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# A SIMPLE SPECTROPHOTOMETRIC METHOD FOR THE DETERMINATION OF COBALT (II) USING 1-NITROSO-2-NAPHTHOL IN ANIONIC AQUEOUS SOLUTION OF SODIUM DODECYL SULPHATE

**GUL AFSHAN SOOMRO[a] and GHULAM ABBAS SHAR[*,a,b]**

[a]Department of Chemistry, Shah Abdul Latif University, KHAIRPUR – 66022, Sindh, PAKISTAN
[b]Department of Chemistry, Virginia Commonwealth University, Richmond,
VIRGINIA – 23284-2006, USA

## ABSTRACT

A simple rapid new spectrophotometric method has been developed for the determination of cobalt at trace level using 1-nitroso-2-naphthol (NNPh) in presence of anionic aqueous micellar solution surfactant 1.0% sodium dodecyl sulphate (SDS). NNPh reacts with cobalt (II) to form green coloured tris (1-nitroso-2-naphtholato) cobalt complex. The importance of this method is the use of micellar system which 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 $2.05 \times 10^4$ L $mol^{-1}cm^{-1}$ and 3.49 ng $cm^{-2}$at $\lambda_{max}$ 436.2 nm. Linear calibration graph was obtained over the concentration range 0.12-4.0 μg$mL^{-1}$, the stoichiometric composition of the chelate was 1:3 (Co: $[NNPh]_3$. The developed method was successfully applied for the determination of cobalt from alloy and pharmaceutical samples.

**Key words**: Spectrophotometric, Cobalt, NNPh, Anionic micellar, SDS.

## INTRODUCTION

Cobalt play essential role in biological systems[1]. Cobalt is the major constituent of vitamin $B_{12}$ or cyanocobalamine. Cobalt deficiency causes thalassemia, sickle cell anemia, hematological disorders, and polycythemia disease[2]. Excess dose of cobalt is toxic and causes vomiting, nausea, pulmonary diseases and skin diseases[3]. Special cobalt- alloys are used for prosthetic parts such as knee and hip replacements[4]. Cobalt ion in small concentration is essential for enzymatic functions in all mammals. Cobalt is very toxic, when it is given to plants and moderately toxic to mammals in high dose. Now days, it has been

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[*] Author for correspondence; E-mail: gabbas.shar@salu.edu.pk

great concern about the role of cobalt in biochemical and environmental systems. Determination of cobalt concentration and its effects on system is of great importance and scope. In spectrophotometric analysis of metal ions, the metal is complexed with chelating agent and solublized in solvent extraction is easy method for studying the metal ions because of its simplicity and rapidity[5]. Several spectrophotometric methods have been developed to replace the old solvent extraction method by using the surfactants[6]. Micellar methods due to solubility of several metal complexes have shown improvement in the analytical merits of techniques for the determination of metal ions. Micellar media is introduced to enhance the molar absorpitivities, sensivities and replaces the previous steps of toxic solvent extraction[7-15]. Many spectrophotometric methods for the determination of cobalt using various chelating reagents are available. Some of the recently developed spectrophotometric methods for the determination[16-21] are less selective and less sensitive. We have developed new simple, sensitive and selective spectrophotometric method for the determination of cobalt (II) in various materials by using 1-NNPh as chromogenic agent in anionic micellar aqueous solution of 1.0% SDS.

## EXPERIMENTAL

### Apparatus

A Cecil CE 9500 UV-Vis 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. I.R spectrophotometer (260 Hitachi*)* was utilized for study of metal chelates. Besides, pH/conductivity meter (Sension 156 HACH) with Sension Gel-filled pH electrodes was used.

### Preparation of reagents

NNPh (Merck) was made by dissolving 75 mg in 50 mL and was dissolved in minimum volume of 1.0% SDS, this was stock solution of 15000 ppm (1500 µgmL$^{-1}$). SDS 1.0% was prepared by taking 1.0 g in volumetric flask of 100 mL. Cobalt (II) nitrate was made prepared by dissolving 4.93 g in (1000 µgmL$^{-1}$) 1L. Copper (II) nitrate stock solution was prepared by taking 3.85 g in (1000 µgmL$^{-1}$) 1L. Nickel (II) nitrate was made by dissolving 4.94 g in (1000 µgmL$^{-1}$) 1L and iron (II) chloride was prepared by taking 4.84 g in 1 L (1000 µgmL$^{-1}$). 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[22]. Buffer solutions of pH 1-10 were prepared by using appropriate methods[23], with appropriate volumes of the mixtures of 0.2 M KCl-0.2 M HCl for (pH 1-4.0), 0.2 M $CH_3COOH$-0.2 M $CH_3COONa$ for (pH 5-6.0), 0.1 M $KH_2PO_4$-0.1 M NaOH for (pH 6.5-8.0) and 0.025 M sodium borate and 0.1 M HCl for (pH 9-10.0).

