Spectrophotometric Determination of Cobalt (II) as Complexes with Bromopyrogallol red in Micellar Media of Tween 80

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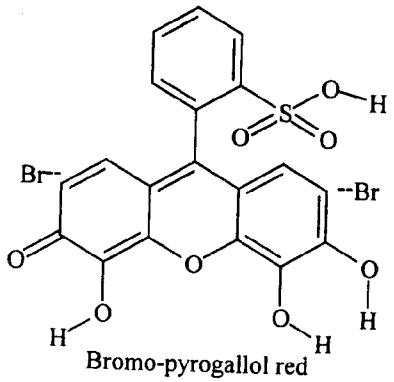
(Received 28th April, 2004, revised 28th July 2004)

Summary: Cobalt (II) was determined spectrophotometrically with bromopyrogallol red as complexing reagent in aqueous phase in presence of a non-ionic surfactant Tween 80. Beer's law is obeyed, over the concentration range 0.25-4.0 μg mL^{-1} with the detection limit of 1.0 ng mL^{-1}. Validation of this method has been made by comparing the results with those obtained by flame Atomic Absorption Spectroscopy; no significant difference was noted between the two methods at 95% confidence interval. The method is simple, accurate and economical and has been applied for the determination of cobalt (II) in pharmaceutical samples.

Introduction

In chemical analysis, metal chelation followed by solvent extraction and spectrophotometric detection is the preferred mode of analysis for a number of metal ions due to rapidity, simplicity and wide applications [1-2]. However, during last decade several spectrophotometric methods have been developed in which the solvent extraction step is conveniently replaced by the use of a surfactant [3-4]. 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 [5-12]. Micellar media is mainly used to enhance the absorption sensitivities, thus simplifying the system by replacing the use of toxic organic solvent for extraction. The bromopyrogallol red is used as chelating agent in the determination of metal ions by spectroscopy. However bromopyrogallol red metal complexes are water insoluble and therefore a solvent extraction with either chloroform or carbon tetrachloride is required. Xirong *et al.*, [13, 14] reported a spectrophotometric determination of Mo (VI), W (V) and Sb (III) as complexes of bromopyrogallol red in aqueous media using anionic, cationic and non-ionic surfactant respectively. The determination of copper (II), cobalt (II) and nickel (II) as M (II)-ammonium pyrrolidinedithiocarbamate complex in micellar media has been reported recently [15]. Bromopyrogallol red has a hydrogen atom of hydroxyl group that is replaceable by a metal, and oxygen atom, which forms stable complexes with several metal ions.

In the present work, a spectrophotometric determination of Co (II) as their bromopyrogallol red complexes in micellar aqueous solution of surfactant Tween 80 is described. The method was successfully applied for the determination of Co (II) ions in pharmaceutical samples.



Bromo-pyrogallol red

Results and Discussion

Fig. 1 shows the absorption spectra of reagent bromopyrogallol red at 431 nm, (b) absorption spectra of Co (II)-bromopyrogallol red complex at 388 nm. The optimized reagent concentration 0.01 % was used throughout the complex study. The surfactant of concentration 5 % Tween 80 was used throughout the metal-complex formation. The absorption maxima were obtained at optimized pH of 2.0 for Co (II) ion. Fig. 2 shows a calibration graph of Co (II)-bromopyrogallol red complex obtained by plotting absorption maxima against varying concentration of this metal ion. The Beer's law holds in the range 0.25-4.0 μgmL^{-1}. The complex was stable for at least 2 hours. Molar absorptivity and Sandells'

