Derivative Spectrophotometric Determination of Cobalt(II) with 1-(2 Pyridylazo)-2-Naphthol in Micellar Medium

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Summary: A spectrophotometeric and first derivative spectrophotometeric determination of cobalt (II) is carried out with 1-(2 pyridylazo)-2-naphthol as complexing reagent in aqueous phase using non-ionic surfactant Tween 80. The cobalt is determined in the range 1.7 - 225 ng ml^{-1} with detection limit (2σ) of 1.7 ng ml^{-1}. The molar absorptivity and Sandell's sensitivity are $0.87 \times (10^4\ mol^{-1}cm^{-1})$ and 6.8 $ngcm^{-2}$ at 580 nm. The optimum pH of the complex is 5. The critical micelle concentration (cmc) of Tween 80 is 5 %. Absorption studies in the first derivative mode is carried out to determine the absorption maximum of the complex and to overcome interference due to the presence of certain 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 Co (II) in pharmaceutical samples.

Introduction

Cobalt is an important essential micronutrient for all living systems [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 surfacetants), many analytical techniques for determination of metal ions in aqueous system have been developed and modified [6-14]. 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 [15]. The determi-nation of metal complexes of 1-(2 pyridylazo)-2-naphthol in micellar media has been reported earlier [16]. Tween series surfactants are very soluble in aqueous systems than other non-ionic surfactants. 1-(2 pyridylazo)-2-naphthol (PAN) forms coloured water-insoluble complexes with a large number of metal ions [17-19] and these are suitable for extractive spectrophotometric analysis. The use of surface-active reagent increases the solubility of PAN has been reported earlier [20-23]. Derivative mode spectrophotometry is recently shown to be more useful than classical spectrophotometry for solving several analytical problems [24]. 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 [25, 26]. 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. The Co (II) forms the coloured complexes with APDC, I-nitroso-2-naphthol, bromopyrogallol red, xanthate and DDTC [27].

In the present work, results of the determination of Co(II) as PAN complexes, in a non-ionic surfactant Tween 80 using first derivative mode spectrophotometric method is reported. The method is successfully applied for the determination of Co (II) in pharmaceutical samples.

Results and Discussion

Fig. 1 shows absorption spectra of 1-(2 pyridylazo)-2-naphthol (PAN) at 450 nm and Co (II)-$(PAN)_2$ complex at 460 nm (i.e. a shift from 580 nm) in first derivative mode spectroscopy. The derivative spectra show a sharp cross-over point at 460 nm, corresponding to the submerged peak of the complex in the zero-order spectrum. It can be seen in the Fig.

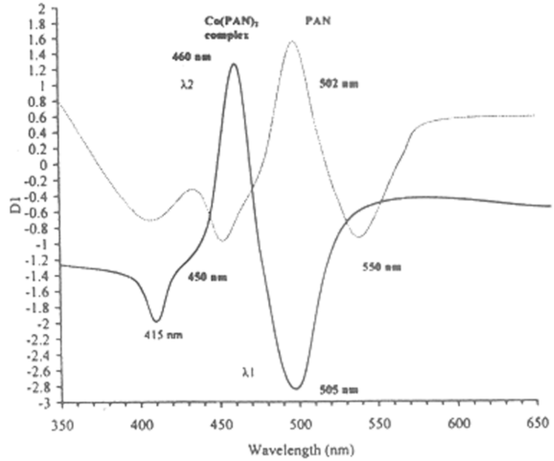

Fig. 1. First derivative mode absorption spectra of PAN and Co (II)-PAN complex in 5 % Tween 80 at pH 5.