**Table 1: Analytical parameters of Co(II)- $[NNPh]_3$ in 1.0% SDS**

| **Parameters** | **Co(II)** |
|---|---|
| Wavelength, $\lambda_{max}$ nm | 436.2 |
| pH | 5 |
| SDS | 1.0 % |
| NNPh (μgmL$^{-1}$) | 185 |
| Reagent ( M:R) | 1:3 |
| Linear range/μgmL$^{-1}$ | 0.12 -4 |
| Molar absorption coefficient/mol$^{-1}$cm$^{-1}$ | $2.05 \times 10^4$ |
| Sandell's sensitivity/ngcm$^{-2}$ | 3.49 |
| Detection limit/μgmL$^{-1}$ | 0.12 |
| Correlation coefficient ($R^2$) | 0.999 |
| Reproducibility (% RSD)$^*$ | 0.91 |

**Table 2: Effect of foreign ions on the Co(II)-$[NNPh]_3$**

| **Ion/salt** | **Co(II)** |
|---|---|
| $Na_2$ tartarate, KSCN, $KClO_3$ | 800 |
| Mg(II) | 600 |
| $Na_2C_2O_4$ | 200 |
| $Na_2$ citrate | 500 |
| Mn(II) | 200 |
| Zn(II) | 50 |
| Cu(II) | 5 |
| KCN | 50 |
| Al(III) | 10 |
| Ni(II) | 5 |
| Cr(IV) | 8 |
| Fe(III) | 5 |
| Pb(II) | 3 |
| Cd(II) | 2 |

## Determination of cobalt ions in alloy sample

Alloy sample of cobalt ions 0.1-0.5 g of reference material JSS 607-6 was digested with concentrated HCl (15 mL) and concentrated $HNO_3$ (5.0 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 as JSS 607-6 (Co 4.72, W 16.96, V 0.82)[24] data values are shown in Table 3.

**Table 3: Determination of Co(II) in reference material**

| Certified (%) composition | Metal ion | Metal (µg) present | Metal (µg) found | RSD % | Relative error % | Recovery % |
|---|---|---|---|---|---|---|
| JSS 607-6 | Co(II) | 14.01 | 14.03 | 0. 80 | 0.14 | 100.14 |

## Pharmaceutical samples

Neurobion injection (Merck) (vitamin $B_{12}$) sample 1.0 mL ampoule injection was transferred into 50 mL flask adding 10 mL nitric acid and sulphuric acid ratio (10+1), sample was heated to dryness[25]. The sample residue was leached with dilute $H_2SO_4$ and diluted to the solution till it reaches final colorless residue[26]. Sample solution was neutralized with sodium hydroxide and was made working solution in 50 mL volumetric flask. However, it was transferred in volumetric flask, and added adequate volume of NNPh 185 ppm, 1.0% SDS and pH 5 buffer solutions for the complex formation. The results are given in Table 4.

**Table 4: Determination of Co(II) in pharmaceutical samples**

| Sample | Analyte ion | Proposed method µgmL$^{-1}$ | RSD % | AAS method µgmL$^{-1}$ | RSD % | Recovery % |
|---|---|---|---|---|---|---|
| Neurobion (Inj)<br>21.74 µg mL$^{-1}$ | Co(II) | 21.70 | 0.5 | 21.71 | 0.8 | 99.81 |

## Determination of Co (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 $HNO_3$ to avoid precipitation. Cobalt metal was skipped in tap water in the volumetric flask added appropriate volumes of NNPh 185 ppm, 2.0 mL buffer solution of pH 5 and 2 mL 1.0% SDS the complex absorbance was measured as given in Table 5.

