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Comparison of adsorptive stripping voltammetry with sensitized spectrophotometric for determination of copper ion using phenyl-2-pyridil ketone oxime

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ABSTRACT

A simple accurate and sensitive micellized spectrophotometric method and sensitive and selective voltammetric procedure for determination of copper (II) ion using phenyl-2-pyridil ketone oxime (PPKO) has been compared. The spectrophotometric determination of copper using PPKO in the presence of anionic surfactant SDS has been performed. The influence of type and amount of surfactant, pH, complexation time and amount of ligand on sensitivity of spectrophotometric method were examined. The voltammetric procedure involves an adsorptive accumulation of Cu²⁺-PPKO on a hanging mercury drop electrode, followed by a stripping voltammetric measurement of reduction current of adsorbed complex at about -0.30V (vs. SCE). The optimum conditions for the analysis of copper (II) was fixed in pH (5.8-7.0), 60 μM PPKO, accumulation potential and time of -0.5V (vs. SCE) and 60s. The peak current is proportional to the concentration of copper over the range 0.3-76 ng mL⁻¹ with a detection limit of 0.01 ng mL⁻¹. In spectrophotometric method the Beers law is obeyed over the concentration range of 0.3-21.0 μg mL⁻¹ in surfactant median with detection limits of 1.4 ng mL⁻¹. Finally in both methods, the repeatability, accuracy and the effect of interfering ions on the determination of copper ion were evaluated. The proposed methods successfully with recovery yield of almost 100% have been applied for the rapid and simple determination of copper in the real samples. There is a good agreement between methods and atomic absorption spectrometry.

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KEYWORDS

Phenyl-2-pyridilketon oxime (PPKO);
Spectrophotometric method;
Surfactant media;
SDS;
Copper ion;
Adsorptive stripping voltammetry.

INTRODUCTION

The importance of the determination of trace metal concentration in natural water samples is increasing in contamination monitoring studies. In many cases, the

analysis of heavy metals in environmental samples presents a notable difficulty due to both the low levels of metals in the samples and the high complexity of the matrices^[1]. Copper is a gastrointestinal tract irritant but is generally not harmful to humans at low concentra-

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tion. However, in concentration less than 1 ppm can be toxic to aquatic plants and some fishes^[2], so that, copper tends to be much more of an environmental hazard than a human hazard. The determination of trace amounts of copper has received considerable attention in many samples especially environmental pollution. Many method including ICP-MS, ion chromatography, atomic absorption spectrometry, extraction and separation method, ion selective electrode, supported liquid membrane^[3-15] has been used for copper determination. Many of these methods are time consuming or require complicated and expensive instrument and some of them has low repeatability and need careful construction of membrane electrode. Due to low concentration of copper content and view to the above mention problem, development of new sensitive and selective methods for selective, sensitive, rapid and convenient determination of this ion in sub-micron levels is still a challenging requirement.

Organic surfactant media are very useful in analytical application, especially in UV-Visible spectrophotometry^[16-17] and fluorescence process^[18], because they are stable in aqueous solution and transparent optically, enhance sensitivity and readily available^[19]. In Surfactant media complexes of metal ions with complexing agent are most stable and formed aggregates that cause an improvement in sensitivity and detection limits^[19].

On the other hand, in recent years, adsorptive or cathodic stripping voltammetry (CSV) has attracted considerable attention for trace and ultra trace metal ions or organic compounds, because of excellent sensitivity, accuracy, precision and the low cost of instrument. Stripping analysis following adsorptive accumulation of metal chelates is becoming a widely accepted analytical tool, as it extends the scope of selective stripping analysis toward additional trace metals and offers an effective alternative method for monitoring other metals^[20-22].

It was reported that adsorption of some species on HMDE is due to either sparingly solubility and/or Π orbital interaction, especially in aromatic ring containing compounds, selecting a suitable adsorption potential, suggesting that sometimes combination of electrostatic and Π orbital interaction is important and increases the figure of merit of a method^[23]. Due to the advantages including good sensitivity, portability and low cost,

incorporation of PPKO in solution lead to high sensitivity for adsorptive method.

In the present research using PPKO two different methods including spectrophotometry as low cost and even accessible instrument with adsorptive stripping voltammetry their comparison for copper determination has been carried out.