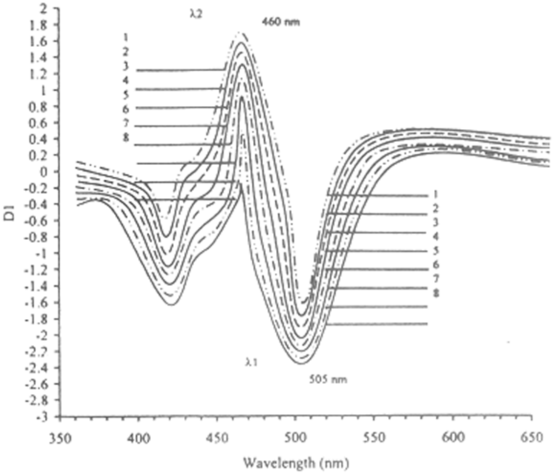

Fig. 2. First derivative mode absorption spectra of Co (II)-PAN complex with increasing conc. (1-8) in 5 % Tween 80 at pH 5. Co (II) conc. 3.1, 6.3, 12.5, 25.0, 43.8, 62.6, 125.2 and 250 ngmL^{-1}.

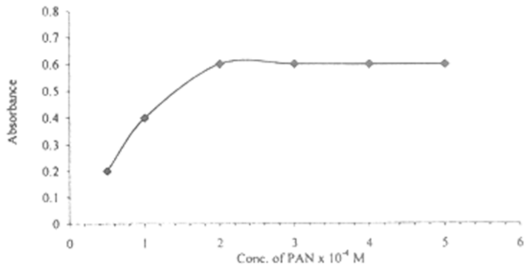

Fig. 3 Effect of PAN conc.on the absorbance of Co (II) PAN complex.

1 the height of the peak at 460 nm (TD) and the depth of the trough at 505 nm were linearly related to the metal ion concentration. It can be seen that the first derivative spectra are more resolved than those obtained for the normal mode. 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; other close peaks are changed from normal mode wavelength to new ones 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. PAN 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 80 solution was above (0.0013 %, w/v) concentration [28]. Fig. 2 shows the first derivative spectra of Co (II)-$(PAN)_2$ complex at 460 nm with increasing concentration of cobalt (II). Fig. 3 shows effect of varying concentration of PAN, increase absorption from 2×10^{-4} M in presence of constant Co (II) concentration. Fig. 4 shows the optimum pH for Co (II) is 5.0.

Fig. 5 shows the calibration graph of Co (II)-$(PAN)_2$ complex in first derivative spectroscopy in the range of 1.7-225 ng ml^{-1} at 460 nm. The detection limit is lowered significantly from normal mode 6.7 to 1.7 ng ml^{-1}, which is the great success of the present method. Comparison of detection limit of the present method with other sensitive methods is given in Table-1.

Table-1: Comparison of sensitivities of various methods

Present method	Fluorimetric Method [Ref. 30]	Spectroscopic method [31]	AAS method [32]	Electrothermal atomization-AAS method [33]	FAAS method [34]	(ICP-AES) method [35-37]
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

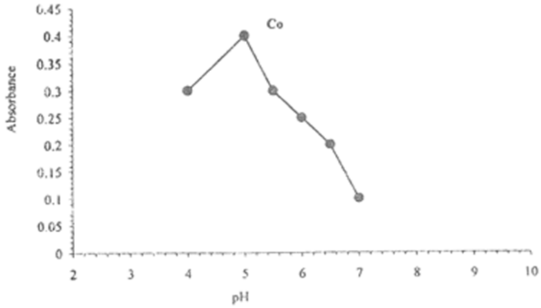

Fig. 4 Effect of pH on the absorbance of Co (II)-PAN complex.

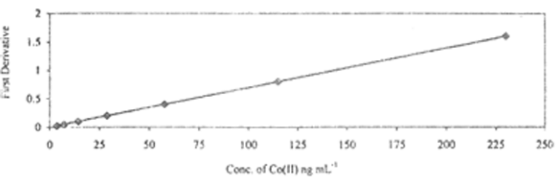

Fig. 5 Calibration graph for Co (II)-PAN complex in 5 % Tween 80 at pH 5 in first derivative spectroscopy mode.

All other experimental conditions are same as in normal mode molar absorptivity, Co (II) 0.87 × (10^4 mol^{-1} cm^{-1}), Sandell's sensitivity (6.8 ng cm^{-2}) and Beer's law linear range in normal mode is 0.5-4.0 μg ml^{-1} already given in Table-2

Composition of the complex formed under experimental conditions was investigated by Job's method of continuous variations. Composition of the complex formed under experimental conditions was investigated by Job's method of continuous variations. From Fig. 6 it can be inferred that metal: ligand ratio is 1:2.