**Table 5: Percent recovery of known amount of Co(II) added to tap water**

| Metal ions | Amount added (µgmL$^{-1}$) | Amount found (µgmL$^{-1}$) | Recovery (%) |
|---|---|---|---|
| Co(II) | 1.0 | 0.99 | 99 |

**Table 6: Comparison of cobalt determination methods using NNPh**

| Metal | Method | Reference |
|---|---|---|
| Co | In Triton X-100, ε 3.18 × 10$^{4}$ mol$^{-1}$cm$^{-1}$, Sandell's sensitivity 2.05 ngmL$^{-1}$, linear range 0.20-3.0 µgmL$^{-1}$, and D.L 1.68 ngmL$^{-1}$ | 28 |
| Co(II) | in Tween 80, D.L. 0.016, µgmL$^{-1}$ | 35 |
| Co(II) | In Triton X-100, ε 2.05 × 10$^{4}$ mol$^{-1}$cm$^{-1}$, $\lambda_{max}$ 425 nm D.L., 0.02 µgmL$^{-1}$ | 27 |
| Co(II) | In 1.0% SDS, ε 2.05×10$^{4}$, mol$^{-1}$cm$^{-1}$, 436.2 nm, D.L. 3.49, µmL$^{-1}$ | Present method |

## RESULTS AND DISCUSSION

NNPh is an excellent colour forming chelating agent reacts with cobalt forms tris (1-nitroso-2-naphtholato) cobalt complex structure is shown in Fig. 1. UV-vis spectra of NNPh transitions (n→π*) from ligand-to ligand charge transfer (LLCT)[27-29] of N-O molecule and C-O-H group at $\lambda_{max}$ 377.0 nm is shown in Fig. 2. UV-vis spectra (1-nitroso-2-naphtholato) cobalt complex of green colour is formed at $\lambda_{max}$ 436.2 nm charge transfer transitions (n→π*), from ligand-to metal (LMCT) (pπ-dπ) is shown in Fig. 3. Cobalt (II)-[NNPh]$_3$ complexes showing increasing concentration of cobalt ions in 1.0 % SDS at ($\lambda_{max}$ 436.2 nm) are shown in Fig. 4.

The stoichiometry of the complex was found 1:3 (Metal : Ligand) by Job's method[30] of continuous variation method of metal and chelate ratio[31] forming tris[1-nitroso-2-naphtholato]cobalt shown in Fig. 5. NNPh concentration was varied at fixed concentration of 1 m.mole Co(II) ions and NNPh molar ratios 5.0 to 80.0 m.mole, where 20-50 mM NNPh was optimized concentration found for the complex formation is shown in Fig. 4. For surfactant optimization, 1 µgmL$^{-1}$ Co(II)-chelate, 2 mL of 1.0% SDS showed constant maximum absorbance in 10 mL volume, this 1.0% SDS was optimized for the whole procedure, which value is greater than the cmc value 8.3 × 10$^{-3}$ M than reported[32]. Co-[NNPh]$_3$ complex showed maximum constant absorbance at pH 5.0, which was selected for subsequent studies as shown in Fig. 7.

