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DETERMINATION OF COBALT(II) AND NICKEL(II) WITH ISOAMYLXANTHATE AS A COMPLEXING REAGENT IN MICELLAR MEDIA

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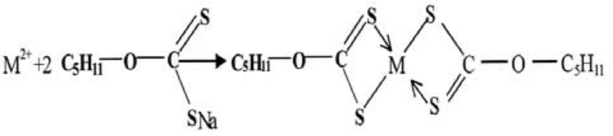
Cobalt(II) and nickel(II) were determined spectrophtometrically using sodium isoamylxanthate as a complexing reagent in aqueous phase in the presence of anionic surfactant sodium dodecylsulphate (SDS). Beer's law was obeyed for Co(**I**I) and Ni(II) over the concentration range 3.0-35 and 2.0-37 μgmL^{-1} respectively. The λ_{max}, molar absorptivity and Sandell's sensitivity of Co(**I**I) and Ni(II) were 360 nm and 416 nm; ε is 0.19 and 0.2 ($\times 10^4 mol^{-1}cm^{-1}$) 31.1 and 29.3 ng cm^{-2} respectively. Maximum absorbance at 1:2 (M: L) molar ratio suggested the formation of $M(C_6H_{11}OS_2)_2$ where M = Co(II) and Ni(II). The complex remained stable for more than 2 h. The optimized reagent concentration 0.5 % was used throughout the study. Surfactant concentration of 1.0 % SDS caused significant enhancement in absorbance. Maximum absorption was observed at 360 nm and 416 nm for Co and Ni complexes, respectively. The absorption maxima were obtained at optimized pH of 7.0. Validation of method has been made by comparing the results with Atomic Absorption Spectrometry; no significant difference was obtained between the two methods at 95 % confidence interval. The method is simple, accurate, economical and has been applied to the determination of cobalt(II) and nickel(II) in industrial wastewater, pharmaceutical and edible oil samples.

Keywords: Anionic, Micelle, SDS, M(II), Isoamylxanthate complex, Spectrophotometry

1. Introduction

For the determination of trace elements in biological, industrial and environmental materials at low concentration, there is a need for the development of more rapid and sensitive analytical methods. Metal chelation followed by solvent extraction and spectrophotometric detection is the preferred mode of analysis for a number of metal ions [1-2]. However, during the 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 [5-11]. Micellar media is mainly used to enhance the absorption sensitivities, thus simplifying the system by replacing the use of toxic organic solvent for extraction.

Thio compounds are highly sensitive to colour reactions, stability and selectivity towards various metal ions [12-13]. Xanthate have $-CS_2$ group which makes them more reactive towards various metals and is used as chelating agents in the determination of metal ions by spectroscopy since long. However, sodium isoamylxanthate metal complexes are water insoluble and therefore, a solvent extraction with either chloroform or carbon tetrachloride is required. Atamjyot et al. [14] reported spectrophotometric determination of metal ions as complexes of isoamylxanthate in aqueous media using nonionic, anionic and a cationic surfactants respectively. The determination of metal complexes of 1-(2-pyridylazo)-2-naphthol complex in micellar media has been reported recently [15-19]. Sodium isoamylxanthate forms stable complexes with several metal ions, a typical reaction is shown below:



In the present work, a spectrophtometric determination of Co(II) and Ni(II) as their isoamylxanthate complexes in micellar aqueous solution of sodium dodecylsulphate (SDS) is described. The method was successfully applied to the determination of these metal ions in industrial wastewater, pharmaceutical and edible oil samples.

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2. Experimental

2.1. Reagents

All chemicals used were of analytical grade reagents (Merck and Fluka) unless otherwise stated. Standard Co(II) and Ni(II) stock solutions of (100 μgmL^{-1}) were prepared by dissolving their nitrates of 0.493 and 0.494 g / L respectively. Other metal ion solutions were prepared from their nitrate or chloride salts. SDS (1.0 %) solution was prepared by dissolving 1.0 g of SDS in a 100 mL volumetric flask and diluting to the mark with double distilled water. Stock solution of 0.5 % of sodium isoamylxanthate reagent was prepared. The buffer solution of pH 7 was prepared by taking 0.1M KH_2PO_4 (50 mL) and 0.1M NaOH (29.1 mL) mixture and adjusting the volume to 100 mL according to Perrin and Dempsey [20].

2.2. Apparatus

A UV / Vis Spectrophotometer Super Aquarius Cecil CE 9500 was used throughout this study. Atomic absorption Spectrometer, Analyst 100 Perkin Elmer was used for metal ion determination. FTIR Spectrum One Perkin Elmer was used for IR study. The Sension 156 multimeter HACH was used for pH study.

