



## A Simple Spectrophotometric Determination of Nickel(II) Using 1-Nitroso-2-naphthol in Anionic Micellar Solution

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A simple rapid new spectrophotometric method has been developed for the determination of nickel at trace level using 1-nitroso-2-naphthol as complexing reagent in presence of anionic aqueous micellar solution surfactant 1 % sodium dodecyl sulphate. 1-Nitroso-2-naphthol reacts with nickel(II) to form *bis*(1-nitroso-2-naphtholato) nickel complex. The use of micellar system replaces the previous solvent extraction steps while enhancing the sensitivity, selectivity and the molar absorptivity which reduces the cost and toxicity. The average molar absorption coefficient and Sandell's sensitivity was found to be  $1.02 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$  and  $5.7 \text{ ng cm}^{-2}$  at  $\lambda_{\text{max}}$  471.6 nm. Linear calibration graph was obtained over the concentration range  $0.25\text{--}4.0 \mu\text{g mL}^{-1}$ , the stoichiometric composition of the chelate was 1:2 (Ni:[NNPh]<sub>2</sub>). The developed method was successfully applied for the determination of nickel from alloy and real samples.

**Keywords:** Spectrophotometric, Nickel, 1-Nitroso-2-naphthol, Anionic micellar, Sodium dodecyl sulphate.

### INTRODUCTION

Nickel plays necessary role in the biological living systems and in the formation of bio-molecules. Nickel synthesis many bio-molecules and is the major constituent of some important bio-active complexes of enzymes<sup>1,2</sup>. Important coenzymes NiFe constituted hydrogenases, urease, acetyl coenzyme and methyl coenzyme<sup>3</sup> are more prominent. Bio-molecules of nickel are counted important bioenzymes and have important role in the biological system<sup>4</sup>. In determination of Ni<sup>2+</sup>, the metal ion is chelated and formed insoluble complex which is solubilized by the solvent extraction for the analysis. Spectrophotometric techniques widely employed due to its simplicity, rapidity and low cost and maintenance. Micellar systems enhance the molar absorptivities, sensitivities and replaces the old previous steps of toxic solvent extraction<sup>5-10</sup>. Several spectrophotometric methods have been developed to replace the old solvent extraction method by using the micellar surfactants<sup>11-16</sup>. Micellar media is introduced to enhance the molar absorptivities, sensitivities and replaces the previous steps of toxic solvent extraction<sup>17-21</sup>. We have developed new simple, sensitive and selective spectrophotometric method for the determination of nickel(II) in various materials by using 1-nitroso-2-naphthol as chromogenic agent in anionic micellar aqueous solution of 1 % sodium dodecyl sulphate.

### EXPERIMENTAL

A Cecil CE 9500 UV-visible scanning spectrophotometer equipped with a 10 mm path length quartz cell was utilized. Atomic absorption spectrophotometer (Analyst-100 Perkin Elmer) with multi-elemental hollow cathode lamps was used. FTIR (Spectrum-One Perkin Elmer) was used. Besides, pH/conductivity meter (Sension 156 HACH) with Sension Gel-filled pH electrodes was used.

**Preparation of reagents:** A solution of 1-nitroso-2-naphthol (Merck) was made by dissolving 75 mg of 1-nitroso-2-naphthol in 50 mL of 1 % sodium dodecyl sulphate, this was stock solution of 15000 ppm ( $1500 \mu\text{g mL}^{-1}$ ). Sodium dodecyl sulphate 1 % was prepared by taking 1 g in volumetric flask of 100 mL. Nickel(II) nitrate solution was made by dissolving 4.94 g in ( $1000 \mu\text{g mL}^{-1}$ ) 1L. Other metal ions solutions were made by dissolving their nitrate and chloride salts and insoluble compounds were made dissolved in acids or according to special dissolution method<sup>22</sup>. Buffer solutions of pH 1-10 were prepared by using appropriate methods<sup>23</sup>, with appropriate volumes of the mixtures of 0.2 M KCl – 0.2 M HCl for (pH 1-4), 0.2 M CH<sub>3</sub>COOH – 0.2 M CH<sub>3</sub>COONa for (pH 5-6), 0.1 M KH<sub>2</sub>PO<sub>4</sub> – 0.1 M NaOH for (pH 6.5-8.0) and 0.025 M sodium borate and 0.1 M HCl for (pH 9-10).

