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RESEARCH PAPER

Eco-friendly method for the estimation of cobalt (II) in real samples using 1-(2-Thiazolylazo)-2-naphthol

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Key words: Cobalt, 1-(2-Thiazolylazo)-2-naphthol (TAN), Micellar, Cetyltrimethylammonium bromide.

Abstract

An easy and quick spectrophotometric method is developed for the investigation of cobalt at trace level using 1-(2-Thiazolylazo)-2-naphthol (TAN) in presence of surfactant cetyltrimethylammonium bromide (CTAB) aqueous micellar solution. The cobalt forms bis [1-(2-Thiazolylazo)-2-naphthol] cobalt complex reacting with 1-(2-Thiazolylazo)-2-naphthol. Proposed method is of great importance because use of micellar system instead of solvent extraction steps that were toxic, expensive and time consuming. The method shows improved sensitivity, selectivity and molar absorption. The coefficient of molar absorption and Sandell's sensitivity was found to be ε 1.89×10^4L mol^{-1} cm^{-1} and 3.1ngcm^{-2} at λ_{max} 572.7nm. Graph of Linear concentration calibration was obtained in the range 0.02-9.0µgmL^{-1}; stoichiometric metal ligand ratio was found 1:2 for the complex Co-[TAN]$_2$ formation. The proposed method was applied for the investigation of cobalt from different alloys, biological, environmental and pharmaceutical samples.

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Introduction

Metals play important role in biological and daily life. Metals may potentially be essential like cobalt, zinc, nickel, manganese copper, iron etc and toxics such as cadmium, arsenic, mercury , lead, etc (Dogan Uluozlu *et al.*, 2007). Sometimes intake of essential metals in excessive amount can also produce toxic effects over human health (Singh *et al.,* 2011). Cobalt is significant element for biological (Amin, 2014) as well as industrial processes. In living systems, it is an essential micronutrient. It is an important constituent of vitamin B_{12} (El Sheikh, 2015; Nekouei, F and Nekouei S, 2014), it plays vital role in the production of RBC and pernicious anemia can be prevented by the use of cobalt in suitable amounts. Cobalt (II) in low concentration is necessary for functions of enzyme in all mammalians (Bhattacharya *et al.,* 2016). Insufficiency of cobalt may cause thalassemia, sickle cell anemia, hematological and polycythemia disorders (Prashanth *et al.*, 2015).

Although the higher amounts of cobalt may be toxic and may causes, nausea, vomiting, dermatitis and pulmonary disorders (Czarnek *et al.,* 2015; Naeemullah *et al.,* 2012). Cobalt has a narrow difference between essential and toxic concentration levels, its determination and analysis at micro-levels in diverse matrices is required to evaluate and the development of analytical procedures that are more reliable is necessary. 0.3 to 4.0mg of cobalt is required per day as a cyanocobalamine (Korai, 2019).

Nowadays, it has been immense concern about the function of cobalt in bio-chemical (Scharf *et al.*, 2014) and ecological systems (Reddy *et al.*, 2011). Special alloys of cobalt are employed as prosthetic pieces like knees and hips replacement (Devi and Reddy, 2012).

In spectrophotometric study of cobalt (II), the metal is reacted with complexing reagent and insoluble metal complex is formed then solubilized with solvent extraction (Drozd and Leonova, 2014; Teng *et al.,* 2012; Zoubi, 2013). Various methods for spectrophotometric determination of cobalt have been developed to substitute the previous method of solvent extraction with the use of micellar system (surfactants) (Soomro and Shar, 2015). Micellar methods show enhancement in the investigative qualities of methods for the analysis of metal ions in solubilizing the complex (Hosseinzadeh *et al.,* 2013; Hosseinzadeh and Gheshlagi, 2009; Ketola, 2016; Khammas, 2009; Olkowska and Polkowska, 2012; Wani *et al.,* 2017). Several procedures for the spectrophotometric analysis of cobalt with different complexing agents are presented (Afifi *et al.,* 2014; Chandramouleeswarn and Ram Kumar, 2014; Guzar and Jin, 2008; Hussein *et al.,* 2016; Modawe and Eltayeb, 2013; Raju *et al.,* 2013). Recently some less sensitive and less selective spectrophotometric methods are developed for the determination (Fornea *et al.,* 2016). We have developed a convenient, quick, selective and sensitive method for the investigation of Co (II) in different substances by utilizing TAN as chelating agent in surfactant CTAB micellar media.