2.3. Synthesis of reagent sodium isoamylxanthate

Stoichiometric quantities of (1:1:1) of isoamyl alcohol (1M), sodium hydroxide (1M) and carbon disulphide (1M) were used. Isoamyl alcohol (22mL) was taken in a 200 mL beaker and kept in an ice-salt mixture. Saturated solution of sodium hydroxide (8g) in water was added while stirring and carbon disulphide (12 mL) was added gradually with vigorous shaking for about 40 minutes and the xanthate formed was filtered by suction through a sintered funnel. Sodium isoamylxanthate was dissolved in acetone, and filtered. Benzene was added to the filtrate slowly, while stirring. The precipitate formed was filtered by suction. The product was recrystallised by dissolving again in acetone and petroleum ether (b.p. 40-60 ^{o}C) was added to obtain precipitates, which were filtered and transferred to a vacuum dessicator and dried for 24 hours. The purity of the reagent prepared (sodium isoamylxanthate) was checked by FTIR and compared with reference reagent (sodium isoamylxanthate) 95 % purity was observed. A 0.5% solution of sodium isoamylxanthate was prepared in distilled water and standardized titrimetrically [21] using mercuric acetate as a titrant and diphenylcarbazone as an indicator.

3. Procedure

3.1 Spectrophotometric metal ion determination in micellar solution

Appropriate volumes of stock solutions of metal ions**,** sodium isoamylxanthate and surfactant SDS 1.0 % were added and made upto 25 mL volume with distilled water, having metal ions concentration 2-38 μgmL^{-1}, sodium isoamylxanthate 0.5 % and SDS surfactant 1.0 %. The pH values and analytical wavelength used are listed in Table 1.

Table1. Analytical characteristics of metal(II)-isoamylxanthate complexes in presence of SDS.

Characteristics	Co(II)	Ni(II)
Beer's law range (μgmL^{-1})	3.0-35	2.0-37
Absorption maxima (λ_{max}, nm): (a) micellar (b) CCl_4	 360 355	 416 412
Molar absorptivity in micellar × (10^4 mol^{-1} cm^{-1})	0.19	0.2
Molar absorptivity in CCl_4 × (10^4 mol^{-1} cm^{-1})	0.18	0.19
Sandell's sensitivity (ngcm^{-2})	31.1	29.4
Detection limit (ngmL^{-1})	31.01	29.3
pH	7	7
Surfactant	SDS	SDS
0.5% reagent (mL)	0.5	2
RSD ±	0.3	0.2

At 95 %, n = 6.

3.2. Spectrophotometric metal ion determination in CCl_4

Appropriate volumes of stock metal ions, sodium isoamylxanthate and aqueous buffer solutions were placed in 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, absorbance was measured at the 355 nm and 412 nm wavelength for metal ions. Applications for the validation of method are given in Table 3.

3.3. The industrial waste water

Industrial waste water sample, 1L obtained from industrial effluent collected from Sukkur site area was filtered using Whatman filter paper. Concentrated HNO_3 4.0mL and 30% H_2O_2 2mL were added to the filtrate. The resulting solution was preconcentrated in an oven at 110 °C to a final volume of 25mL. Appropriate amounts of surfactant and sodium isoamylxanthate were added to a 25mL calibrated flask to obtain final concentration of 1.0 % 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. The same sample, 5.0 mL was diluted to 25 mL with double distilled water for AAS analysis [22].

3.4. Pharmaceutical sample

A sample, each of injectable Neurobion (Merck, Pakistan) was digested with HNO_3 in a covered beaker. The residue of the sample was leached with dilute H_2SO_4 and diluted to the mark in a calibrated flask. Working solutions were prepared by taking an appropriate amounts of the samples. Appropriate amounts of surfactant and sodium isoamylxanthate were added to a 25 mL calibrated flask to obtain final concentration of 1.0 % 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 [23]. Cobalt content was determined by proposed method and by AAS (Table 3).

