitivity of PQSC with other well known methods is made in Table-1.

TABLE-1
COMPARISON OF SENSITIVITY OF SOME REAGENTS FOR NICKEL(II)

| Reagent | Sensitivity μg Ni/cm$^2$ for log $I_0/I = 0.001$ |
|---|---|
| Dimethylglyoxime + oxidising agent | 0.0042/445/465 nm |
| Dimethylglyoxime/$CHCl_3$ | 0.017/375 nm 0.012/325 nm |
| Dithiooximide | 0.0046/640 nm |
| 2,3-Quinoxalinedithiol | 0.0034/656 nm |
| α-Furli dioxime | 0.0045/435 nm |
| Salicylaldoxime | 0.011/387 nm |
| 3-Hydroxy-1,3-diphenyltriazine | 0.0038/422 nm |
| (Pyridyl-2-azo) chromotropic acid | 0.0017/570 nm |
| Acenaphthenequinone monoxime (AQM) | 0.007/390 nm |
| Phenanthrenequinone monoxime (PQM) | 0.0098/450 nm |
| Phenanthrenequinone monothiosemicarbazone (PQSC) (present method) | 0.0035/490 nm |

## ACKNOWLEDGEMENT

Authors are thankful to the Principal, L.S. College, Muzaffarpur for providing library and laboratory facilities.

## REFERENCES

1. E.B. Sandell, Colorimetric Determination of Traces of Metals, Interscience Publishers, Inc., New York (1959).
2. E.D. Snell and C.T. Snell, Colorimetric Methods of Analysis, Van Nostrand, Princeton, Vol. II, p. 352 (1964).
3. I. Chakraborti and H.C. Rai, *Asian J. Chem.*, **15**, 1572, 1665, 1687 (2003).

(*Received*: 8 May 2003; *Accepted*: 18 October 2003) AJC-3183