EXPERIMENTAL

Instrumentation

Cathodic stripping voltammetry (CSV) was carried out with a metrohm 746VA trace analyzer, using a Multi-Mode electrode in the hanging mercury drop electrode (HMDE) mode and SCE as the reference electrode. All potentials are measured and quoted relative to this reference electrode. The three-electrode system was completed by means of a platinum auxiliary electrode. Differential pulse voltammetry was carried out with pulse amplitude of 100mV with scan rate of 80mV s⁻¹ and a pulse interval of 0.1s.

A shimadzu UV-vis 160 spectrophotometer was used to measure the absorbance of complex in Brij 58 media. A 691 pH /Ion meter with a combined glass and calomel electrode has been used for measurement and adjustment of test solutions pH. The AAS determinations were carried out on a Shimadzu 680 A atomic absorption spectrometer with a hallow cathode lamp and a deuterium background corrector, at a wavelength of 324.8nm (resonance line) using an air-acetylene flame.

Reagent and solution

All chemical such as nitrate of copper and other cations were of the analytical grade purchased from Merck Company and used as received. A 0.5% (w/v) all surfactant all from Merck company including sodium dodecyl sulfate (SDS), Triton X-100, cetyltrimethyl ammonium bromide (CTAB), n-dodecyltrimethylammonium bromide (DTAB) was prepared by dissolving 0.5g of surfactant in 100mL volumetric flask with stirring. The organic solvents such as chloroform were purchased from Merck company. The ligand phenyl-2-pyridilketon oxime (PPKO) was synthesized according to literature^[24]. Nitrate salts of other cations or potassium salts of anions (1000mg L⁻¹) in distilled water were prepared.

More dilute solutions were prepared by diluting the stock solutions with distilled water. The buffer solutions were adjusted to the required pH value with sodium hydroxide and hydrochloric acid and were electrolyzed for 48 h at -1.6V in a mercury pool for removing the trace metal ions. Doubly distilled water was used throughout.

Procedure

The general procedure used to obtain cathodic adsorptive stripping voltammograms was as follows. Appropriate volume of sample solution containing $640.0\mu\text{g mL}^{-1}$ copper(II) ion was poured into a 25.0mL volumetric flask and the pH was adjusted to 5.8 by the addition of 2.5mL 0.1M acetate buffer(pH=5.8). Then 0.15mL of PPKO solution(1.96mg mL^{-1}) was added and the volume was adjusted to 25.0mL with distilled water. The solution was then transferred to a voltammetric cell. The stirrer was switched on and the solution was purged with argon gas for 5min. After forming a new drop, accumulation was affected for 60 s at -0.5 V while stirring the solution. At the end of accumulation time the stirrer was switched off, and after 10 s to allow the solution to become quiescent, the potential was scanned in the negative direction.

Procedure for spectrophotometric copper ion determination in surfactant media

Standard copper solutions of $100\mu\text{g mL}^{-1}$ were prepared and several aliquots of this copper ion solution were added to 25mL volumetric flask in the range of 0.05-25.0 $\mu\text{g mL}^{-1}$. To these solutions, 0.25mL of 0.01M PPKO and 0.25mL of 10mM SDS were added and with phosphate buffer (pH 7.0) was filled to the mark and the absorbance were measured. The calibration curve of copper ion was constructed tracing the absorbance versus the copper concentration.

Procedure for investigation of complex nature to pH

The pH measurement method for speciation of different form of complex and calculating dissociation constant of PPKO and stability constant of complexes was performed according to literature^[25,26]. Two separate solution were prepared as following: the first solution contains, 5mL 0.02735 M PPKO, 10mL 0.5M potassium nitrate, 2mL 0.1M hydrochloric acid and 33mL

water; the second solution contain 5mL 0.02735 M PPKO, 5mL 0.01346M CuCl_2 , 10mL 0.5M potassium nitrate, 2mL hydrochloric acid and 28mL water. Both solutions were titrated potentiometrically with 0.0965M sodium hydroxide. From the titration curve of the first solution the acidic dissociation constants of the ligand and from the second titration curve the formation constant of different form of complex were evaluated. According to IUPAC recommendation detection limit has been calculated^[5].