Material and method

UV-Vis Cecil CE 9500 spectrophotometer having quartz cells with path length of 10 mm. Atomic absorption spectrophotometer (Analyst-800 Perkin Elmer) model. FTIR spectrophotometer (NICOLET iS10). pH/conductivity meter (Sension 160 HACH Company USA) model.

Preparation of Reagents

The cobalt (II) ion stock solution (1000µg/L) was prepared from high purity $Co(NO_3)_2.6H_2O$, supplied by (Merck, Darmstadt, Germany) in double distilled water (Ghali, 2014), while other required metal ion solutions were prepared from their nitrate and chloride salts. TAN soIution (4×10^{-3}M) was prepared by adding its 0.50g with small amount of methanol in 500mL measuring flask and the volume was made with CTAB 0.02M up to the mark (Ferreira and Nano, 1994). 0.02M solution of CTAB was prepared by taking its 7.28g in 1000mL measuring flask and the final volume was made up to the mark with deionized water (Korai, 2019). Insoluble chemicals were solubilized in particular acids as to technique special dissolution (Shar and Soomro, 2014). Buffers of pH 1 to 10 were made according methods (Perrin, 2012), by mixing appropriate volumes of KCl (0.2 M)-HCl (0.2M) of both for pH 1.0 to 4.0, CH_3COOH (0.2 M)-CH_3COONa (0.2 M) volumes for solution of pH 5.0 to 6.0, KH_2PO_4 (0.1 M)-NaOH (0.1 M) volumes for solution of pH 6.5 to 8.0 and sodium borate (0.025 M)-HCl (0.1 M) volumes for preparation of the solution of pH 9.0 to 10.0. All the chemicals were used of analytical grade with high purity (Merck / Fluka).

General method for determination of cobalt (II) metal ions

The different concentrations of cobalt ions ranges from 0.06-10µgmL^{-1}, 0.5 to 9×10^{-4} M concentration of TAN solution (1-4×10^{-4} M), 2mL of buffer solutions of different pHs and 1-2mL of cetyltrimethylammonium bromide (0.02M) were mixed into measuring flask of 10mL, mixture was shaken and final volume was made with deionized water (Korai, 2019). The absorbance for cobalt metal ions at optimum conditions for metal complexes formation were observed at particular λ_{max} with UV-vis spectrophotometer (double beam CE-9500) having bandwidth of 2 nm and 5 nms^{-1} speed in 10 mm quartz cells.

Investigation of Co (II) ions in alloys sample

The cobalt alloy sample of 0.1 to 0.5g of reference substance JSS 607-6 was added in 15mL of concentrated HCl and 5.0mL of concentrated HNO_3 in beaker. The volume of sample solution was reduced to 5mL by placing it on a hot plate. Then 10mL of concentrated HCl was mixed, filtered and diluted to 25mL volume by adding double distilled water (Shar and Soomro, 2014). The sample was transferred in measuring flask, mixed 2ml volume TAN 3×10^{-4} M, CTAB 0.02M and 2mL buffer of pH 9.5 in formation of complex. The outcomes are given in Table 3.

Investigation of cobalt (II) ion in Pharmaceutical sample

Neurobion ampoule injection (Merck company) (vitamin B_{12}) sample 1.0mL was taken in 50mL of flask adding 10mL of HNO_3 and H_2SO_4 by the (10:1) ratio, the solution was warmed to dryness (Mallah *et al.,* 2012). The residue was leached with dilute sulphuric acid and diluted to the solution till it reaches final colorless residue. Then NaOH was mixed to neutralize the sample and working solution was made in 50mL measuring flask. Though the solution was transferred in measuring flask and mixed 2mL volumes of TAN 3×10^{-4} M, CTAB 0.02M and 2mL buffer of pH 9.5 in formation of complex. The outcomes are given in Table 4.

