

Derivative Spectrophotometric Determination of Nickel (II) with 1-Nitroso-2-naphthol in Aqueous Phase

G. A. SHAR AND G. A. SOOMRO

Department of Chemistry

Shah Abdul Latif University Khairpur, Sindh, Pakistan

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Summary: A spectrophotometric and first derivative spectrophotometric determination of Ni (II) is carried out with 1-nitroso-2-naphthol as complexing reagent in aqueous phase using non-ionic surfactant Tween 40. The nickel is determined in the range 1.7-120 ng mL⁻¹ with detection limit (2σ) of 1.7 ng mL⁻¹. The molar absorptivity and Sandell's sensitivity are ϵ_{\max} 1.0 \times (10⁴ mol⁻¹cm⁻¹) and 5.8 ng cm⁻² at 452 nm. The optimum pH of the complex is 8. The critical micelle concentration (cmc) of Tween 40 is 5 %. Absorption studies in the first derivative mode is carried out to determine the absorption maximum of the complex for higher sensitivity and to overcome interference due to the presence of certain other metal ions. The present method is compared with that of AAS and no significant difference is noted between the two methods at 95 % confidence level. The method has been applied for the determination of Ni (II) in industrial waste water and edible oil samples.

Introduction

Deficiency of nickel may lead to health problems such as dermatitis, deformities of bones, while excess intake may cause lung cancer and myocardial infarction [1]. In chemical analysis, metal chelation followed by solvent extraction and spectrophotometric detection is preferred mode of analysis for a number of metal ions [2-3] due to rapidity, simplicity and wide applications. Several spectrophotometric methods have been developed in which the solvent extraction step is conveniently replaced by the use of a surfactant [4-5]. Due to the solubility of several compounds in micelles (aggregates of surfactants), many analytical techniques for determination of metal ions in aqueous system, have been developed and modified [6-16]. Micellar media is mainly used to enhance the absorption sensitivities, thus simplifying the system by replacing the toxic organic solvents. Determination of iron and ruthenium as ternary complexes by extractive second derivative spectrophotometry has been reported [17]. Derivative spectrophotometric determination of copper (II) in non-ionic micellar medium has been reported [18]. Tween series surfactants are very soluble in aqueous systems than other non-ionic surfactants. 1-nitroso-2-naphthol forms coloured water-insoluble complexes with a large number of metal ions and the use of surface-active reagent increases the solubility of 1-nitroso-2-naphthol [19]. Derivative mode spectrophotometry is recently shown to be more useful than classical spectrophotometry for solving several analytical problem [20]. The use of derivative mode spectrophotometry

offers a useful means of enhancing the sensitivity and selectivity of the method besides convenient solution to well defined analytical problems such as resolution of multi component systems, overcoming interference due to sample turbidity, matrix back ground and enhancement of spectral details [21-22]. The scale of this increase depends on the shape of the normal absorption spectra of the analyte and the interfering substances, as well as on instrumental parameters and the measurement techniques (e.g. peak-to-trough or zero-crossing), chosen by the analyst in a given analytical procedure.

In the present work, determination of Ni (II) as 1-nitroso-2-naphthol complex in a non-ionic surfactant Tween 40 using first derivative mode spectrophotometric method is reported. The method was successfully applied for the determination of Ni (II) in industrial waste and edible oil samples.

Results and Discussion

Fig. 1 shows absorption spectra in first derivative mode spectroscopy of Ni (II)-1-nitroso-2-naphthol complex at 470 nm (i.e. a shift from 452 nm). It can be seen in the Fig. 1 the height of the peak at (pH) 470 nm and the depth of the trough (TD) at 400 nm were linearly related to the metal ion concentration. It can be seen by comparing Fig. 1 that the first derivative spectra are more resolved than those obtained for the normal mode. However, even higher derivative orders yield sensitive but irrepro-

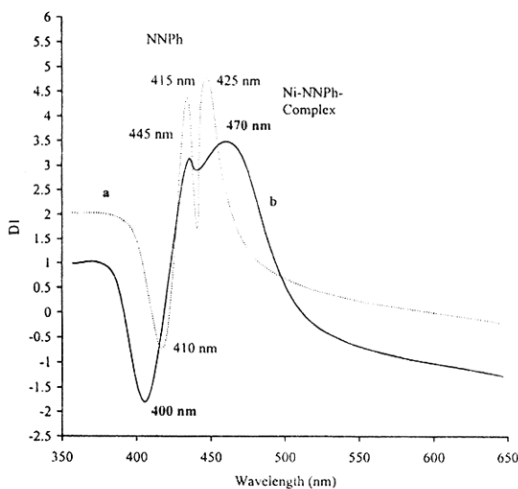
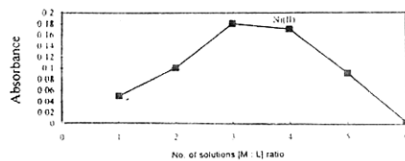


