Spectrophotometric Determination of Copper(II) and Palladium(II) Complexes with Isoamylxanthate in Micellar Media of SDS/Tween 80

[1]G. A. SHAR, [1]G. A. SOOMRO AND [2]M. I. BHANGER
[1]*Department of Chemistry*
Shah Abdul Latif University Khairpur, Sindh, Pakistan
[2]*Center of Excellence in Analytical Chemistry*
University of Sindh, Jamshoro, Pakistan

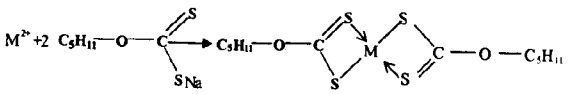
(Received 15th December, 2003, revised 24th Feburary, 2004)

Summary: Copper (II) and palladium (II) were determined spectrophotometrically with sodium isoamylxanthate as complexing reagent in aqueous phase in presence of anionic/nonionic surfactant SDS/ Tween 80. Beer's law was obeyed, for Cu(II) and Pd(II) over the range 2.0 - 30 and 2.0 - 38 μg ml^{-1} respectively. The λ_{max}, molar absorption, molar absorptivity and Sandell's sensitivity of Cu(II) and Pd(II) were 420 nm and 380 nm; ε_{max} = (× 10^4 mol^{-1} cm^{-1}) is 0.36 and 0.45 and 17.7 and 23.6 ng cm^{-2} respectively. Maximum absorbance at, 1:2 (M: L) mole ratio. The complex remained stable for more than 2 h. Reagent concentration optimized 0.5% was used throughout the study. Surfactant concentration 1% SDS yields higher enhancement in absorbance of Cu(II) and 5% Tween 80 was used for maximum absorption of Pd(II) complex. The absorption maxima were obtained at optimized pH of 7.0 for all metal ions. Validation of this method has been made by comparing the results with those obtained by flame AAS, no significant difference was observed in the two methods at 95% confidence interval. The method is simple, accurate, economical and has been applied to the determination of copper(II) and palladium(II) in industrial waste samples.

Introduction

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 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.

Thio compounds play a vital role in analytical chemistry due to highly sensitive colour reaction, stability and selectivity towards various metal ions [13-23]. Xanthate have $-CS_2$ group which makes them more reactive towards various metals and for long used as chelating agents in the determination of metal ions by spectroscopy. However sodium isoamylxanthate metal complexes are water insoluble and therefore a solvent extraction with either chloroform or carbon tetrachloride is required. Atamjyot. *et al.* and A.K. Malik *et al.* [24,25] reported a spectrophotometric determination of metal ions as complexes of isoamylxanthate in aqueous media using nonionic, anionic and a cationic surfactant respectively. The determination of metal complexes of 1-(2 pyridylazo)-2-naphthol complex in micellar media has been reported recently [26]. Sodium isoamylxanthate form stable complexes with several metal ions, a typical reaction is followed:



Proposed reaction of metal (II) with sodium isoamylxanthate to form metal (II) isoamylxanthate complex

In the present work, a spectrophotometric deter-mination of copper(II) and palladium(II) as their isoamylxanthate complexes in micellar aqueous solution of anionic/nonionic sodium dodecylsulphate (SDS) /Tween 80 is described. The method was successfully applied for the determination of these metal ions in industrial waste samples.

Results and Discussion

Fig. 1 (a) Shows the spectra of isoamylxanthate, the absorption maxima is at 360 nm and of a Cu(II)-isoamylxanthate complex with absorbance maxima at 420 nm with greenish colour, (b) Pd(II)-

