

## Spectrophotometric determination of nickel in alloys using 5-mercapto-3-methyl-4-[2-pyridylideneamino]-1,2,4-triazole (MMPT)

Ronald A Nazareth & B Narayana\*

Department of Studies in Chemistry, Mangalore University,  
Mangalagangothri 574 199, India  
E-mail : nbadiadka@yahoo.co.uk

Received 3 August 2001; revised 10 December 2002

A simple and rapid spectrophotometric method for the determination of nickel has been developed using 5-mercapto-3-methyl-4-[2-pyridylideneamino]-1,2,4-triazole (MMPT). The green coloured 1:2 complex formed shows the absorption maximum at 400 nm. The method is free from interference from many of the associated metal ions. It obeys the Beer's law in the range of 3 ppm to 11.5 ppm of Ni(II) with molar absorptivity and sandell sensitivity of  $8.51 \times 10^3 \text{ dm}^3/\text{mol}/\text{cm}^{-1}$  and  $0.03 \mu\text{g}/\text{cm}^2$  respectively. Analyses of various alloys have been carried out with satisfactory and reproducible results.

Nickel occurs in meteoric iron and in the minerals josephinite  $\text{FeNi}_3$ , awaurite  $\text{FeNi}_2$ . It occurs in arsenates, antimonates, silicates, sulphides and phosphates together with cobalt, iron, copper, chromium and zinc. Nickel occurs to an estimated 0.016% in the 10 mile depth of the earth's crust, ranking 24<sup>th</sup> in the order of abundance of the elements. The total amount of nickel is greater than that of copper, zinc and lead combined.

Nickel is extensively used either as the metal or its alloys. Nickel-plated articles, nickel coating on copper or iron are in daily use. In finely divided form it serves as a valuable catalyst in hydrogenation of oils. The alloy monel metal (Ni, Cu, Fe), German silver (Cu, Ni, Zn), Nichrome (Ni, Cr), the US Nickel coin are familiar uses of the metal. Nickel is also used in the storage batteries. Nickel is the most widely used electrodeposited metal. Nickel cyanide is used in silver and gold plating baths to obtain their hard deposition. It is also added to zinc plating baths for enhancing brightness of zinc deposition.

Because of these extensive applications of nickel and its various alloys and compounds, a rapid and

accurate analytical method for determining nickel in micro and semi micro levels is essential. Although there are a number of gravimetric and complexometric reagents known for the determination of nickel, the difficulty encounters when sample containing trace amounts of nickel needed to be analysed. In such cases spectrophotometric methods may be readily adopted using a selective and sensitive reagents.

A survey of literature reveals that a large number of reagents are suitable either directly or after extraction into a solvent for the spectrophotometric determination of nickel. The condition for maximum colour development, sensitivity and selectivity of the proposed method differ very widely. Among the earliest reagents used for spectrophotometric determination of nickel are the extraction of nickeldimethylglyoximate<sup>1</sup> complex into chloroform and the quantitative determination of nickel at the pH 5 to 9. In this process Fe(III), Cr(III), and Cu(II) cause interference. Some of the other reagents used for the spectrophotometric determination of nickel include salicylaldoxime<sup>2</sup>, phenanthraquinonemonoxime<sup>3</sup>, 6-chloro-1,2-naphthaquinonedioxime<sup>4</sup>, 1,1,1-trifluoromercaptapent-3-en-2-one<sup>5</sup>, thionyl-trifluoroacetone<sup>6</sup>, 1-(2-pyridylazo)-2-naphthol<sup>7</sup>, diamoniummethylene-bisdithiocarbamate<sup>8</sup>, ammoniumpyridine-1-carbodithionate<sup>9</sup>,  $[\alpha, \alpha'-(o\text{-phynyldimino})\text{bis}(o\text{-cresol})]$ <sup>10</sup>, isonitrosoacetophenone<sup>11</sup>, isonitroso-acetylacetone<sup>12</sup>, benzyl- $\alpha$ -monoxime<sup>13</sup>, isonitrosothiocamphor<sup>14</sup>, 3-hydroxy-2-methyl-1,4-naphthaquinone-monoxime<sup>15</sup>, 6'-hydroxy-2', 4'-dimethyl acetophenone-oxime<sup>16</sup>, and indane-1, 2, 3-trione<sup>17</sup>. Some of the recently used reagents for the spectrophotometric determination of nickel are sodium diethyldithiocarbamate<sup>18</sup>, 2-(4, 6-dimethyl-2-pyrimidylazo)-1-naphthol-4-sulphonate<sup>19</sup>, (2-nitrophenyl)-3-(4-nitrosophenyl)triazene<sup>20</sup>, diethylenetriamine and imidazole<sup>21</sup>, 1,2-*o*-isopropylidene-4-aza-7-aminoheptane<sup>22</sup>, sodium isoamylxanthate<sup>23</sup>.