**General procedure:** The sample solution was taken in calibrated volumetric flasks, added appropriate amounts of nitroso-2-naphthol (185 ppm), appropriate amounts of 1 % sodium dodecyl sulphate and 2 mL buffer solution of varying pH was added for the complexes formation and the absorbance's were measured.

**Determination of nickel ions in reference material:** Alloy sample of nickel ions 0.1-0.5 g of reference material stainless steel No. 306 was digested with concentrated HCl (15 mL) and concentrated HNO<sub>3</sub> (5 mL) in beakers. The sample solution was heated to reduce the volume to 5 mL on a hot plate. Then mixed 10 mL concentrated HCl, solutions in the sample solutions by filtering and diluting to a final volume of 25 mL. Alloy sample of reference material having the composition stainless steel no. 306 (Ni 12, Mo 2.0-3.0, Cr 16.5 and Fe 7.0-71.0)<sup>24</sup>.

**Determination of nickel ions in alloy sample:** The sample solution 4-20 g oil was taken and dissolved in concentrated HNO<sub>3</sub>. The dried sample solution was heated on furnace at 600 °C for 1 h and then was cooled. Few drops of concentrated HNO<sub>3</sub> were added in to the sample solution and was dried again heated to 700 °C for 1 h. The solution was made by digesting ash in concentrated HCl and diluted up to mark. Sample solution in 10 mL flask was made after filtering and the final volume make up to mark<sup>25</sup>. The sample solution was taken in calibrated volumetric flasks, added appropriate amounts of 1-nitroso-2-naphthol (185 ppm), appropriate amounts of 1 % sodium dodecyl sulphate and 2 mL buffer solution of varying pH was added for the complexes formation and the absorbance's were measured.

**Determination of Ni (II) in tap water samples:** Sample solution of tap water was collected from Khairpur city. Then samples were filtered through 0.45 µm filter paper and then were acidified with 1 mL concentrated HNO<sub>3</sub> to avoid precipitation. Nickel was skipped in tap water in the volumetric flask added appropriate volumes of nitroso-2-naphthol 185 ppm, 2 mL buffer solution of pH 8 and 2 mL 1 % sodium dodecyl sulphate the complex absorbance was measured<sup>26</sup>.

## RESULTS AND DISCUSSION

1-Nitroso-2-naphthol is an excellent colour forming chelating agent reacts with nickel forms *bis*(1-nitroso-2-naphtholato) nickel complex structure is shown in Fig. 1. UV-visible spectra of nitroso-2-naphthol transitions ( $n \rightarrow \pi^*$ ) from ligand-to ligand charge transfer (LLCT)<sup>27-29</sup> of N-O molecule and C-O-H group at  $\lambda_{\max}$  377 nm is shown in Fig. 2. UV-visible spectra (1-nitroso-2-naphtholato) copper complex is formed at  $\lambda_{\max}$  471.6 nm charge transfer transitions ( $n \rightarrow \pi^*$ ), from ligand-to-metal (LMCT) ( $p\pi-d\pi$ ) is shown in Fig. 3. The stoichiometry of the complex was found 1:2 (Metal: Ligand) by Job's method 30 of continuous variation method of metal and chelate ratio 3:1 forming *bis*[1-nitroso-2-naphtholato]-nickel (Fig. 4). 1-Nitroso-2-naphthol concentration was varied at fixed concentration of 1 mmol Ni(II) ions and 1-nitroso-2-naphthol molar ratio 5 to 80 mmol, where 40-70 mM 1-nitroso-2-naphthol was optimized concentration found for the complex formation (Fig. 5). For surfactant optimization, 1 µg mL<sup>-1</sup> Ni(II)-chelate, 2 mL of 1 % sodium dodecyl sulphate showed constant