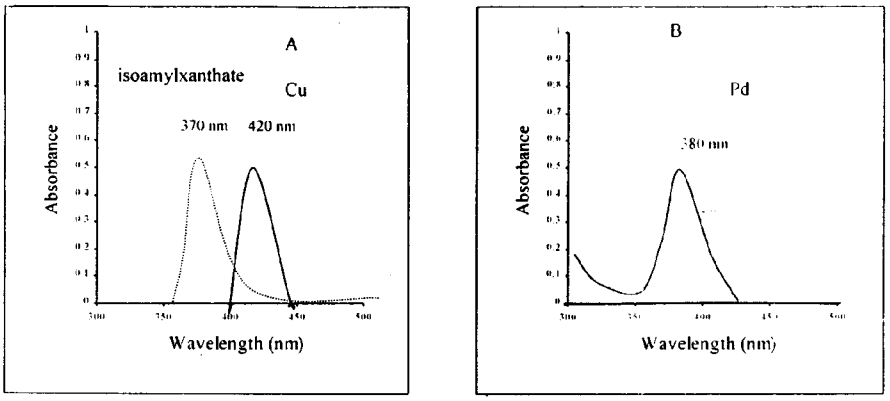


Fig. 1: Absorption spectra of metal (II) ions with isoamylxanthate in 1% (SDS)/5% Tween 80 (A) dotted lines for isoamylxanthate (0.5%), permanent lines for Cu(II-isoamylxanthate complex (B) Pd(II)-isoamylxanthate complex at (λ_{max} 390 nm).

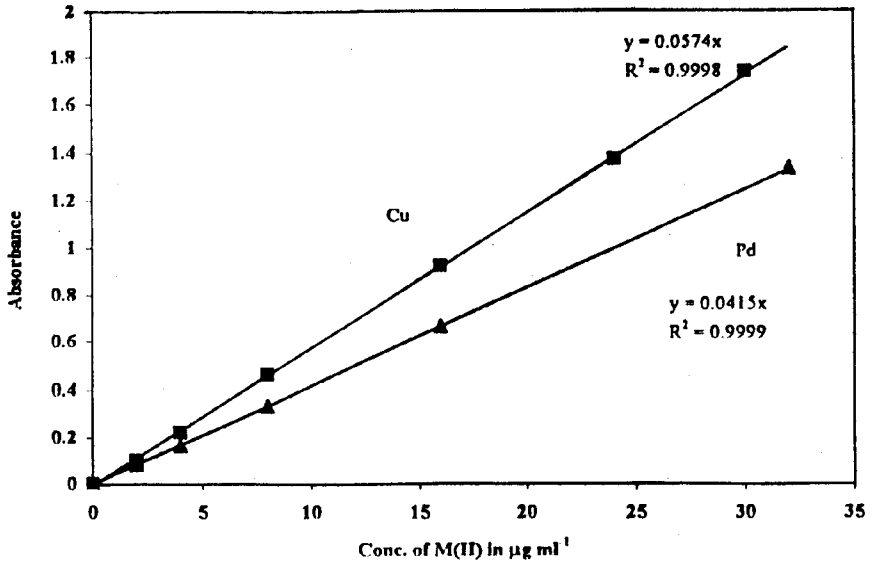


Fig. 2: Calibration graph of metal(II)-isoamyl-xanthate complexes in 1% SDS/5% Tween 80

isoamylxanthate complex with an absorbance maxima at 380 nm .

Composition of the complexes

Composition of the complexes was investigated by Job's method of continuous variations. Maximum absorbance at a 1:2 (M: L) mole ratio suggested the formation of $M(C_6H_{11}OS_2)_2$ where M = Cu(II) and Pd(II). The complex remained stable for more than 2 h. Reagent concentration optimized 0.5% was used throughout the study. Surfactant concentration 1% SDS yields higher enhancement in absorbance and was used for maximum absorption of Cu(II) and Pd(II) complex. The absorption maxima were obtained at optimized pH of 7.0 for all metal ions. Fig. 2 Shows a calibration graphs of Cu(II) and Pd(II)-isoamylxanthate complexes obtained by plotting absorption maxima against varying concentration of these metal complexes. Beer's law linear range was found to be 2.0 - 30 µg $ml^{-1}$and 2.0 - 38 µg ml^{-1} respectively for Cu(II) and Pd(II)-isoamyl-xanthate complexes. Molar absorptivity and Sandell's sensitivity of Cu(II) and Pd(II)-isoamyl-xanthate

complex is ε_{max} = ($\times 10^4$ $mol^{-1}cm^{-1}$) 0.36 and 0.45 and 17.1 and 23.6 ng cm^{-2}. All other analytical parameters such as detection limit, surfactant, and reagent concentrations are given in Table 1.