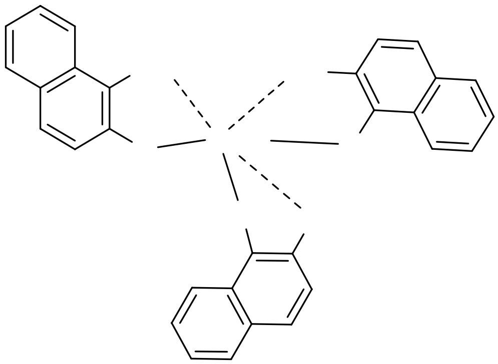

**Fig. 1: Structure of tris(1-nitroso-2-naphtholato) cobalt**

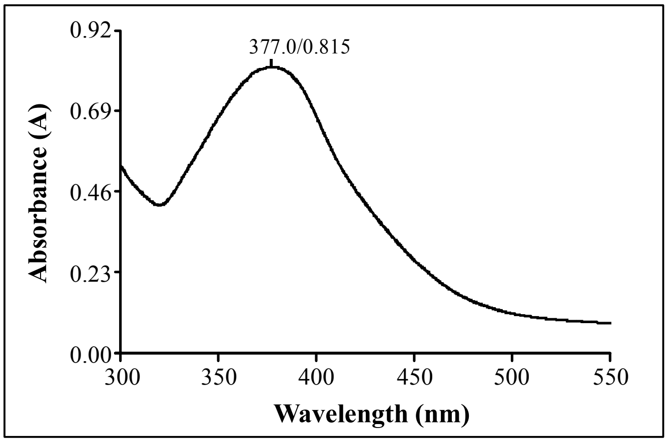

**Fig. 2: UV-vis spectrum of NNPh reagent at ($\lambda_{max}$ 377.0 nm) in 1.0% SDS**

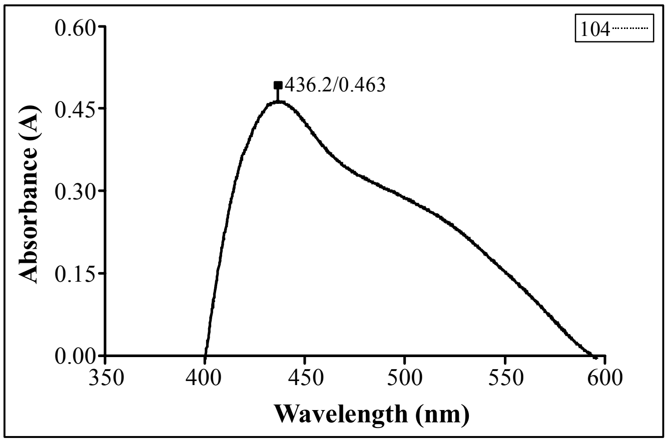

**Fig. 3: UV-vis spectrum of Co(II)-[NNPh]$_3$ complex at ($\lambda_{max}$ 436.2 nm) in 1.0% SDS**

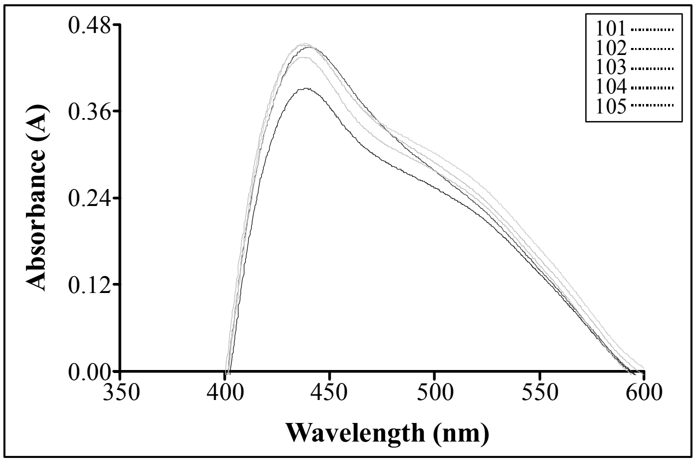

**Fig. 4: UV-vis spectra of Co(II)-[NNPh]$_3$ with increasing concentration at ($\lambda_{max}$ 436.2 nm)**

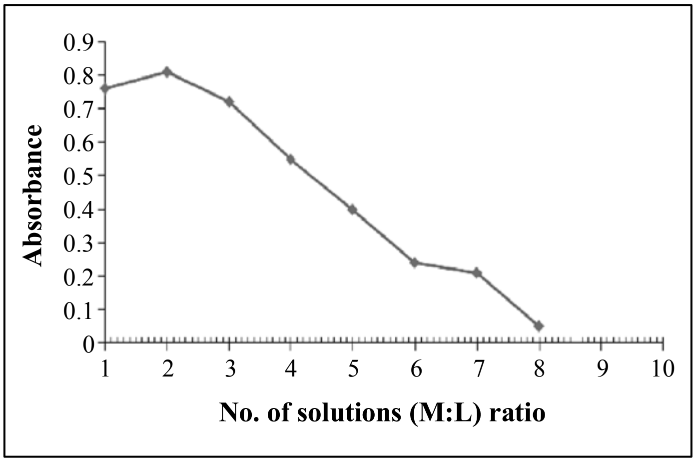

**Fig. 5: Composition of Co(II)-[NNPh]$_3$ by mole ratio method (Job's plot of metal : ligand ratio)**

Calibration graph showed linear concentration over the range 0.12-4.0 µgmL$^{-1}$, the correlation coefficients with experimental data was 0.999 as shown in Fig. 5. Molar absorptivity of the complex was found ($2.05 \times 10^4$) L mol$^{-1}$ cm$^{-1}$ is given in Table 1 and showed significant improvement in the molar absorptivities[33,34]. Detection limit and Sandell's sensitivity was found 0.12 µgmL$^{-1}$ and 3.49 ngcm$^{-2}$ as given in 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.