Analysis of cobalt in environmental water samples

1L of samples of waste water were collected from the different places of Pano Akil District Sukkur and industrial area of Mirpur Mathelo district Ghotki, Pakistan and were filtered and acidified by adding 2mL of H_2O_2 30% concentrated and 4mL of HNO_3 (conc.) (Iqbal *et al.*, 2017). Then the obtained solution was promoted for pre-concentration by placing in oven at about 110°C to get 25mL of solution at last. The solution was transferred into volumetric flask, mixed with 2mL of reagent TAN, 2mL of CTAB of 0.02M concentration and 9.5 pH buffer. Then the Co-TAN complex formed and the cobalt metal complex absorbance was recorded against blank (reagent). The obtained data is shown in Table 9.

Analysis of Co (II) ion in tap water sample

Tap water sample was taken from area of Khairpur, Sindh. Then the solution was filtered using 0.45µm filter paper and acidified by adding 1mL of concentrated HNO_3 to prevent from precipitation. Metal cobalt was added in the sample in measuring flask, mixed 2mL volumes TAN 3×10^{-4}M, 2.0mL of pH 9.5 buffer solution and 2mL of CTAB 0.02M then absorbance for complex was measured as shown in Table 5.

Investigation of Co (II) metal ions in biological samples

The sample of tea leaf 0.1 g was taken in a measuring utensil and digested with 5mL volume of HNO_3 conc. with warming. Then filtered and diluted the sample solution and the solution were transferred into measuring flask and mixed 2mL volume TAN volume, 0.02 M CTAB 2mL volume and 2mL of buffer solutions of 9.5 pH for formation of metal chelate. Then absorbances were observed spectrophotometrically for cobalt (II) metal ion. The amount of cobalt was calculated and is shown in Table 6.

Investigation of Cobalt (II) in hair samples

The hair samples were washed and subjected to ultrasonic vibration for 1 hour in acetone, water, water and acetone separately in the 100mL volume. The samples were filtered and dried. After weighing the samples, they were digested in nitric acid 2.5mL volume and kept at 60°C overnight in oven. These samples were taken in calibrated flask (DaAntonio, 1982). Then NaOH was mixed to neutralize the samples and working solutions were made in 50mL measuring flask. Though the solutions were transferred into measuring flask and mixed 2mL volume TAN, 0.02 M CTAB 2mL volume and 2mL of buffer solutions of 9.5 pH for formation of metal chelate and determined spectrophotometrically for cobalt (II) metal ion. The amount of cobalt was calculated and the results are shown in Table 7.

Determination of Cobalt (II) in nail samples

The samples were collected, washed with double distilled water and dried in oven. Then the samples were digested by adding the 10mL of nitric acid conc. and perchloric acid in the ratio of 6:1 ratio of mixture and kept them at room temperature overnight. Then the obtained solution was promoted for pre-concentration by placing in oven at about 160-180°C to get 1mL of solution at last (Mehra and Juneja, 2005). Then NaOH was mixed to neutralize the samples and working solutions were made in 50mL measuring flask. Though the solutions were transferred in measuring flask and mixed the suitable TAN volume, 0.02 M CTAB 2mL volume and 2mL of buffer solutions of 9.5 pH for formation of metal chelate and determined spectrophotometrically for cobalt (II) metal ion. The amount of cobalt was calculated and is shown in Table 7.

Investigation of Cobalt (II) in Pharmacological tablet samples

The samples of known amount were taken and digested with 3mL volume of HNO_3 0.01M, heated to dryness and residue was dissolved in alcohol. The solution was then filtered and made it diluted upto 100mL with deionized water. The stock solutions of the lower concentrations were made by suitable successive dilution method. Then the sample was transferred in measuring flask and mixed the 2mL volume TAN, 0.02 M CTAB 2mL volume and 2mL of buffer solutions of 9.5 pH for formation of metal chelate and determined spectrophotometrically for cobalt (II) metal ion. The amount of cobalt was calculated and the results are shown in Table 8.