Table-1: Analytical characteristics of metal(II) isoamylxanthate complexes in presence of surfactants

Characteristics	Cu(II)	Pd(II)
Beer's law range (μgml^{-1})	2.0- 30	2.0- 38
Absorption maxima (λ_{max}, nm): in micellar	420	380
Molar absorptivity in micellar $\times (10^4$ mol^{-1} $cm^{-1})$	0.36	0.45
Sandell's sensitivity ($ngcm^{-2}$)	17.7	23.6
pH range	7	7
Surfactant used	SDS	Tween 80
Amount of 0.5% reagent used (ml)	3	0.3
RSD ±	0.004	0.003

Interferences

The effects of foreign ions on the determination of these metal ions were studied in detail. To test the effect of diverse ions, Cu(II) and Pd(II) were determined by general procedure, in the presence of their respective 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), Co(II), Cd (II), Cr(II), Mg(II), Mn(II), Pb(II), Sr(II), Rh(III), Zr(IV) and Zn(II). Amongst the anions examined (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 (95). Iron (II and III) (50 fold in excess) in the determination of these metal ions was masked with 2.0 ml of 5% sodium fluoride solution. Cobalt(II) was masked by adding sodium cyanide (2ml, 5%) and interference due to nickel(II) was overcome by decomposing the nickel(II) complex with 2 - 4 M HCl. EDTA interfered strongly in the determination of these metal ions due to its ability to form stronger complexes than isoamylxanthate.

Validation of method

Proposed method was verified by % recovery test by standard addition method, results were compared with AAS, which are in good agreement (AAS) given in Table 2.

Application

The proposed spectrophotometric method was applied to the determination of Cu(II) and Pd(II) in industrial waste water samples. Results are shown in Table 3.

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 (%)
Cu(II)	1.0	0.99	99 ± 1
Pd(II)	1.0	0.97	97 ± 3

At 95%, n = 6

Table-3: Determination of Cu(II) ions in industrial waste water samples

Sample	Amount of Cu(II) determined (mg)		
	Present method	AAS	C.V. %
*Industrial waste	58.70 ± 0.32	58.90	2.57

At 95%, n=6* Kotri site area

Experimental

Reagents

All chemicals used were analytical grade reagents (Merck and Fluka) unless otherwise stated. Standard Cu(II) and Pd(II) stock solutions of (100 μg ml^{-1}) were prepared dissolving their nitrates respectively. Other metal ions solution were prepared from their nitrate or chloride salts. Surfactant SDS 1 % and Tween 5% solution was made that weighing, dissolved in a 100 ml volumetric flask, and was diluted to the mark with double distilled water.

Stock solution of 0.5% solution 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) mixtures and adjusting the volume to 100 ml according to Perrin and Dempsey [27].

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 comparative metal ion determination. The Pye Model 292 pH meter was used.

Synthesis of reagent sodium isoamylxanthate [28]

Stoichiometric quantities of isoamyl alcohol (1M), sodium hydroxide (1M) and carbon disulphide (1M) (1:1:1) were used. Isoamyl alcohol (22 ml) was taken in 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) was added to obtain precipitates, which were filtered and transferred to a vacuum dessicator and dried for 24 hours. A 0.5% solution of sodium isoamylxanthate was prepared in distilled water and standardized titrimetrically [29] using mercuric acetate as a titrant and diphenylcarbazone as an indicator.

Procedure

Spectrophotometric metal ion determination in micellar solution.

Appropriate volumes of stock solutions of metal ions, sodium isoamylxanthate, and selected surfactants SDS 1%, 5% Tween 80 were added and made up to 25 ml volume with distilled water having metal ions concentration used 2 - 38 $\mu g\ ml^{-1}$, conc. of sodium isoamylxanthate 0.5%, 1% SDS, 5% Tween 80 surfactant. The pH values and analytical wavelength used are listed in Table- 1.

Spectrophotometric metal ion determination after extraction with CCl_4

Appropriate volumes of stock metal, sodium isoamylxanthate and buffer aqueous 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 appropriate wavelength for metal ions. Validation and application are given in Table-3.

Determination of Cu (II) in industrial waste water *samples*

Industrial wastewater sample, 1L obtained from industrial effluent collected from Kotri site area was filtered using Whatman filter paper. Concentrated nitric acid (4 ml) and 30 % hydrogen peroxide (2 ml) were added to the filtrate. The resulting solution was concentrated in an oven at 110°C to a final volume of 25 ml. Appropriate amounts of surfactant and sodium isoamylxanthate were added to a 25 ml calibrated flask to obtain final concentration of 1% SDS, 5% Tween 80 and 0.5% sodium isoamylxanthate. Then 5 ml of the sample was added and the absorbance was measured against water. The same sample, 5 ml was diluted to 25 ml with double distilled water for AAS analysis (Table 3).