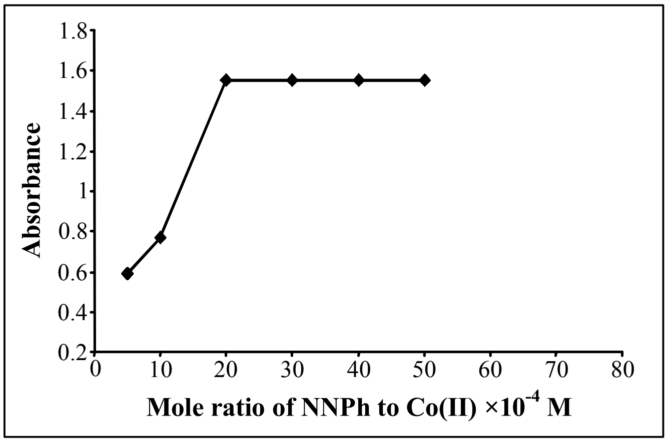

**Fig. 6: Effect of amounts of NNPh on the absorbance of Co(II)**

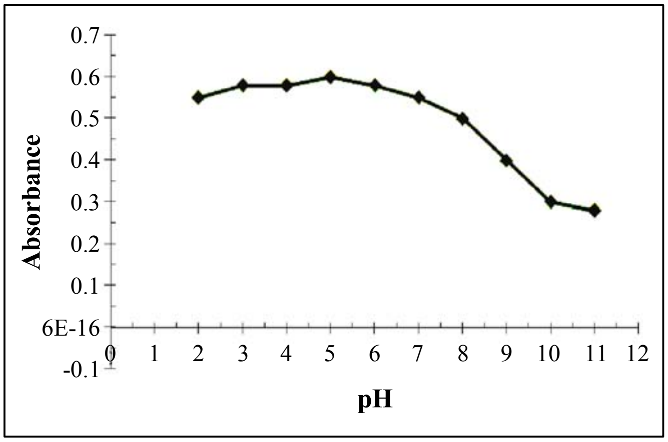

**Fig. 7: Effect of pH on the absorbance of Co (II)**

## Effect of foreign ions in the determination of cobalt

Above the amount 800 μgmL$^{-1}$ KSCN, sodium tartarate and $KClO_3$ showed interference in the Co(II)-chelate formation. Cadmium(II), copper(II), lead(II), iron(II) and nickel(II) showed interference at low trace level concentration. Ascorbic 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. Cu(II) solutions interference was removed by using buffer solution of $NH_3$ as masking agent. Cu(II) interference was completely removed by using their specific masking agents results are shown in Table 2.

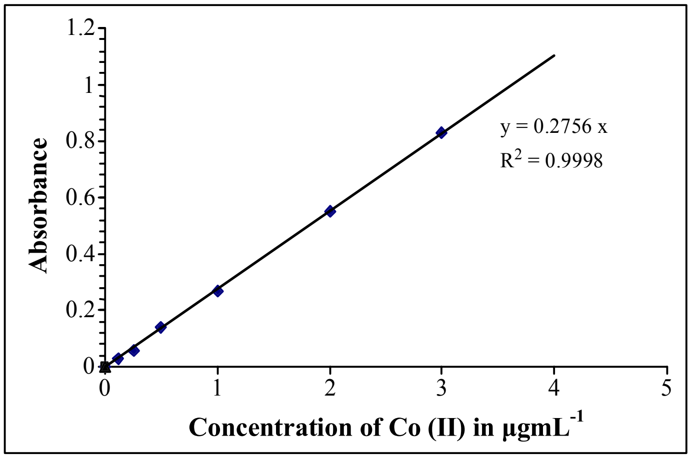

**Fig. 8: Calibration graph for Co(II)-$[NNPh]_3$ complex in 1.0% SDS**

### Validation of method to the determination of cobalt (II) ions

The method developed was validated to the determination of cobalt ions by present spectrophotometric method from certified reference material JSS 607-6 and in Neurobion injection and also standard addition method of % age recovery test was applied for the verification of the accuracy and the precision of the method. The average Co ions found (n 7) in the reference material with a precision as relative standard deviation RSD was upto 0.80 % is given in Table 3-5.

## CONCLUSION

The results obtained in the determination of cobalt (II) were comparable with the recently reported methods, while the present method showed significant improvement in Beer's law linear concentration range than reported[33-36]. Sensitivity and 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 as given in Table 6.

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