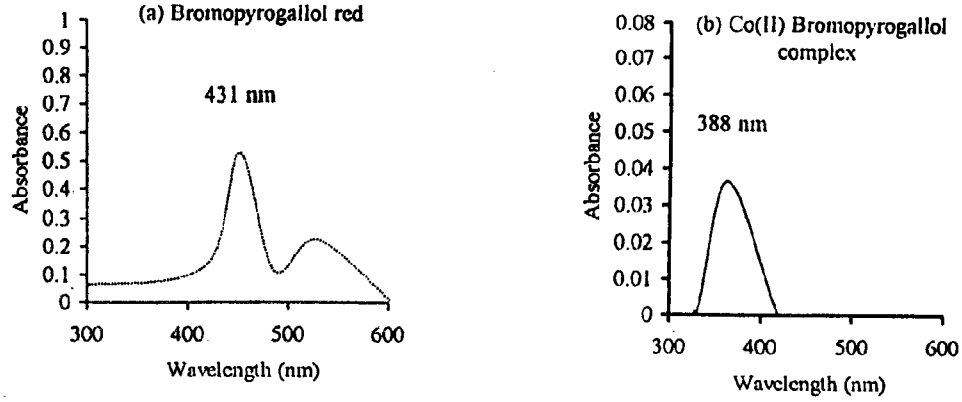


Fig. 1: Absorption spectra of (a) Bromopyrogallol red (b) Co (II)-bromopyrogallol red complex in micellar solution of 5% Tween 80.

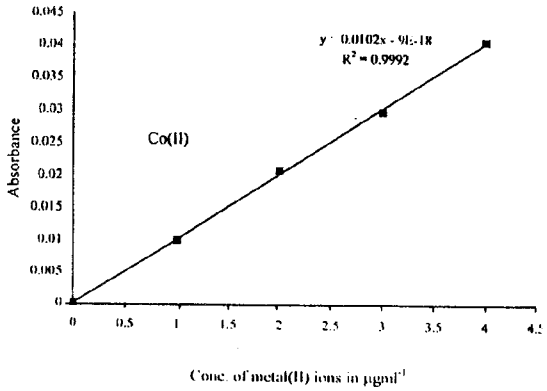


Fig. 2: Calibration graph of Co (II)-bromopyrogallol complex in 5% Tween 80.

sensitivity of Co (II)-bromopyrogallol red complex is ε_{max} ($\times 10^4$ $mol^{-1}cm^{-1}$) 0.06; 9.9 ng cm^{-2}. All other analytical parameters such as, wavelength, surfactant, reagent concentration are given in Table-1.

Detection limit

Detection limit was found to be 1.0 ng mL^{-1} using the present method. There is a slight improvement as compared to the method reported by Xirong Huang *et al.*, [14].

Interference

As we can see from Table-2 interferences of metal ions of Zr (IV), Sn (IV), Ti (IV), Bi (III), V (V), Mo and Sn (II) were serious. The interference was removed using EDTA and ascorbic acid as masking agents.

Table-1: Analytical characteristics of Co (II)-bromopyrogallol red complex in Tween 80

Characteristics	Co(II)
Beer's law range (μgmL^{-1})	0.25 - 4.0
Absorption maxima (λ_{max} nm):in micellar	388
Molar absorptivity in micellar $\times (10^4$ $mol^{-1}cm^{-1})$	0.06
Sandell's sensitivity ($ngcm^{-2}$)	9.9
Detection limit ($ngcm^{-1}$)	1.0
pH	2.0
5 % Tween 80 used in mL	3.0
0.01% Bromopyrogallol red used in mL	2 .0
RSD ±	0.03

At 95 % confidence limit, * n = 6

Table- 2: Effects of foreign ions on the determination of 5 µg of Co (II)

Foreign metal ions	Tolerance Limits μgmL^{-1}	Foreign non metal ions (0.01 M)	Tolerance limits (mL)
As(III) Cr(III) Ni(II)	>100	Nitrite	1.0
Ca(II) Mg(II)	>100	Silicate	1.0
Cu(11) Pb(II)	80	Phosphate	1.0
Mn (II)	60	Oxalate	0.25
Zn(II) Al(III)	40	Citrate	0.5
Sb(V) Fe(II)	20	Flouride	>2.5
Sn (IV) Cr(VI) Fe(III)	10	Ascorbate	>2.5
Zr (IV)Sn(11) Ti (IV)	4	EDTA	>2.5
V (V)	2		
Sb(III)	1		