maximum absorbance in 10 mL volume, this 1 % sodium dodecyl sulphate was optimized for the whole procedure, which value is greater than the cmc value  $8.3 \times 10^{-3}$  M than reported<sup>30-32</sup>. Ni-[NNPh]<sub>2</sub> complex showed maximum constant absorbance at pH 8, which was selected for subsequent studies (Fig. 6). Calibration graph showed linear concentration over the range 0.25-4 µg mL<sup>-1</sup>, the correlation coefficients with experimental data was 0.999 (Fig. 7). Molar absorptivity of the complex was found ( $1.02 \times 10^4$ ) L mol<sup>-1</sup>cm<sup>-1</sup> (Table-1) and showed significant improvement in the molar absorptivities<sup>33,34</sup>. Detection limit and Sandell's sensitivity was found 0.25 µg mL<sup>-1</sup> and 5.7 ng cm<sup>-2</sup> (Table-1). The metal-complex showed absorbance maximum constant up to 5 min. At ordinary temperature metal complex showed stable absorbance measurement till 24 h.

TABLE-1  
ANALYTICAL PARAMETERS OF Ni(II)-[NNPh]<sub>2</sub> IN SDS

Parameters	Ni(II)
Wavelength, $\lambda_{\max}$ (nm)	471.6
pH	8
SDS	1 %
1-Nitroso-2-naphthol (NNPh) (µg mL <sup>-1</sup> )	185
Reagent (M:R)	1:2
Linear range (µg mL <sup>-1</sup> )	0.25-4
Molar absorption coefficient (mol <sup>-1</sup> cm <sup>-1</sup> )	$1.02 \times 10^4$
Sandell's sensitivity (ng cm <sup>-2</sup> )	5.7
Detection limit (µg mL <sup>-1</sup> )	0.25
Correlation coefficient (R <sup>2</sup> )	0.999
Reproducibility (% RSD)*	0.91

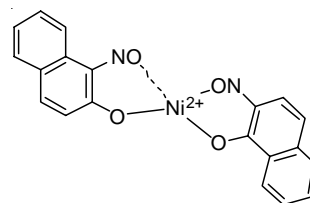


Fig. 1. Structure of *bis*(1-nitroso-2-naphtholato) nickel

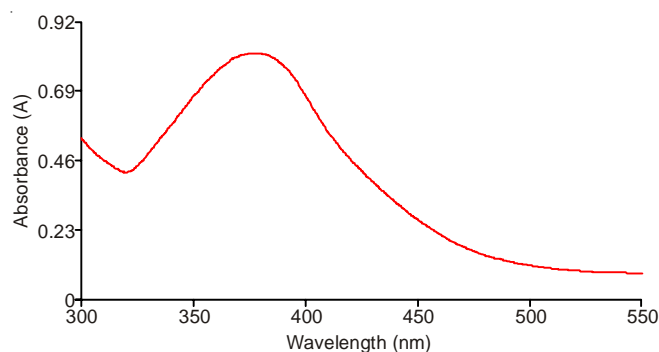


Fig. 2. UV-visible spectrum of NNPh at ( $\lambda_{\max}$  377 nm) in 1 % SDS; CECIL CE 9500; Time: 18:46 07/05/14; Wavelength: 400 nm; Speed: 5 nm/s; Averaging: 1 nm; Bandwidth: 2 nm; Operator: G.A.S; Reference: Eth + SDS; Sample: NNPh

### Effect of foreign ions in the determination of nickel:

Above the amount 800 µg mL<sup>-1</sup> KSCN, sodium tartarate and KClO<sub>3</sub> showed interference in the Ni(II)-chelate formation. Cadmium(II), cobalt(II), lead(II), iron(II) and copper(II) showed interference at low trace level concentration. Ascorbic

