



DETERMINATION OF COBALT(II) WITH 1-NITROSO-2-NAPHTHOL IN MICELLAR MEDIUM BY FIRST DERIVATIVE SPECTROPHOTOMETRY

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A first derivative spectrophotometric determination of cobalt(II) is carried out with 1-nitroso-2-naphthol as complexing reagent in aqueous phase using non-ionic surfactant Tween 40. The cobalt 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 1.86 × 10⁴ mol⁻¹cm⁻¹ and 3.6 ng cm⁻² at 444.5 nm. The optimum pH of the complexation is 5. 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 interferences. 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 Co(II) in pharmaceutical samples.

Keywords: Co(II), Non-ionic-Tween 40, Micelle, 1-nitroso-2-naphthol, First derivative spectrophotometry.

1. Introduction

Cobalt is an important essential micronutrient for all living systems. In chemical analysis, metal chelation followed by solvent extraction and spectrophotometric detection is preferred mode of analysis for a number of metal ions [1-3] 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 the determination of metal ions in aqueous system, have been developed and modified [6-10]. Micellar media is mainly used to enhance the absorption sensitivities, thus simplifying the system by replacing the toxic organic solvents. The use of polyoxyethylene sorbitan mono-oleate (Tween 40) is reported for the determination of metal ions using 1-nitroso-2-naphthol as a complexing agent [11]. The determination of metal complexes of 1-(2-pyridylazo)-2-naphthol in micellar media has been reported earlier [12]. Tween series surfactants are very soluble in aqueous systems than other non-ionic surfactants. The use of surface-active reagent increases the solubility of 1-nitroso-2-naphthol has been reported [13]. Derivative mode spectrophotometry is recently shown to be more useful than

classical spectrophotometry for solving several analytical problems [14]. 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 Co(II) as 1-nitroso-2-naphthol complex in a non-ionic surfactant Tween 40 using first derivative mode spectrophotometric method is reported. The method is successfully applied for the determination of Co(II) in pharmaceutical samples.

2. 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 for pH measurement.

2.1. Reagents

All chemicals used were analytical grade reagents (Merck and Fluka A.G) unless otherwise stated. Standard Co(II) stock solutions of (100 μg mL⁻¹) were prepared dissolving their nitrate salts.

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Other metal ion solutions were prepared from their nitrate or chloride salts. 5 % Tween 40 solution was prepared in double distilled water. Buffer solution 100 mL of pH 5 was prepared by taking 0.2 M sodium acetate (35.2 mL) and 0.2 M acetic acid (14.8 mL) [15].

2.2. Procedure

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

Two sets of solutions, one containing $3 \mu\text{g mL}^{-1}$ metal ion and other without it, and each containing fixed amount of the reagent ($185 \mu\text{g mL}^{-1}$) and Tween 40 (5 %) in the pH range 2.0 -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-Co(II) complex, a set of solutions containing increasing amounts of Tween 40 (2 %-10 %), and $3.0 \mu\text{g mL}^{-1}$ Co(II) and $185 \mu\text{g mL}^{-1}$ 1-nitroso-2-naphthol, at the pH 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 1×10^{-2} to 8×10^{-2} M of the reagent at the optimum pH.

Table 1. Analytical characteristics of Co(II)-1-nitroso-2-naphthol in presence of Tween 40 in normal mode spectroscopy.

Characteristics	Co(II)
Beer's law range ($\mu\text{g mL}^{-1}$)	0.12 –3.0
Absorption maxima (λ_{max} , nm): (a) micellar	444.5
(b) CCl_4	447.8
Molar absorptivity ($10^4 \text{ mol}^{-1} \text{ cm}^{-1}$)	1.6
Sandell's sensitivity ng cm^{-2}	3.6
Detection limit (ng mL^{-1})	3.1
pH	5
Concentration of Tween 40	5 %
Concentration of 1-nitroso-2 naphthol ($\mu\text{g mL}^{-1}$)	185
RSD \pm	12.9

At 95 %, n = 6

Range of linear proportionality of absorbance of the system with Co(II) ion concentration has been ascertained based on a set of solutions containing varying amounts of the metal ions ($1.0\text{-}120 \text{ ng mL}^{-1}$ and 0.06 to $4.0 \mu\text{g mL}^{-1}$), $185 \mu\text{g mL}^{-1}$ 1-nitroso-2-naphthol and 5 % Tween 40 at pH 5 condition of maximum complex formation.