In the present investigation, 5-mercapto-3-methyl-4-[2-pyridylideneamino]-1,2,4-triazole (MMPT) has been used as a selective, rapid and sensitive spectrophotometric reagent for the determination of nickel. The method tolerates a large number of cations and anions.

## Experimental

All the reagents were of analytically pure grade. Standard stock solution (1000 ppm) of nickel(II) was prepared by dissolving nickel ammonium sulphate hexahydrate in water and standardized<sup>24</sup>. The stock solution was then diluted suitably to prepare the standard solutions.

MMPT was prepared by refluxing a mixture of 7.92 g of 3-methyl-4-amino-5-mercapto-1, 2, 4-triazole<sup>25</sup> and 6.10 g of pyridine-2-aldehyde in 50 ml methanol containing 3 drops of conc. H<sub>2</sub>SO<sub>4</sub>, for 3 hours<sup>26</sup>. The solid product obtained was separated and recrystallised from methanol as light yellow coloured needles (M.P.:145°C). A 0.2% alcoholic solution of MMPT was used. Buffer solution of suitable pH were prepared by mixing borax, potassium hydrogenphthalate, potassium dihydrogen phosphate, KCl, HCl and NaOH in proper proportions<sup>27</sup>.

A Secomam Anthelie NUA 0.22PP UV-visible spectrophotometer was used with 1 cm quartz cell.

### Preparation of alloy solutions

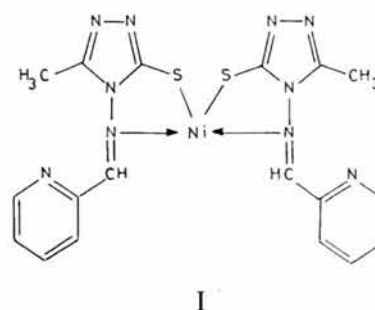
Samples of nickel-based alloys were dissolved in concentrated nitric acid and the oxides of nitrogen are expelled with the use of concentrated sulphuric acid until the evolution of brown fumes ceased. The residue was extracted with distilled water and made up to 100 ml in a standard flask and was analyzed for the composition of nickel. The results obtained were compared with the results obtained from the standard method.

### Procedure

Aliquots of 0.1-2.0 ml of the stock solution containing 2.0-2.0 ppm of nickel (II) were pipetted out into a series of 25 ml standard flasks. To each of the flasks, 5 ml of 0.2% alcoholic solution of MMPT was added and made up to the mark using buffer solution of pH 8.0. The solutions were shaken well and the absorbance was measured at 400 nm using 1 cm matched cells against a reagent blank.

## Results and discussion

MMPT forms a soluble 1:2 complex with nickel(II) (Structure I). The green coloured complex has an absorption maximum at 400 nm ( $\epsilon=8.51 \times 10^3 \text{ l mol}^{-1} \text{ cm}^{-1}$ ). Nickel (II) forms chelates especially with nitrogen and oxygen donor ligands. Nickel (II) reacts with MMPT instantaneously at room temperature. The colour development is observed only at pH 7-10. The maximum absorbance was found at pH 8.



Beer's law is obeyed up to 11.5 ppm of nickel. The optimum range for accurate determination is deduced from Ringbom's plot<sup>28</sup> and is found to be 3.0-11.5 ppm. The molar absorptivity and Sandell's sensitivity<sup>29</sup> for 5 ppm are  $8.51 \times 10^3 \text{ l mol}^{-1} \text{ cm}^{-1}$  and  $0.03 \mu\text{g/cm}^2$  respectively.