Results and discussion

TAN is tridentate chelate reacts with Co(II) by bonding through two atoms of nitrogen and one atom of oxygen in TAN after deprotonation. The structure of the complex bis [1-(2-Thiazolylazo)-2-naphthol] cobalt is shown in Fig. 1. UV-vis spectrum of TAN showed broad peak (π→π*) electron transitions from one ligand to another (L→L) of nitrogen atom of nitro group at λ_{max} 488.5 of C=N group, OH group and N=N double bonds is shown in Fig. 2. UV-Vis spectrum of Co(II)-TAN compound gave bathochromic shift termed as red shift by 84.2 nm. Transformation of charge from TAN to Co(L→M) was observed from the orbitals of TAN (pπ) to Co(dπ) at λ_{max} 572.7 ($\varepsilon 1.89\times10^4$L $mol^{-1}cm^{-1}$). Co(II)-TAN spectra showed that after deprotonation of -OH atom and C=N group and N=N are taking part in TAN-chelate are shown in Fig. 3. The Co-complex gave reddish brown colour rapidly and gave the same constant maximum absorbance up to 60 minutes. Co-TAN complex at room temperature showed no any change in absorbances until 24 h. The TAN reagent concentration effect on the Co-TAN complex formation was investigated by varying TAN reagent concentration (Khadem *et al.,* 2010) 0.5 to 10.0×10^{-4} M, while Co (II) ions concentration was kept constant 1m.mole. Concentration of the reagent TAN was optimized by taking 1m.mole Co ions reacted with TAN in molar ratio of 1:3×10^{-4} M forming Co-TAN complex showing maximum absorbance. TAN 3×10^{-4} M concentration showed Co-TAN complex formation with maximum absorbance is shown in Fig. 4. Therefore concentration of TAN reagent was kept 3×10^{-4} M constant in the throughout studies. Stoichiometric Co-TAN compositions were determined using Job's method (Cherdantsevaa *et al.,* 2010; Jayanna *et al.,* 2010; Patel *et al.,* 2016; Reddy *et al.,* 2016) by varying both Co and TAN concentrations by molar-ratio method**.** Co-TAN metal against ligand ratio was found 1:2 (M:L_2). 0.02M CTAB 2mL volume of surfactant solution showed maximum constant absorbance, which was above the cmc value. In complex formation different pH was kept and investigated the optimum pH where the absorbance was showed maximum. pH 9.5 was measured optimum pH (Kuliyev, 2016) for Co (II)-$(TAN)_2$ complex formation is given in Fig. 5. Calibration linear concentration graph was obtained at 0.02-9.0µgmL^{-1}, with correlation coefficients 0.9991 is given in Fig. 6. Coefficient of molar absorptivity was obtained ε1.89×10^4 L mol^{-1}cm^{-1} at λ_{max} 572.7 is shown in Table 1. The Sandell's sensitivity was found 3.1ngcm^{-2} is shown in Table 1, showed improvement. Detection limit was obtained to be 3.1ngmL^{-1} is given in Table 1.

Table 1. Analytical parameters of Co(II)- $[TAN]_2$ in CTAB 0.02M.

Parameters	Cobalt
Wavelength (λ_{max})	572.7 nm
pH	9.5
CTAB (Surfactant) 0.02M	2.0mL
TAN concentration	3.0×10^{-4} M
Metal to Reagent ratio (M:R)	1:2
Linear range	0.02-9.0 µgmL^{-1}
Coefficient of molar absorptivity	1.89×10^4 Lmol^{-1}cm^{-1}
Sandell's sensitivity	3.1 ngcm^{-2}
Detection limit	3.1 ngmL^{-1}
(R^2)	0.9991
(% RSD)	0.80

2.0µg/mL of metal complex was chosen to examine the effect of interference under definite for the formation of metal complex was measured. The cations copper(II) and chromium(IV) were merely interfering species that exhibited the great influence in the formation of metal complex. 1.0mL of masking agent EDTA was used to remove before more perchloric acid addition. Both copper (II) and cadmium (II) showed greater interference at minute level, which was lowered using 0.01M NaCN 1.0mL volume masking agent solution (Jain and Memon, 2017). The high concentrations of SCN$^-$, Br$^-$, Cl$^-$, ascorbic acid and I$^-$ have not experienced interference. 1500µg/mL concentration of sodium tartrate has not revealed any interfering influence in the formation of metal chelate absorbance. Various masking agents such as thiocyanate, phosphate, citrate, and fluoride were utilized to eliminate the more effect of foreign interfering species (Rajni and Usha, 2012) as shown in Table 2.