2.3. Spectrophotometric metal ion determination in micellar solution

Absorption spectra were recorded against reagent as reference to generate analytical calibration curves in normal mode ($\lambda_{\text{max}} = 444.5 \text{ nm}$) or in first derivative mode (peak height (PH) at 440 nm) or (trough depth (TD) at 390 nm). Cobalt contents of the standard and the sample were determined using AAS with an air acetylene flame. The pH and wavelength used are listed in Table 1.

2.4. The determination of Co(II) in pharmaceutical samples

2.4.1. Pharmaceutical sample:

A tablet of Theragran-M (Bristol-Myers Squibb, Pak) was transferred to a crucible to which was added 0.5 g potassium bisulphate, dissolved in 2 mL water, 6 mL hydrochloric acid (37 %) and 3 mL nitric acid (65 %). The mixture was heated on flame. The white powder obtained was dissolved in 25 mL water. Working solutions were adjusted to 10 mL solution for analysis of cobalt, spiked with $20 \mu\text{g}$ cobalt(II) and then determined by proposed method and by AAS (Table 2).

Table 2. Determination of Co(II) ion in pharmaceutical sample.

Sample	Cobalt determined ($\mu\text{g /tab}$)	
	Present method	AAS method
Theragran-M tablet (Bristol-Myers Squibb Pak.) ($39.0 \mu\text{g /tab}$)	39.0 (0.4)	39.1 (1.4)

At 95 %, n = 6, coefficient of variation is given in parenthesis.

3. Results and Discussion

The absorption spectra in first derivative mode spectroscopy of 1-nitroso-2-naphthol reagent at 425 nm and Co(II)-1-nitroso-2-naphthol complex at 440 nm are shown in Fig. 1. It shows that the height of the peak at 440 nm (TD) and the depth of the trough at 390 nm were linearly related to the metal ion concentration and the first derivative spectra are more resolved than those obtained for

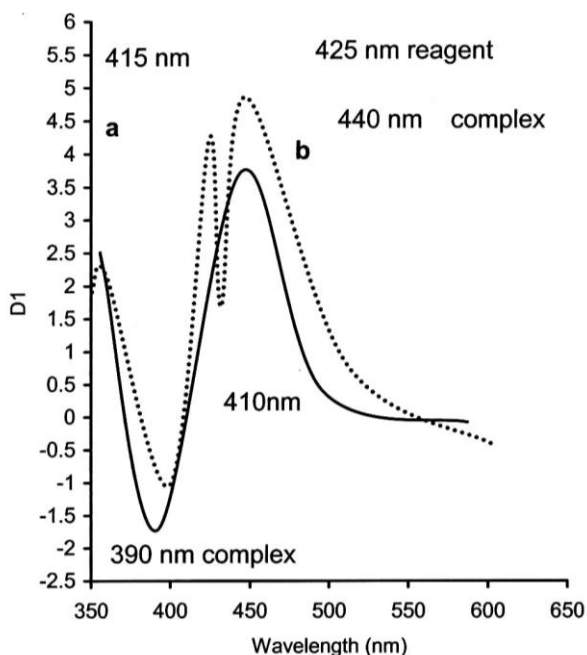


Figure 1. First derivative spectra of (a) 1-nitroso-2-naphthol (b) cobalt (II) – 1-nitroso-2-naphthol complex in 5% Tween 40.

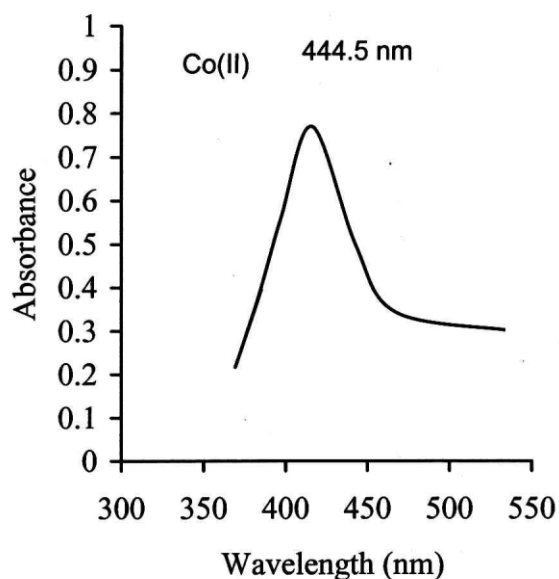


Figure 2. Absorption spectrum Co(II)-1-nitroso-2-naphthol complex in 5% Tween 40 at pH5 Co(II) 3 $\mu\text{g mL}^{-1}$.