Study of interferences by foreign ions

Interferences in the determination of Co (II) with 1-(2 pyridylazo)-2-naphthol in presence of 5 % Tween 80 were studied and the results are shown in the Table-2. The criterion for the studies was a ± 4.0 % change in absorbance for 2.0 μg ml^{-1}of metal (II) in final 10 ml solution. The amount of foreign ion tolerated (i.e which changes absorbance by ≤ ± 4.0 %) is given in the Table-2; cations of Fe, Cd, Hg, Mn and Zn interfere. As has been reported, the complexation reaction between metal (II) and PAN is completely masked by EDTA and cyanate at low concentration, whereas ascorbic acid, Br$^-$, Cl$^-$, I$^-$, and SCN$^-$ do so at relatively higher concentrations. As the iron (II) chelate is unstable, furthermore, no suitable masking reagents were found for iron (II), while iron (III) can be eliminated by the addition of ammonium

Table-2: Analytical characteristics of Co (II)-1-(2 pyridylazo)-2-naphthol complex in Tween 80 in normal mode spectroscopy

Characteristics	Co(II)
Beer's law range (μgml^{-1})	0.5-4.0
Absorption maxima (λ_{max}, nm): (a) micellar	580
(b) $CHCl_3$	590
Molar absorptivity ε_{max} × (10^4 mol^{-1} cm^{-1})	0.87
Sandell's scale sensitivity (ngcm^{-2})	6.8
Detection limit (ng ml^{-1})	6.7
pH	5
RSD ±	0.04

At 95%, n= 6

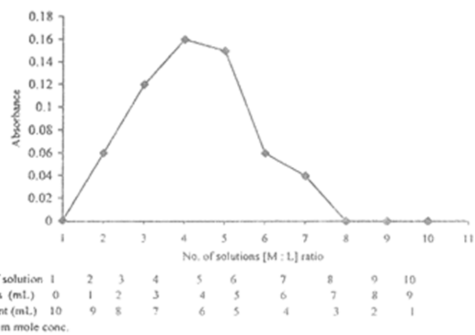

Fig. 6 Job's plot of metal : ligand ratio.

oxalate or citrate before colour development. Alkali and alkaline-earth metal ions donot interfere. Though, masking agents such as citrate, phosphate, fluoride and thiocyanate are generally useful to overcome interference due to cations, only citrate is found suitable in the present case, presence of 1.0×10^{-3} M of citrate enhances the tolerance limits of Fe (III), and Pb (II) from 100, and 500 μg to ≥ 500 and 1000 μg respectively. The interference due to absorption by Hg and Ni (II)-PAN complexes in normal mode is thus removed by the first derivative spectra which are more resolved than those obtained for the normal mode.

Table-3: Tolerance limits (μg ml^{-1}) for interference's of metal ions and salts with 1-(2 pyridylazo)-2-naphthol in Tween 80 in normal mode spectroscopy.

Ion / salt	Co(II)	Remark
Chlorides	200	
Iodide	200	
Ascorbate	400	
Cyanate	100	c
Bromide	200	
Borate	200	
KSCN	1000	
NaF	600	
$Na_2C_2O_4$	200	
$KClO_3$	1000	
Na_2tartarate	1500	
EDTA	100	c
Acetate	600	
Na_2citrate	500	
KCN	500	b
Mg(II)	3000	
Al(III)	300	
Cd(II)	100	
Co(II)	-	
Cr(III)	50	
Cr(VI)	8	
Fe(III)	100	a, b
Mn(II)	100	b
Ni(II)	100	b
Pb(II)	500	a
Zn(II)	100	b
Hg(II)	100	b
Fe(II)	100	b
Cu(II)	100	

a masked by citrate,
b interferences strongly,
c masked the complexation between Co (II) and PAN.
The concentration of metal ions is 2.0 μg ml^{-1}

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-4.

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

Application

The proposed spectrophotometric method was applied to the determination of Co (II), in pharmaceutical samples. Results are shown in Table-5.