Fig. 1: First derivative spectra of (a) 1-nitroso-2-naphthol (b) nickel (II)-1-nitroso-2-naphthol complex in 5% Tween 40.

ducible signal, so this possibility was discarded. Derivative spectroscopy provides additional possibilities because it enhances the detectability of minor spectral features, thus this technique was adopted. The first order derivative spectrum is of great significance as it exhibits the λ_{max} of the complex which is otherwise difficult to ascertain due to several absorbing species and only a shoulder appears in the normal absorption spectrum due to the desired component. Weak and broad peaks give higher sharpest peak; other close peaks are changed from normal mode wavelength to new waves length showing no closeness to other neighbour peaks. The micelle of non-ionic surfactant with polyoxyethylene group comprises two parts. One is the hydrocarbon tail directed to the interior core of micelle and the other is the hydrated polyoxyethylene group located at outer sphere. Organic compounds and metal chelates having large affinity towards polyoxyethylene group may be incorporated. 1-nitroso-2-naphthol could be dissolved by this phenomenon, because this species has a hydroxyl group, which interacts with the ether oxygen of polyoxyethylene group, by hydrogen bonding. It seems that micelle in solution was formed because 5 % Tween 40 solution was above this concentration (0.0013 % w/v) [23]. Composition of the complex formed under experimental conditions was investigated by Job's method of continuous variations. From Fig. 2 it can be inferred that metal: ligand ratio is 1: 2. Fig. 3



No. of solution	1	2	3	4	5	6	7	8	9	10	11
M ions (mM)	0	1	2	3	4	5	6	7	8	9	10
Ligand (mM)	0	9	8	7	6	5	4	3	2	1	0
Both 1m mole conc.											

Fig. 2: Job's plot of metal:ligand ratio

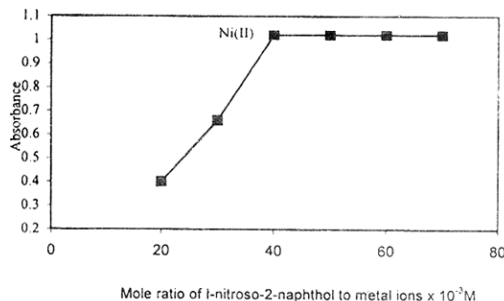


Fig. 3: Effect of amounts of 1-nitroso-2-naphthol on the absorbance of metal ions.

indicates the effect of mole ratio of 1-nitroso-2-naphthol for Ni (II) in the complex formation and is observed that different metals have different mole ratios. For nickel it is 40 to 70 m. moles of the reagent. There fore, 40 m. mole of the reagent require 1m.mole of the metal ion. Fig. 4 shows the optimum pH 8.0 for Ni (II) 1-nitroso-2-naphthol complex formation. Fig. 5 shows the calibration graph of Ni (II)-1-nitroso-2-naphthol complex in the range of 1.7-120 ng mL^{-1} at 470 nm in first derivative mode spectroscopy.

The detection limit is lowered significantly from 5.8 to 1.7 ng mL^{-1} . All other experimental conditions are same as in normal mode spectroscopy. Molar absorptivity is $1.0 \times (10^4 \text{ mol}^{-1}\text{cm}^{-1})$, Sandell's sensitivity (5.8 ng cm^{-2}). Beer's law linear range in normal mode is 0.5-4.0 $\mu\text{g mL}^{-1}$.

Comparison of detection limit of the present method with other sensitive methods is given in Table-4 [27-31].

Study of interference's by foreign ions

In the Ni (II) determination with 1-nitroso-2-naphthol in presence of 5 % Tween 40 were studied

Table-1: Analytical characteristics of Ni (II)-1-nitroso-2-naphthol in 5 % Tween 40 in normal mode spectroscopy

Characteristics	Ni (II)
Beer's law range ($\mu\text{g mL}^{-1}$)	0.5 - 4.0
Absorption maxima (λ_{max} , nm): (a) micellar (b) CCl_4	452
Molar absorptivity ϵ_{max} : ($10^4 \text{ mol}^{-1} \text{ cm}^{-1}$)	1.0
Sandell's sensitivity ng cm^{-2}	5.8
Detection limit (ng mL^{-1})	5.8
pH range	8
Conc. of Tween 40	5 %
Conc. of 1-nitroso-2 naphthol ($\mu\text{g mL}^{-1}$)	185
RSD \pm	9.05.23

At 95 %, n = 6

Table-2: Tolerance limits for interference's of metal ions and salts with 1-nitroso-2-naphthol in 5 % Tween 40 in normal mode spectroscopy Tolerance limits $\mu\text{g mL}^{-1}$