Table 2. Effect of foreign ions on the Co(II)-$[TAN]_2$.

Metal ions / salts	Cobalt
Na_2tartarate	1500
KSCN, $KClO_3$	1100
NaF, CH_3COO^-	2100
Na_2citrate, Pb(II)	500
Al(III)	100
Bromide, Iodide, Chloride, Borate, $Na_2C_2O_4$	200
EDTA, Cyanate, Cd(II), Mn(II), Hg(II),	10
Fe(II)	100
Ni(II)	100
Zn(II)	100
Co(II)	-
Cu(II)	10
Cr(III)	60
Cr(IV)	8

FTIR spectra of TAN aqueous gave absorption band at 3342.70cm^{-1} for ν (OH) group and 2948.39 for ν (C-H) (C-N) and 1651.39 for aromaticity are shown in Fig. 7. 4000 cm^{-1}-1500 cm^{-1} showed the stretching while while 1500 cm^{-1}-550 cm^{-1} showed finger print region (Korai, 2019). The Co (II)-TAN complex showed lower wave numbers by 3335.77 cm^{-1} for ν (OH) group and 2940.55 for ν(C-H) (C-N) and decrease to 1657.06 for aromaticity of ν(Co-TAN). New bands suggested Co (II)-TAN bonding as shown in Fig. 8.

Precision and accuracy

Neurobion injection (Merck), Alloy JSS 607-6 and Tap water were tested for reliability and accuracy of method, % age recovery test by adding calculated amount of Co (II) ions are given in Table 3-5.

Table 3. Determination of Co(II) in reference material.

Alloys (%) Certified composition	Metal ions	Metals Present	Metals found	% RSD	% Relative error	% Recovery
JSS 607-6	Co(II)	14.01 µg	13.98 µg	0.40	0.14	99.78

Table 4. Determination of Co(II) in pharmaceutical samples.

Samples	Analyte ions	Proposed method µg/mL	RSD %	AAS method µg/mL	RSD %	Recovery %
Neurobion (Inj) 21.74 µg/mL	Co(II)	21.68	0.4	21.69	0.4	98.0

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

Metal ions	Co (II) added	Co (II) found	% Recovery
Co(II)	0.60 mg/mL	0.59 mg/mL	98.33

Table 6. Determination of Co(II) in biological samples.

Sample	Amount of cobalt (mg/g)	
	Certified value	Present method
Tea leaves	0.12	0.11

Table 7. Determination of Co (II) metal ions in hair and nail samples.

Samples	Analyte ions	Proposed method (µg/L)	RSD%
Hair	Co(II)	29.23	0.3
Nail	Co(II)	2.72	0.4

Table 8. Determination of Co (II) metal ions in pharmaceutical tablet samples.

Sample (mg/tablet)	Cobalt content (µg/mL)	
	Reported	Found
Neurobion forte (cyanocobalamine 15 mg)	7.45	7.44
Basiton forte (cyanocobalamine 15 mg)	7.42	7.43

Table 9. Determination of cobalt in environmental water sample.

Alloy/ sample Certified (%) composition	Analyte ions	Proposed method (µg/mL)	RSD %	A.A.S method (µg/mL)	RSD%	%Recovery
Municipal water	Co(II)	0.22	0.30	0.22	0.28	93.0
Industrial waste water sample, from Mirpur Mathelo	Co(II)	2.0	0.20	1.99	0.30	99.5

Table 10. Comparison of cobalt(II) analysis procedures using TAN.