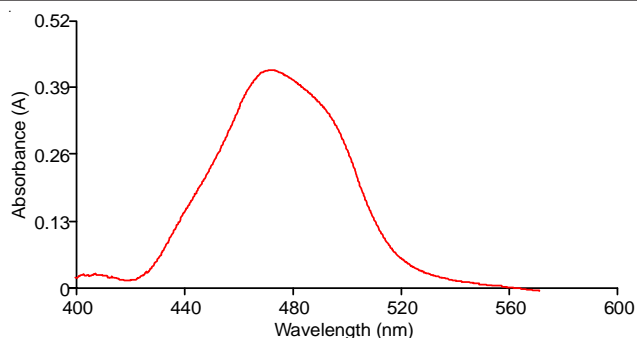


Fig. 3. UV-visible spectrum of Ni(II)-[NNPh]<sub>2</sub> at ( $\lambda_{\max}$  471.6 nm) in 1 % SDS; CECIL CE 9500; Time: 23:04 12/04/14; Wavelength: 400 nm; Speed: 5 nm/s; Averaging: 1 nm; Bandwidth: 2 nm; Operator: G.A; Reference: NNPh; Sample: Ni(NNPh)<sub>2</sub>

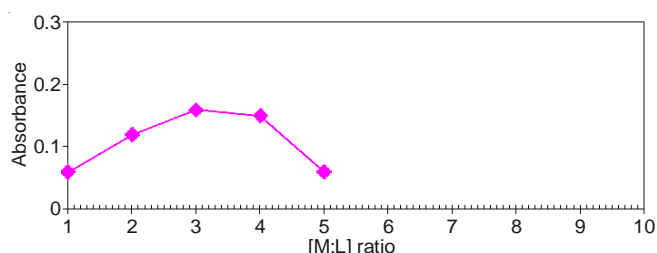


Fig. 4. Composition of Ni(II)-NNPh complex by the mole ratio method (Job's plot of metal: ligand ratio)

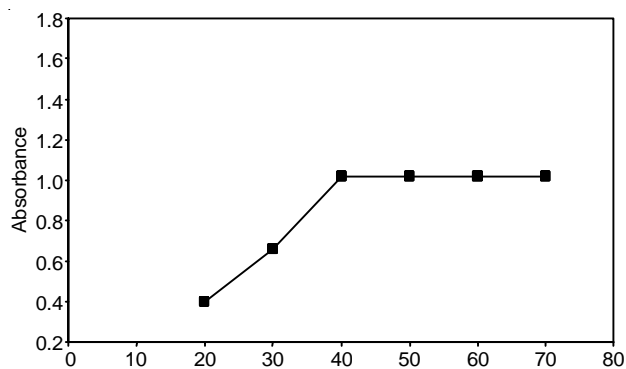


Fig. 5. Effect of amounts of NNPh on the absorbance of Ni(II); Mole ratio of NNPh to Ni(II)  $\times 10^4$  M