Table-5: Determination of Co (II) ion in pharmaceutical sample

Sample	Cobalt determined (μg /tab)	
Theragran-M tablet	Present method	AAS method
(Bristol-Myers Squibb Pak.)	39.0	39.1
(39.0 μg /tab)	(0.4)	(1.4)
Neurobion (Inj) Merck	21.70	21.70
71.24 μg ml^{-1}	(0.8)	(2.5)
Certied value		

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

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.

Reagents

All chemicals used were analytical grade reagents (E. Merck and Fluka A.G) unless otherwise stated. Standard Co (II) stock solutions of (100 μg ml^{-1}) were prepared dissolving their nitrate salts. Other metal ions solutions were prepared from their nitrate or chloride salts. 5% Tween 80 solution was prepared by dissolving it in a 100 ml volumetric flask, and was diluting to the mark with double distilled water. Buffer solution of pH 5 was prepared by taking 0.2 M sodium acetate (35.2 ml) and 0.2 M acetic acid (14.8 ml) mixtures and adjusting the volume to 100 ml according to Perrin and Dempsey [29].

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 PAN-Co (II) complex.

Two sets of solutions, one containing 3.0 μg ml^{-1} metal ion and other without it, and each containing fixed amount of the reagent (2×10^{-4} M) and Tween 80 (5 %) in the pH range 4.0 -7.0, 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 PAN-Co (II) complex, a set of solutions containing increasing amounts of Tween 80 (2%-10%), and 4.0 μg ml^{-1} Co (II) and 2×10^{-4} M PAN, at the pH of the maxi-mum complex formation, was prepared.

Effect of varying ligand concentration on the absorbance of the system was investigated by preparing a set of solutions containing 8×10^{-6} to 2×10^{-4} M of the reagent at the optimum pH.

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 (1.0-215 ng ml^{-1} and 0.06 to 4.0 μg ml^{-1}) 2×10^{-4} M PAN, and 5 % Tween 80 at pH 5 condition of maximum complex formation.

Spectrophotometric metal ion determination in micellar solution.

Appropriate volumes of stock solutions of metal ions, 1-(2 pyridylazo)-2-naphthol, and surfacetant Tween 80 were added and made up to 25 ml volume with distilled water having metal ions concentration of 1.0 - 215 ng ml^{-1} and 0.06 to 4.0 μg ml^{-1}, PAN 2×10^{-4} M and 5 % Tween 80. Absorption spectra were recorded against reagent as reference to generate analytical calibration curves in normal mode (λ_{max} 580 nm) or in first derivative mode (peak height (pH) at 460 nm) or (trough depth (TD) at 505 nm). Cobalt content of the standard and the sample was determined using AAS equiped with an air acetylene flame. The pH and wavelength used are listed in Table-2.

The determination of Co (II) in pharmaceutical samples.

(a) Pharmaceutical sample

A tablet of Theragran-M (Bristol-Myers Squibb, Pak) was transferred to a crucible to which it 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 μg cobalt (II), and then determined by proposed method and by AAS (Table-1).

(b) Pharmaceutical sample

(i) A sample, each of injectable Neurobion (Merck Pakistan) was digested with nitric acid in a covered beaker. The residue of the sample was leached with dilute sulfuric acid and diluted to the mark in a calibrated flask. Working solutions were prepared by taking an appropriate amount of the sample. Appropriate amounts of surfactant and sodium isoamylxanthate were added to a 25 ml calibrated flask to obtain final concentration of 1 % SDS, and 0.5 % sodium isoamylxanthate. Then 5 ml of the sample was added and the absorbance was measured against a reagent blank prepared under the same conditions. Cobalt content determined by proposed method and by AAS (Table-4).

Conclusions

Determination of trace amount of Co (II) up to 1.70 ng ml^{-1} can be carried out directly using 1-(2 pyridylazo)-2-naphthol, in non-ionic micellar media of 5 % Tween 80 in aqueous solutions. The method is simple and rapid with greater sensitivity, better selectivity, and improved precision and replaces extraction with toxic organic solvents. Co (II) content in pharmaceutical samples determined by the present method is in agreement with the values obtained by atomic absorption spectroscopy.

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