the normal mode Fig. 2. However, even higher derivative orders yield sensitive but irreproducible signal, so this possibility was discarded. As derivative spectroscopy provides additional possibilities because it enhances the detectability of minor spectral features, this technique was

adapted. 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. 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 (0.0013 %, w/v) concentration [16].

3.1. Composition of complex

Composition of the complex formed under experimental conditions was investigated by Job's method of continuous variations. The plot of mole fraction versus absorbance of the metal ion shows at solution No. 2, which corresponds to 1:3 (M: L) ratio for metal ion in the complex is shown in Fig. 3.

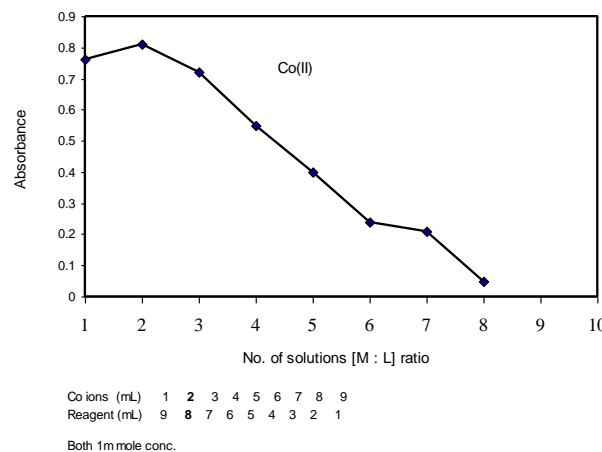


Figure 3. Job's plot of metal : ligand ratio.

Fig. 4 shows increase in the absorption with increase in the concentration of 1-nitroso-2-naphthol solution from $20-50 \times 10^{-3}$ M in presence of constant Co(II) concentration. Fig. 5 shows the optimum pH 5. for Co(II)-1-nitroso-2-naphthol

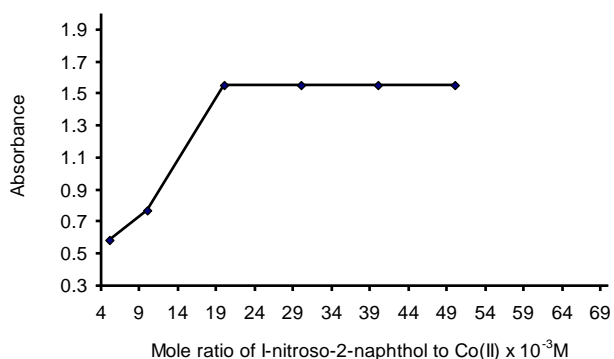


Figure 4. Effect of amount of 1-nitro-naphthol on the absorbance of Co(II).

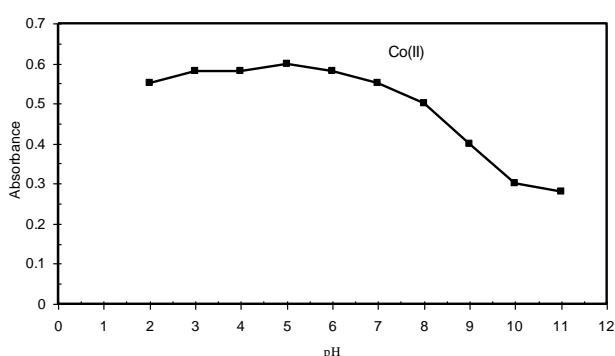


Figure 5. Effect of pH on the absorbance of CO(II)-1-nitroso-2-naphthol.