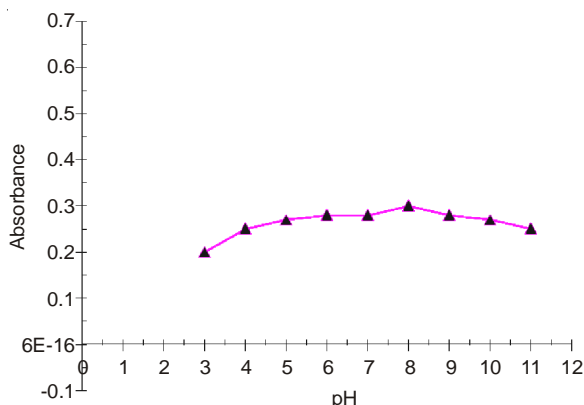


Fig. 6. Effect of pH on the Ni(II)-NNPh complex

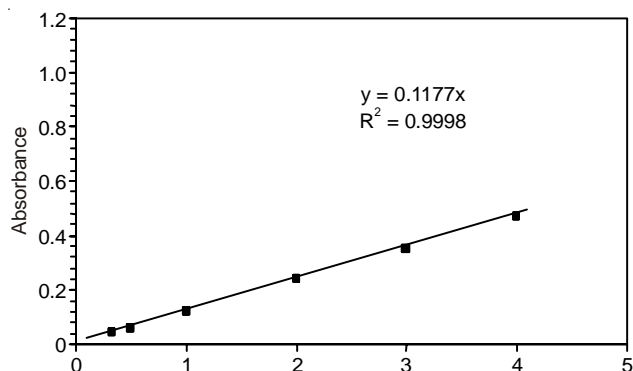


Fig. 7. Calibration curve for Ni(II)-NNPh complex in 1 % SDS; Concentration of Ni(II) ions in  $\text{mg mL}^{-1}$

acid and EDTA removed the interference of other metal ions and were used as masking agents. Fe(II) showed no interference at pH 5, because it interferes at optimized pH 1 by forming metal complex. Co(II) solutions interference was removed by using buffer solution of  $\text{NH}_3$  as masking agent. Co(II) interference was completely removed by using their specific masking agents results are shown in Table-2.

TABLE-2  
EFFECT OF FOREIGN IONS ON Ni(II)-[NNPh]<sub>2</sub>

Ion/salt ( $\mu\text{g mL}^{-1}$ )	Ni(II)
$\text{Na}_2$ tartarate, KSCN, $\text{KClO}_3$	800
Mg(II)	600
$\text{Na}_2\text{C}_2\text{O}_4$	200
$\text{Na}_2$ citrate	800
Mn(II)	500
Zn(II)	100
Co(II)	80
KCN	30
Al(III)	100
Cu(II)	100
Cr(IV)	8
Fe(III)	10
Pb(II)	3
Cd(II)	2

#### Validation of method to the determination of nickel(II)

**ions:** The method developed was validated to the determination of nickel ions by present spectrophotometric method from certified reference material stainless steel No. 306, alloy and standard addition method of % age recovery test was applied for the verification of the accuracy and the precision of the method as given in Tables 3-5. The average Ni ions found (n 7) in the reference material with a precision as relative standard deviation RSD was up to 0.91 % as given in Tables 3 to 5.

#### Conclusion

The results obtained in the determination of nickel(II) were comparable with the recently reported methods, while the present method showed significant improvement in Beer's law linear concentration range than reported<sup>24,35-37</sup>. Sensitivity and

TABLE-3  
DETERMINATION OF Ni(II) IN REFERENCE MATERIAL

Alloy certified (%) composition	Metal ion	Metal ( $\mu\text{g}$ ) present	Metal ( $\mu\text{g}$ ) found	RSD (%)	Relative error (%)	Recovery (%)
Stainless steel No. 306	Ni(II)	24.05	23.96	1.59	0.38	99.62

TABLE-4  
DETERMINATION OF Ni(II) IN REAL SAMPLE

Sample	Analyte ion	Proposed method ( $\mu\text{g mL}^{-1}$ )	RSD (%)	AAS method ( $\mu\text{g mL}^{-1}$ )	RSD (%)	Recovery (%)
Edible oil ( $\mu\text{g mL}^{-1}$ )	Ni(II)	8.50	0.8	8.58	0.6	99.07

TABLE-5  
PERCENT RECOVERY OF KNOWN AMOUNT OF Ni(II) ADDED TO TAP WATER

Metal ions	Amount added ( $\mu\text{g mL}^{-1}$ )	Amount found ( $\mu\text{g mL}^{-1}$ )	Recovery (%)
Ni(II)	1.0	0.99	99

the selectivity of the present method is higher than the reported expensive and toxic solvent extraction methods. The present method is simple, rapid, sensitive, selective, reproducible and non-extractive than existing methods of spectrophotometric analysis.

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