Conclusions

Determination of trace amount of Cu(II) and Pd(II) is carried out directly using sodium isoamylxanthate in anionic/nonionic micellar media of (SDS)/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. Cu(II) and Pd(II) content in various matrixes can be determined by the present method.

References

1. J. Jago, P. E. Wilson B. M. Lee, *Analyst*, **96**, 349 (1971).
2. W. J. Simmons, *Anal. Chem.*, **45**, 1947 (1973).
3. M. P. San Andres, M. L. Marina, and S. Vera, *Talanta*, **41**, 179 (1994).
4. M. A Sanz and M. F. Fernandez, *Anal. Chem.*, **58,** 216 (1986) 1.
5. H. C. Gin, L. Hong and P. J. Mai, *Talanta*, **41** 1357 (1994).
6. A. Lopez Garcia, E. Blanco Gonzalez, J. L. Garcia Alonso and A. Sanz Medel, *Anal. Chim. Acta*. **264**, 241 (1992).
7. T. Okada, Anal. Chem., 64 (1992) 2138.
8. E. Paramauro, A. Bianco Prevot and E. Pelizzetti, *Anal. Chim. Acta*, **264**, 303 (1992).
9. L. J. Cline Love, J. G. Habarta and J. G. Dorsey, *Anal. Chem.* **56**, 1133A (1984).
10. X. Jin, M. Zhu and E. D. Conte, *Anal. Chem.*, 71 514 (1999).
11. Jinsook Yun and Heeseon Choi, *Talanta,* **52,** 893 (2000).
12. A. K. Malik, K. N. Kaul, B.S. Lark, W. Faubel and A.L.J. Rao, *Turk. J. Chem.*, **25**, 99 (2001).
13. B. K. Puri, C. L. Sethi and A.Kumar, *J. Chinese Chem. Soc.*,**29**, 173 (1952).
14. T. Khyamin, A. A. Ensafi and B. Hemmmateenjad, *Talanta,* **49**, 587(1999).
15. C.W. Kim and C.S. Kim, *Anal. Sci. Technology*, **12**, 1, (1999).
16. H. C. He, Guanguxue Yu Guangpu, *Fenxi*, **17** (2), 111 (1997).

17. S. A. Barakat and D. T. Burnas, *Anal. Chim. Acta*, **355** (2-3), 167 (1997).
18. A. Alexandrova and S. Arpadjan, *Analyst*, **118**, 1309 (1993).
19. A.A. Ensafi, T.K. Khayamian and B. Hemmateenjad, *Anal. Lett.*, **32**, 111 (1999).
20. S. P. Bag, J. Mukherjee and B. Siladitya, Indian. *J. Chem. Sect. A.*, **37**, 185 (1998).
21. E. Qin and L. J. Yang, *Fenxi-Shiyanshi*, **13** (5), 66, (1994).
22. Y. Kradjova, *Microchim, Acta.*, **130**, 185, (1999).
23. S. L. Zhao, X. Q. Xia and Q. F. Hu, *Anal. Chim. Acta*, **391**, 365 (1999).
24. A. K. Malik, K. N. Kaul, B. S. Lark, W. Faubel and A. L. J. Rao, *Turk. J. Chem.* **25**, 99 (2001).
25. Atamjyot , J. D. Shrma and A. L. J. Rao, *Ind. J. Chem.*, **36A**, 725 (1997).
26. G. A. Shar and M. I. Bhanger, *J. Chem. Soc. Pak.*, **25**(1) 28 (2003).
27. P. Beecher, in M. J. Schick (Ed.) Surfactant Science Series, Vol. 1, Marcel Dekker, New York 481 (1966).
28. C.C. Dewitt and E. E. Roper, *J. m. Chem. Soc.*, **54**, 444 (1932).
29. A. L. J. Rao, A. K. Malik and Y. Paul, *J. Ind. Acad. Forensic, Sci.*, **19**, 31(1992).