Metals	Reagent	Methods/Remarks	Reference
Co(II), Cu(II), Ni(II)	TAN	λ_{max} 618, 626 & 621nm , conc. range 0.05-1.05, 0.05-1.30 & 0.05-0.80µg/mL, D.L 0.018, 0.017 & 0.012ng/mL	Niazi *et al.*, 2008
Fe(II), Co(II)	2-hydroxy-1-naphthaldehyde-p-hydroxybenzoichydrazone (HNAHBH)	λ_{max}405 & 425 nm respectively, ϵ 5.6× 10^4& 2.3×10^4Lmol^{-1}cm^{-1} respectively, Beer's law range 0.055–1.373 & 0.118-3.534µg/mL respectively., D.L 0.095 & 0.04 µg/mL	Devi *et al.*, 2012
Co(II)	[2-(4methoxyphenyl) azo (4, 5-dipheny imidazole)] (MPAI)	λ_{max}491 nm, ϵ 0.2703× 10^4 L mol^{-1}cm^{-1}, Beer's law range 3.00-50.00 µg/mL, D.L 2.083 µg/mL	Hussein *et al.*, 2016
Co(II)	5-nitrosalicylaldehyde semicarbazone (NSS)	λ_{max}417 nm, ϵ 2.86× 10^4 L mol^{-1}cm^{-1}, Beer's law obeyed at 0.5-3.0 µg/cm^3	Jain *et al.*, 2017
Co(II)	4-(6-Bromo 2-benzothiazolylazo) Orcinol(6-BrBTAO)	In alcoholic λ_{max}514 nm, ϵ 2.574x10^3L mol^{-1}cm^{-1}, conc. range 0.7-30 µg/mL, D.L 0.51 µg/mL	Ghali, 2014
Co(II)	(N', N''E, N', N''E)- N', N'' - (2, 2' -(propane-1,3diylbis(sulfanediyl)bis(1-(4-chlorophenyl) ethan -2-yl-1 -ylidene))bis(2hydroxybenzohydrazide)(CAPSH)	in aqueous DMF, λ_{max}380 nm, ϵ 7.9x10^4L mol^{-1}cm^{-1}, Beer's law obeyed at 0.059-0.59 µg/mL	Reddy *et al.*, 2016
Co(II), Co(III)	bis (5-bromosalicylaldehyde) orthophenilinediamine (BBSOPD)	λ_{max}458 nm, ϵ 5.3 x10^4L mol^{-1}cm^{-1}, linear range is 0.2-6 mg L^{-1}	Chandramouleeswaran *et al.*, 2014
Co(II)	TAN	λ_{max} 572.7 nm, Molar absorpitivity ϵ1.89×10^4 L mol^{-1}cm^1, linear calibration range 0.02-9.0 µgmL^{-1}, respectively	Present method

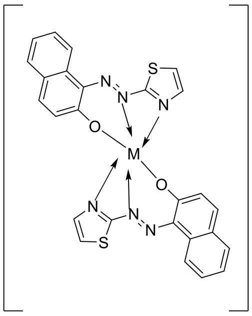

Fig. 1. Proposed structure of bis[1-(2-Thiazolylazo)-2-naphthol]cobalt.

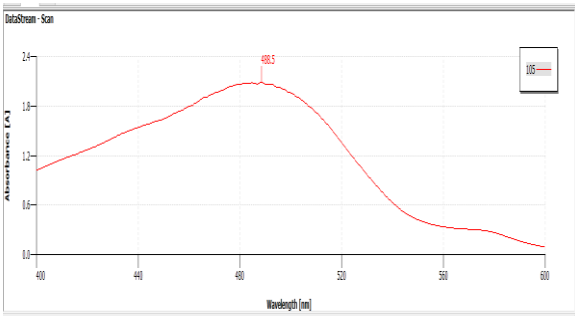

Fig. 2. UV-vis spectrum of TAN reagent at in 0.02M CTAB.

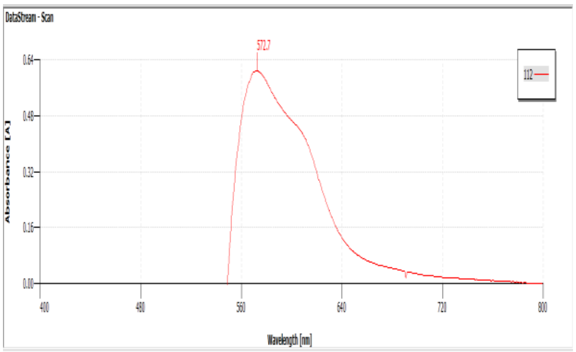

Fig. 3. UV-vis spectrum of Co-TAN in 0.02M CTAB.