Ion / salt	Ni(II)
KSCN	1000
NaF	600
$\text{Na}_2\text{C}_2\text{O}_4$	200
KClO_3	1000
$\text{Na}_2\text{tartarate}$	1000
$\text{Na}_2\text{citrate}$	100
KCN	30
Mg(II)	800
Al(III)	100
Cd(II)	2
Co (II)	80
Cr (III)	30
Cr (VI)	8
Fe (III)	10
Mn(II)	500
Ni(II)	-
Pb (II)	3
Zn (II)	100
Cu (II)	100

At 95 %, n = 6

The conc. of Ni ions is $2 \mu\text{g mL}^{-1}$

Table-3: Percent recovery of known amount added to tap water.

Metal ions	Amount added	Amount found	Recovery (%)
Ni (II)	1.70 ng mL^{-1}	1.69 ng mL^{-1}	99 ± 1
	$0.50 \text{ } (\mu\text{g mL}^{-1})$	$0.49 \text{ } (\mu\text{g mL}^{-1})$	99 ± 1

At 95%, n=6

results are shown in the Table-2, these interference's can be avoided in general by the addition of complexing agent like EDTA which forms stable complexes with many metal ions so that in this medium Ni (II) reaction with 1-nitroso-2-naphthol is highly selective with at pH 8. Cd (II), Fe (III), Cu (II), Co (II) and Pb (II) interfere at low trace level as

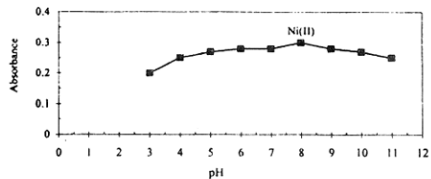


Fig. 4: Effect of pH on the absorbance of metal-1-nitroso-2-naphthol complex.

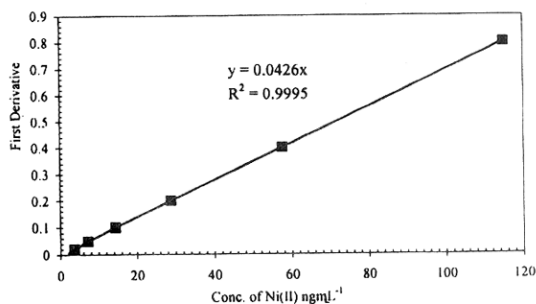


Fig. 5: Calibration graph of Ni (II)-1-nitroso-2-naphthol complex in 5% Tween 40 at pH 8 at (λ_{max} 470 nm and 400 nm) in first derivative mode spectroscopy.

given in Table-2. The interference due to absorption by Fe (III), Cu (II) and Co (II)-1-nitroso-2-naphthol complex in normal mode spectroscopy is thus removed by the use of first derivative mode spectroscopy.

Validation of method

Proposed method was verified by % recovery test by standard addition method, results were compared with AAS, which are in good agreement with (AAS) given in Table-3.

Application

The proposed spectrophotometric method was applied to the determination of Ni(II) and in industrial waste water samples. Results are shown in Table-5.

Experimental

A UV/Vis spectrophotometer Perkin Elmer model Lambda 2 was used for recording normal as well as derivative spectra. Atomic absorption spectrophotometer, model Spectra AA. 20 Varian was used for metal ion determination. The Pye Model 292 pH meter was used in this study.

Table- 4: Comparison of sensitivities of various methods

Present method	Fluorimetric method [24]	Spectroscopic method [25]	AAS Method [26]	Electrothermal atomization-AAS method [27]	FAAS method [28]	(ICP-AES) method [29-31]
1.7 ng mL ⁻¹	7 ng mL ⁻¹	100-800 ng mL ⁻¹	2 ng mL ⁻¹	2-20 ng mL ⁻¹	4 ng mL ⁻¹	0.2 ng mL ⁻¹ , 0.1-80 µg mL ⁻¹

AAS Atomic absorption spectroscopy

FAAS Flame atomic absorption spectroscopy

ICP Inductive couple plasma

AES Atomic emission spectroscopy

Reagents

All chemicals used were analytical grade reagents (Merck and Fluka A.G) unless otherwise stated. Standard Ni(II) stock solution of (100 µg mL⁻¹) was prepared dissolving its nitrate salt. Other metal ions solutions were prepared from their nitrate or chloride salts. 5 % Tween 40 solution was prepared by dissolving it in a 100 mL volumetric flask, and diluting it to the mark with double distilled water. Buffer solution of pH 8 was prepared by taking 0.025M sodium borate (50 mL) and 0.1M hydrochloric acid (20.5 mL) mixtures and adjusting the volume to 100 mL according to Perrin and Dempsey [32].