The determination of nickel in nickel ammonium sulphate solution was performed at different concentrations of nickel(II) using the above reagent. The results are given in Table 1. It shows that the relative error did not exceed  $\pm 0.63\%$  and standard deviation is  $\leq 0.12$  ppm. On comparing the computed value of the student 't' (2.78 for 5% level of significance) with tabulated values, it can be observed that in most of the cases there is no significant difference between the reference values and the value obtained by the proposed method.

The effect of varying amount of the reagent MMPT on the colour development is studied with a solution containing 7.5 ppm of nickel(II). Maximum of 4 ml of 0.2% alcoholic solution of MMPT is needed for the maximum colour development.

The effect of some ions that often accompany nickel(II) were studied by adding different amounts to 5 ppm of nickel(II) solution. The colour is developed

Table 1—Determination of Ni(II) in nickel ammonium sulphate solution

Nickel		Relative error (%)	Standard deviation (ppm)	Students' 't' value**
Present (ppm)	Found* (ppm)			
4.00	4.01	0.25	0.06	0.37
6.00	6.03	0.50	0.12	0.56
8.00	8.05	0.63	0.07	1.6
10.00	9.97	-0.30	0.10	0.67

\* Average of five determinations

as outlined in the procedure. An error of  $\pm 3\%$  in the absorbance readings is considered tolerable. The tolerance limits of various ions are shown in Table 2.

The composition of the complex is obtained by Job's method of continuous variation. Equimolar solutions ( $17.0 \times 10^{-4} M$ ) of nickel(II) and MMPT were mixed in complimentary proportions so that the final volume is 10 ml. The solutions in the flasks are made up to 25 ml with the buffer of pH 8.0. The absorbance is measured at 400 nm. The graph is plotted with the absorbance versus mole ratio of the metal. The plot indicates the composition of the complex as 1:2. Stability constant of the complex was obtained by Turner-Anderson method. Equimolar solutions ( $17.0 \times 10^{-4} M$ ) of nickel(II) and MMPT were mixed in complimentary proportions in such away that the final volume is 10 ml. The contents of the flasks were made up to the mark with the buffer of pH 8.0 and the absorbance was measured at 400 nm. The same experiment is repeated by changing the concentration of nickel(II) and MMPT ( $8.5 \times 10^{-4} M$ ). Graphs were plotted with the absorbance versus mole ratio of the metal. The stability constant of the complex calculated by this method is found to be  $2.417 \times 10^3$ .

#### Application

Nickel forms alloys with a large number of elements. Solutions of some of the nickel alloys were

Table 2—Effect of diverse ions on determination of nickel(II) (5 ppm)

Foreign ion	Tolerance limit (ppm)	Foreign ion	Tolerance limit (ppm)
Cu(II)*	50	Acetate	200
Co(II)	10	Bromide	100
Mn(II)	10	Chloride	100
Hg(II)	25	Fluoride	250
Cd(II)	50	Iodide	250
Al(III)	10	Nitrate	150
Cr(III)	75	Nitrite	200
Fe(III)	60	Perchlorate	200
Tl(III)	25	Oxalate	250
Ti(IV)	75	Sulfate	250
V(IV)	40	Borate	200
Zr(IV)	100	Citrate	250
Mo(VI)	150	Phosphate	200
W(VI)	100		
U(VI)	100		

\* Masked using suitable masking agents.

Table 3—Determination of nickel(II) in alloys

Alloy	Nickel (%)		Relative error (%)	Standard deviation (%)
	Present	Found #		
Permalloy	78.50	78.22	-0.36	0.79
Nomag	11.00	11.10	0.91	0.51
Nichrome	60.00	59.88	-0.20	0.54
Monel metal	67.00	66.76	-0.36	0.78
Alnico	20.00	20.07	0.35	0.86
Constantan	40.00	39.74	-0.65	0.62

# Average of five determinations

prepared and the nickel content was determined by the proposed method. The results are summarized in Table 3.