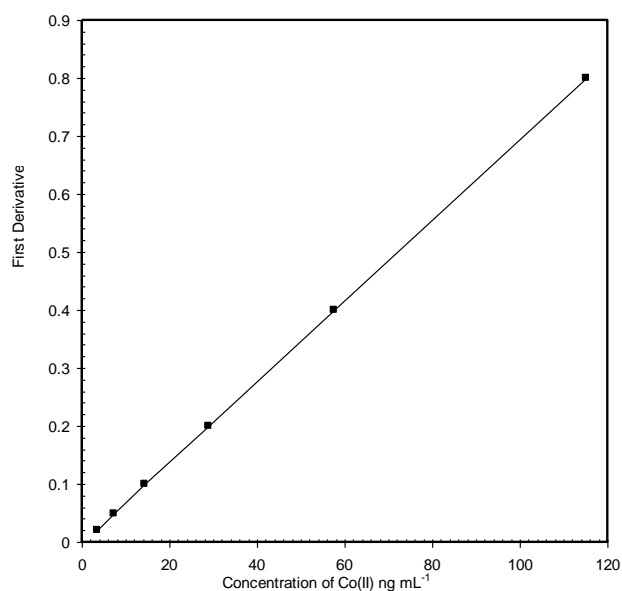


Figure 6. Calibration graph of Co(II)-1-2-naphthol complex in 5% Tween in first derivative spectroscopy.

complex formation. Fig. 6 shows the calibration graph of Co(II)-1-nitroso-2-naphthol complex in the range of 1.7-120 ng mL⁻¹ at 440 nm

with increasing concentration of cobalt(II). In normal mode detection limit is 6.7 ng mL⁻¹ while in first derivative mode it lowered significantly from 6.7 to 1.7 ng mL⁻¹ which is the advantage of the present method. All other experimental conditions are same as in normal mode spectroscopy; molar absorptivity is $1.86 \times 10^4 \text{ mol}^{-1}\text{cm}^{-1}$, Sandell's sensitivity (3.6 ng cm⁻²) and Beer's law linear range 0.12-3.0 μg mL⁻¹ are already given in Table 1 and Beer's law linear range in first derivative mode spectroscopy is 1.7-120 ng mL⁻¹.

Table 3. Tolerance limits of metal ions and salts with 1-nitroso-2-naphthol in Tween 40 in normal mode spectroscopy Tolerance limits μg mL⁻¹.

Ion / salt	Co(II)
KSCN	1000
NaF	600
Na ₂ C ₂ O ₄	200
KClO ₃	1000
Na ₂ tartarate	1000
Na ₂ citrate	500
KCN	50
Mg(II)	800
Al(III)	10
Cd(II)	2
Co (II)	-
Cr (III)	50
Cr (VI)	8
Fe (III)	5
Mn(II)	200
Ni(II)	5
Pb (II)	3
Zn (II)	50
Cu (II)	5

The concentration of metal ions is 2 μg ml⁻¹

Table 4. Percent recovery of known amount added to tap water.

Metal ions	Amount added	Amount found	Recovery (%)
Co(II)	1.70 ng mL ⁻¹	1.69 ng mL ⁻¹	99 ± 1
	0.50 (μg mL ⁻¹)	0.49 (μg mL ⁻¹)	99 ± 1

3.2. Study of interference's by foreign ions

In the Co(II) determination with 1-nitroso-2-naphthol in the presence of 5 % Tween 40 interferences by foreign ions were studied and results are shown in the Table 3. These interferences can be avoided in general by the addition of complexing agent like EDTA which forms stable complexes with many metal ions. In this medium Co (II) reaction with 1-nitroso-2-naphthol is highly selective with buffer at Ph 5. Cd(II), Ni(II), Fe(III) and Pb(II) interfere seriously at trace levels as given in Table. 3. The interference due to absorption by Fe, Ni and Cu(II)-1-nitroso-2-naphthol complex in normal mode spectroscopy is thus removed by the use of first derivative mode spectroscopy.

3.3. Validation of method

Proposed method was verified by % recovery test by standard addition method, results were compared with AAS and no significant difference is noted between the two methods at 95 % confidence level.

4. Conclusions

Determination of trace amount of Co(II) at 1.7 ng mL⁻¹ level is carried out directly using 1-nitroso-2-naphthol in cationic micellar media of 5 % Tween 40 in aqueous solutions in first derivative mode spectroscopy. The method is simple and rapid with greater sensitivity, better selectivity, and improved precision and replaces difficult step of extraction with toxic organic solvents. Co(II) content in various matrixes can be determined by the present method.

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