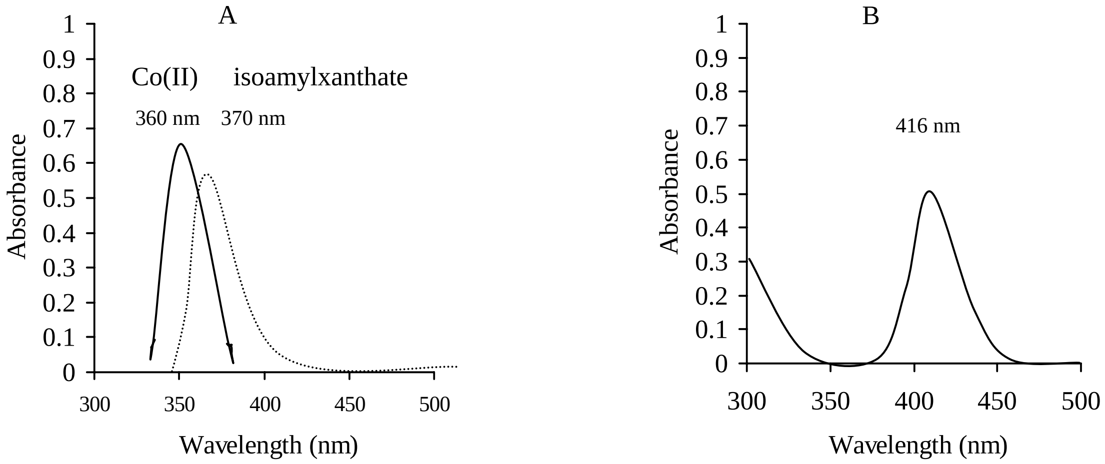
A tablet of Theragran-M (Bristol-Myers Squibb, Pak) was transferred to a crucible to which was added 0.5 g potassium bisulphate dissolved in 2.0 mL water, 6.0 mL HCl (37 %) and 3.0 mL HNO_3 (65 %). The mixture was heated on flame. The white powder obtained was dissolved in 25 mL water. Working solutions were adjusted to 10 mL solution for analysis of cobalt, spiked with 20 μg Co(II) and then determined by proposed method and by AAS (Table 3).

3.5. Determination of nickel in edible oils

A 4.0-20 g of the oil sample (vegetable oil) depending on the nickel content was taken in a beaker and decomposed with concentrated HNO_3. The dried sample was heated in a muffle furnace at 600 °C for 1h and then allowed to cool. After the addition of a few drops of concentrated HNO_3, it was dried and again heated to 700 °C for I h. The ash was dissolved in concentrated HCl and diluted with a small amount of distilled water and filtered, and the final volume was increased to 10 mL in a standard flask. Appropriate amounts of surfactant and sodium isoamylxanthate were added to a 25 mL calibrated flask to obtain final concentration of 1.0 % SDS, and 0.5 % sodium isoamylxanthate. Then, 5.0 mL of the sample was added and the absorbance was measured against a reagent blank prepared under the same conditions [24]. The same sample, 5.0 mL was diluted to 25 mL with double distilled water for AAS analysis (Table 3).

4. Results and Discussion

Fig.1(A) shows the spectra of isoamylxanthate, the absorption maxima is at 370 nm, and of a Co(II)-isoamylxanthate complex with absorbance maxima at 360 nm with greenish yellow colour, (B) Ni(II)- isoamylxanthate complex with an absorbance maxima at 416 nm with yellowish colour. Composition of the complex formed under experimental conditions was investigated by Job's method of continuous variations. Maximum absorbance at a 1:2 (M: L) molar ratio suggested the formation of $M(C_6H_{11}OS_2)_2$ complexes where M = Co(II) and Ni(II). The complex remained stable for more than 2 h. Reagent concentration optimized 0.5 % was used throughout the study. Surfactant concentration 1.0 % SDS yields enhancement in absorbance 360 nm and 416 nm and was used for maximum absorption of Co, and Ni complexes. The absorption maxima were obtained at optimized pH of 7.0 for the metal ions. Fig. 2 shows calibration graphs of Co(II)- and Ni(II)-isoamylxanthate complexes obtained by plotting absorption maxima against varying concentration of these metal complexes. Beer's law was obeyed in the concentration over the range to 3.0-35 $\mu gmL^{-1}$and 2.0-37 μgmL^{-1}, respectively for Co(II)- and Ni (II)-isoamylxanthate complexes. Molar absorptivity and Sandell's sensitivity of Co(II) and Ni(II)-isoamylxanthate complex is ε_{max} ($\times 10^4$ $mol^{-1}cm^{-1}$) 0.19 and 0.2; and 31.1 and 29.3 $ngcm^{-2}$, which shows slightly improvement than solvent extraction method. All other analytical parameters as detection limit, surfactant and reagent concentration are given in Table 1.