The reagent provides a simple rapid and accurate method for the spectrophotometric determination of nickel. The reagent has the advantage of high sensitivity, selectivity, wide optimum pH range and low absorbance of the reagent blank. The method needs neither heating for the complete colour development nor extraction into any organic phase. Interference from copper can be tolerated using thiosulphate as the secondary masking agent. The accuracy of the method is comparable with most methods reported in the literature. Most of the common metal ions, which are associated with nickel either in minerals or in alloys, do not interfere in its determination and hence the method can be used for the analysis of alloys, minerals and artificial mixtures for their nickel content.

#### Acknowledgement

One of the authors (RAN) thanks the University Grants Commission, New Delhi, India for awarding fellowship under Faculty Improvement Program. The authors also thank the Microtron Center of Mangalore University for technical help.

#### References

- 1 Kitagawa H & Shibata N, *Japan Analyst*, 2 (1958) 284.
- 2 Yamamoto Y, Veda K & Ueda S, *J chem. Soc Japan Pure Chem Sec*, 89 (1968) 288.
- 3 Kamil F, Sindhwani S.K, & Singh R P, *Indian J Chem*, 16 (1978) 365.
- 4 Toei K, Motomizu, S. & Hasegaw T, *Bunseki Kagaku*, 27, (1978), 31.
- 5 Gavrilova L G & Zoltov Y A, *Zh Anal Khim*, 25 (1970) 105.
- 6 Mulye R R & Khopkar S M, *Sepr Sci*, 27 (1972) 605.
- 7 Shibata S, Niimi Y & Matsumae T, *Rep Gov Ind Res Inst Nagaya*, 11 (1962) 275.
- 8 Yamamoto D, Tsukada M & Kiraoka S, *Banseki kagaku*, 29 (1980) 396.

- 9 Satake M, Den M & Yashida N, *Fukui Daigaku Kogukubu Kenkyu Hokoku*, 27 (1979) 253.
- 10 Aggatte J & Richardson R A, *Analyst*, 105 (1980) 118.
- 11 Talwar U B & Haldar B C, *Anal Khim Acta*, 51 (1970) 53.
- 12 Talwar U B & Haldar B C, *Indian J Chem*, 9 (1971) 593.
- 13 Ueda K., Nozaki M & Yamamoto Y, *Kanazawa Daigaku Kogukaku Kiyu*, 13 (1980) 103.
- 14 Kathyar G S & Haldar B S, *Indian J Chem*, 22 (1983) 1084.
- 15 Kaamini M, Sindhwani S K & Singh R P, *Analyst*, 107 (1982), 390.
- 16 Eapen M J, Dorai C S & Damodaran V, *Indian J Chem*, 28 (1989) 1022.
- 17 Rao D M, Reddy K H & Reddy D V, *Indian J Chem*, 28 (1989) 12.
- 18 Kaul K N, Malik A K, Lark B S & Rao A L J, *Rev Roumaine Chim*, 45 (2000) 221.
- 19 Singh I & Sushma, *Indian J Chem*, 39 (2000) 557.
- 20 Belyaev E Y, Churkina L N, Robev A M & Lopatina E M, *Russ J Gen Chem*, 70 (2000) 1135.
- 21 Patel R N, Singh N, Shrivatsava, Kumar S & Pandeya, *J molec Ligands*, 89 (2000) 207.
- 22 Sekerci M, *Russ J, inorg Chem*, 45 (2000) 1348.
- 23 Malik A K, Kaul K N, Lark B C, Faubel W, & Rao A L J, *Turkish J Chem*, 25 (2001) 99.
- 24 Vogel A I, *Text book of quantitative chemical analysis*, 4th Edn, (ELBS Longman) 1978.
- 25 Dhaka K S, Mohan J, Chadha V K & Pujari H K, *Indian J Chem*, 12 (1974) 288.
- 26 Abharam Joseph, Madhavi S & Narayana B, *Turkish J Chem*, 18 (1994) 14.
- 27 Robinson R A & Stokes R H, *Electrolyte solutions*, 3<sup>rd</sup> edn. (Butterworth's, London) 1970, 185.
- 28 Ringbom A, *Z Anal Chem*, 115 (1938) 332..
- 29 Sandell B, *Colorimetric determination of traces of metals*, (Interscience, New York) 1959.