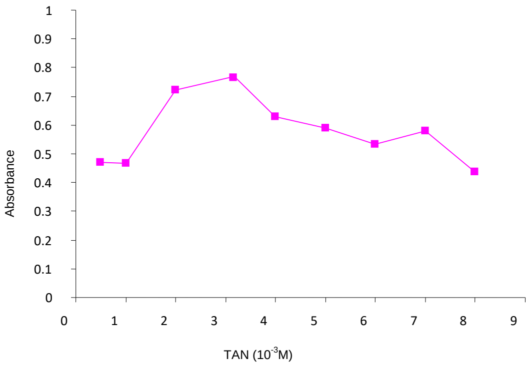

Fig. 4. TAN reagent conc. effect on the absorbance of Co (II)-TAN chelate.

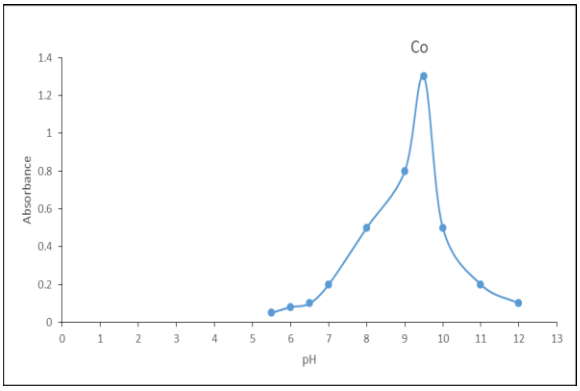

Fig. 5. Effect of pH on the absorbance of Co(II)-TAN.

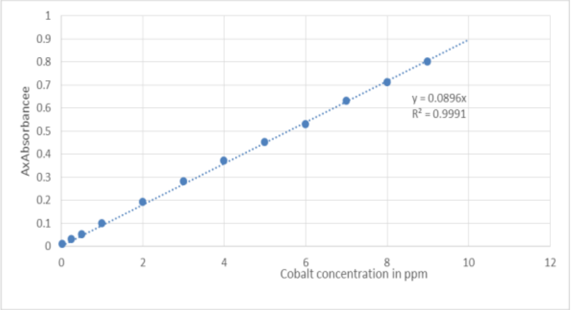

Fig. 6. Calibration graph of cobalt-TAN complex at λ_{max} 572.7nm.

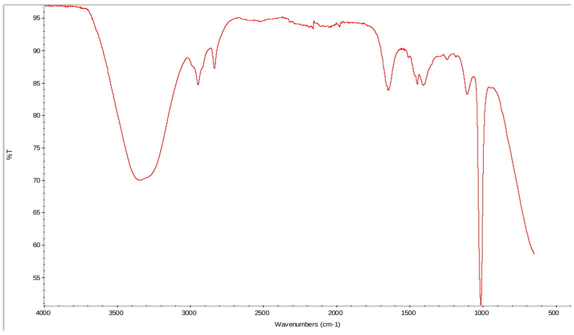

Fig. 7. FTIR spectra of TAN reagent.

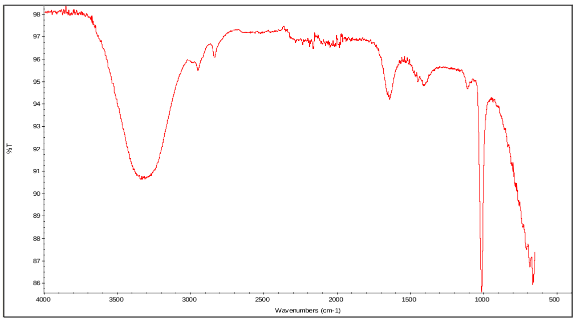

Fig. 8. FTIR spectra of Co-TAN complex.

Conclusions

The Co (II) determination in the present method showed higher selectivity and sensitivity than reported extraction methods that are time taking and costly (Andres *et al.,* 1994). The present method is precise, sensitive, selective, reproducible, non-extractive simple, rapid and versatile spectrophotometric method for determination of cobalt (II) ions as reported in table 10.

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