CECIL CE 9500

Time : 18:46 12/05/08
Wavelength : 400.0 nm
Speed : 5 nm/s
Averaging : 1.0 nm
Bandwidth : 2.0 nm
Operator : G.A.Soomro
Reference : isoamylxanthate
Sample : Co-isoamylxanthate

CECIL CE 9500

Time: 18:50 12/05/08
Wavelength: 400.0 nm
Speed: 5 nm/s
Averaging: 1.0 nm
Bandwidth: 2.0 nm
Operator: G.A. Soomro
Reference: isoamylxanthate
Sample: Ni-isoamylxanthate

Figure 1. Absorption spectra of isoamylxanthate.(A) Dotted lines isoamylxanthate, permanent lines Co(II)-isoamylxanthate complex (B) Ni(II)-isoamylxanthate complex.

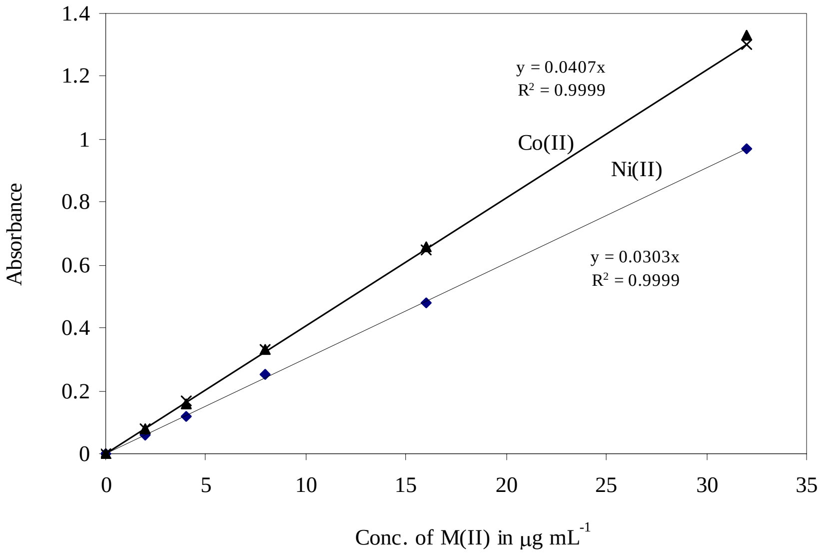


Figure 2. Calibration graph of metal (II) isoamylxanthate complexes in 1%.

4.1. Interferences

The interferences of foreign ions on the determination of metal ions were studied to test the effect of diverse ions, Co(II) (20 µgmL^{-1}) and Ni(II) (37µgmL^{-1}) were determined, in presence of foreign ions. Each of these metal ions can be determined without any interference in the presence of a 50 fold excess of the following cations: Al(III), Bi(III), Ba (II), Cu(II), Pd(II), Cd (II), Cr(II), Mg(II), Mn(II), Pb(II), Sr(II), Rh(III), Zr(IV) and Zn(II). Amongst the anions (amount in mg shown in parenthesis), the following anions did not interfere: acetate (100), sulphate (70), thiosulphate (20) metabisulphite (30), citrate (90), bromide (70), thiocyanate (100), fluoride (95), and chloride ions (95). Iron (II,III) (50 fold in excess) in determination of metal ions was masked with 2.0 mL of 5 % sodium fluoride. EDTA interfered strongly in the determination of these metal ions due to its ability to form stronger complexes than isoamylxanthate.

Table 2. Percent recovery of known amount of metal ions added to tap water.

Metal ions	Amount added (µg mL^{-1})	Amount found (µg mL^{-1})	Recovery (%)
Co(II)	1.0	0.99	99 ± 1
Ni(II)	0.5	0.49	98 ± 1

At 95 %, n = 6

Table 3. Determination of Co(II) and Ni(II) ions in industrial wastewater, drug and edible oils samples.

Sample	Metal ions determined	
Neurobion (Inj) Merck 21.74 µgmL^{-1}) Certified	Proposed method Co(II) (µgmL^{-1})	AAS method Co(II) (µgmL^{-1})
	21.70 (0.3)	21.70 (.03)
Theragran-M Pak.) (µg/tab)	39.0 (0.4)	39.1 (1.4)
Edible oil	Ni(II) (µg)	Ni(II) (µg)
	22.0 (0.3)	22.1 (0.2)
Industrial waste water (µgmL^{-1})	0.40 (0.3)	0.41(0.2)

At 95 %, n 6, c.v. is given in parenthesis.

4.2. 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 Tables 2 and 3.

5. Conclusions

Determination of trace amount of Co(II) and Ni(II) is carried out directly using sodium isoamylxanthate in anionic micellar media of (SDS) aqueous solutions. The method is simple and rapid with greater sensitivity, better selectivity, improved precision and replaces difficult step of extraction with toxic organic solvents. Co(II) and Ni(II) content in various matrixes can be determined by the proposed method.

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