Procedure

Absorption spectra (normal and derivative) of the following solutions were recorded, taking reagent blank as reference, in order to determine photometric characteristics of the 1-nitroso-2-naphthol-Ni (II) complex.

Two sets of solutions, one containing fixed metal ion and other without it, and each containing fixed amount of the reagent (185 µg mL⁻¹) and Tween 40 (5 %) in the pH range 1.0-11.0 were prepared to determine the optimum pH range of the complexation reaction.

To study the impact of varying surfactant concentration on the absorbance of the 1-nitroso-2-naphthol-Ni (II) complex, a set of solutions containing increasing amounts of Tween 40 (2 %-10 %), and fixed Ni(II) and 185 µg mL⁻¹ 1-nitroso-2-naphthol, at the pH 8 of the maximum complex formation was prepared.

Effect of varying ligand concentration on the absorbance of the system was investigated by preparing a set of solutions containing 40×10^{-3} to 70×10^{-3} M of the reagent at the optimum pH 8.

Linear range was set by varying amount of the metal ions in the first derivative mode (1.0-120 ng mL⁻¹) and in the normal mode was 0.06 to 5.0 µg mL⁻¹, 185 µg mL⁻¹ 1-nitroso-2-naphthol, and 5 % Tween 40 at pH 8 condition of maximum complex formation.

Spectrophotometric metal ion determination in micellar solution.

Appropriate volumes of stock solutions of metal ions, 1-nitroso-2-naphthol and surfactant Tween 40 were added and made up to 25 mL volume with distilled water having metal ions concentration of 1.0-120 ng mL⁻¹ and 0.06-5.0 µg mL⁻¹, 1-nitroso-2-naphthol 185 µg mL⁻¹ and 5 % Tween 40. Absorption spectra were recorded against reagent as reference to generate analytical calibration curves in normal mode (λ_{max} 452 nm) or in first derivative mode (peak height (pH) at 470 nm) or (trough depth (TD) at 400 nm). Nickel content of the standard and the sample was determined using AAS equipped with an air acetylene flame. The pH and wavelength used are listed in Table-1.

The determination of Ni (II) in industrial waste and edible oil samples.

(a) The industrial waste

Industrial waste water sample, 1L obtained from industrial effluent was collected from Kotri site area and filtered using Whatman filter paper No. 44. Concentrated nitric acid 4 ml and 30 % hydrogen peroxide 2 ml were added to the filtrate. The resulting solution was preconcentrated in an oven at 110^o C to a final volume of 25 mL. Appropriate amounts of Tween 40 and 1-nitroso-2-naphthol were added to a 25 mL calibrated flask to obtain final concentration of 5 % in Tween 40 and 185 µg mL⁻¹ in 1-nitroso-2-naphthol. Then 5 mL of the sample was added and the absorbance was measured against reagent blank. The same sample, 5 mL was diluted

Table-5: Determination of Ni (II) ions in industrial waste samples

Sample	Amount of Ni (II) determined ($\mu\text{g mL}^{-1}$)		
	Present method	AAS method	C.V. %
*Industrial waste	0.40 \pm 0.06	0.41 \pm 0.03	2.57
Edible oil	22.0 \pm 0.32	22.1 \pm 0.2	2.4

At 95 %, n = 6 *Kotri SITE area

to 25 mL with double distilled water for AAS analysis (Table-5).

(b) Determination of nickel in edible oils

A 4-20 g of the oil sample (vegetable oil) depending on the nickel content was taken in beaker and decomposed with concentrated HNO_3 . The dried sample was heated in a muffle furnace at 600°C for 1h and then allowed to cool. After the addition of a few drops of concentrated HNO_3 it was dried and again heated to 700°C for 1 h. The ash was dissolved in concentrated HCl and diluted with a small amount of distilled water and filtered and the final volume was increased to 10 mL in a standard flask. Appropriate amounts of Tween 40 and 1-nitroso-2-naphthol were added to a 25 mL calibrated flask to obtain final concentration of 5 % in Tween 40 and $185 \mu\text{g mL}^{-1}$ in 1-nitroso-2-naphthol. Then 5 mL of the sample was added and the absorbance was measured against reagent blank. The same sample, 5-mL was diluted to 25 mL with double distilled water for AAS analysis (Table-5).

Conclusions

Determination of trace amount of Ni (II) up to 1.70 ng mL^{-1} can be carried out directly using 1-nitroso-2-naphthol, in non-ionic micellar media of 5 % Tween 40 in aqueous solutions. The method is simple and rapid with greater sensitivity, better selectivity and improved precision and replaces extraction with toxic organic solvents. Ni (II) content samples determined by the present method is in agreement with the values obtained by atomic absorption spectroscopy.

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