With a relative error being less than ± 5 %

Composition

Composition of the complex formed under experimental conditions was investigated by Job's method of continuous variations. From Fig. 3 it can be inferred that metal: ligand ratio in the complex is 1:2 (M: L). Plot of absorbance versus mole fraction

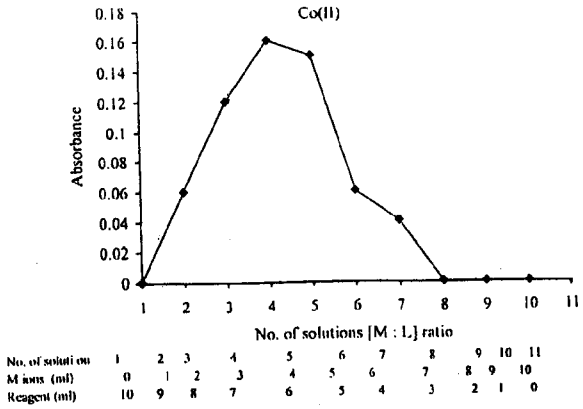


Fig. 3: Job's plot of metal : ligand ratio.

Table-3: Percent recovery of known amount of Co (II) ions added to tap water.

Metal ions	Amount added ($\mu g\ mL^{-1}$)	Amount found ($\mu g\ mL^{-1}$)	Recovery (%)
Co(II)	1.0	0.98	98 ± 2

At 95 %, n = 6

Table- 4: Determination of Co (II) ions in drug samples

Sample	Amount of Co (II) determined (ppm)		
	Certified value	Present method	AAS method
Neurobion (Inj) Merck	21.74	21.70 ± 0.06	21.70

At 95 %, n = 6

of the metal ion shows maximum which corresponds to 1:2 (M: L) ratio in the complex.

Validation of method

Proposed method was verified by standard addition method and the results were compared with AAS, which are in good agreement as given in Table-4.

Application

The proposed spectrophotometric method was applied for the determination of Co (II) in pharmaceutical samples. Results are shown in Table-4.

Experimental

All chemicals used were analytical grade reagents (Merck and Fluka A.G) unless otherwise stated. Standard stock solutions of (100 μgmL^{-1}) of Co (II) were prepared using their nitrate salts. The bromopyrogallol red solutions were freshly prepared in distilled water. Tween 80 5% was prepared by dissolving, 5 g dissolved in a 100 mL volumetric flask and diluting to the mark with double distilled water. The buffer solution was prepared using 0.2 M KCl (25 mL) and 0.2 M HCl (6.5 mL) and adjusting the volume to 100 mL according to Perrin and Dempsey [16]. The pH was obtained as 2.

Apparatus

A UV / Vis Spectrometer Perkin Elmer model Lambda 2 was used throughout this study. Atomic absorption spectrometer model Spectra AA. 20 Varian was used for metal ion determination. The Pye Model 292 pH meter was used.

Spectrophotometric metal ion determination in micellar solution

Appropriate volumes of stock solutions of metal ions, bromopyrogallol red, and surfactant Tween 80 were added to a series of 25 mL calibrated flasks and made up to volume with distilled water. The following concentration ranges of Co (II) ions 0.06-10$\mu g\ mL^{-1}$, concentration of bromopyrogallol red 0.01 % and 5 % Tween 80 optimized value of were used. The surfactant concentration, pH values and analytical wavelength used are listed in Table-1.

Spectrophotometric metal ion determination after extraction with CCl_4

The volumes of stock metal, buffers and bromopyrogallol red solutions were placed into a separating funnel and 10 mL of CCl_4 was added. The organic layer was transferred to a 25 mL volumetric flask. In order to obtain complete extraction, the process was repeated twice with 10 mL and then once with 5.0 mL of CCl_4. For the 25.0 mL total volume of the organic layer, the absorbance was measu-red at the appropriate wavelength for metal ions.

Determination of Co (II) in pharmaceutical samples

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 and its cobalt content were determined by proposed method and by atomic absorption spectroscopy (Table-4).

Conclusions

Determination of trace amount of Co (II) is carried out directly using bromopyrogallol red in nonionic micellar media of Tween 80 in aqueous solutions. 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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