Pretreatment of real samples

Water sample was treated as following: 250mL of water sample was poured in a beaker and 8ml concentrated HNO_3 and 3ml of H_2O_2 of(30%) for elimination and decomposition of organic compound were added. The samples, while stirring was heated to one tent volumes. After adjustment of samples pH to desired value the spectrophotometric experiment and extraction experiments were performed according to general described procedure. Blood sample treatment was carried out as follow: 10mL of deionizer water, 24mL of concentrated HNO_3 and 10mL of H_2O_2 (30%) were added into 20mL of blood sample in a beaker. The volume of mixture while stirring by heating was reduced to tent. Then 3mL of concentrated HNO_3 was added and the solution was filtrated through a watman filter. 200mL of river water after acidification with 6M nitric acid and 3mL H_2O_2 (30%) was heated for 0.5h. After adjustment of pH by addition of appropriate amount of sodium hydroxide or hydrochloric acid, the sample was diluting to 25mL the determination of copper content was performed^[27,28].

RESULTS AND DISCUSSION

Optimizing of condition for determination of copper ion in surfactant media

The ligand PPKO is an N-OH donating ligand base, which is insoluble in water at neutral pH. Due to the presence of oxime group and incorporation of II electron it act as a soft acid and bind selectively to soft acid as copper ion in neutral media. Potentiometric and spectrophotometric studies revealed that it can form a fairly stable and selective complex with copper ion in slightly neutral pH with mole ratio of M: L of 1:2. Figures 1 and

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TABLE 1: Logarithm of cumulative stability constants for the interaction of H^+ and Cu^{2+} with the PPKO at $25^\circ C$

System	m	l	h	Log β
Cu(II)-PPKO	1	1	0	11.53
	1	2	0	21.45
	1	2	1	26.51
	1	2	2	29.81

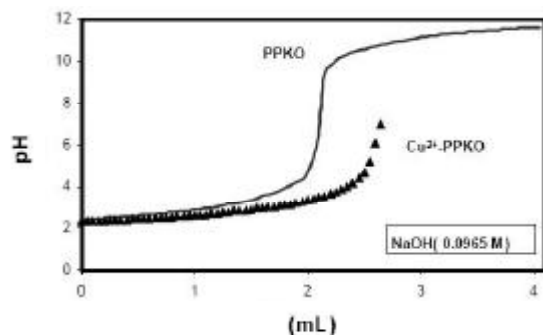


Figure 1 : Titration of PPKO solutions in the presence and absence of copper ion with NaOH 0.0965M

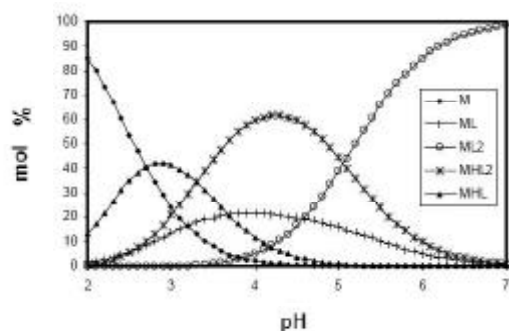


Figure 2 : Speciation of complexes of copper ion with PPKO obtained from figure 1

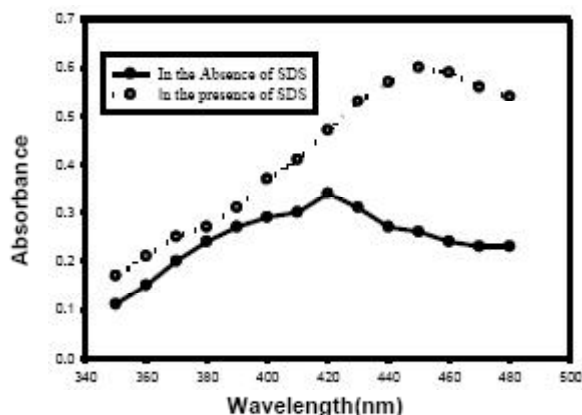


Figure 3: Spectra of Complex in different media 2 Conditions: 8 mM PPKO, 0.1mM SDS, pH 7.0 and $1.0\mu g mL^{-1}$ copper ion in organic media and $15\mu g mL^{-1}$ in SDS

2 display a representative set of potentiometric titration curves obtained for Cu^{2+} -PPKO systems. The forma-

tion constants of copper ion with PPKO binary complexes were determined under stable conditions of 0.1M ionic strength and $25^\circ C$ and values are shown in TABLE 1. The concentration distribution diagrams of binary systems are obtained in terms of percent metal ion as a function of pH, and are shown in figure 1. The high stability constant of ML_2 for copper: PPKO complexes makes it superior as a suitable ligand for developing an analytical method for selective determination of copper ion. In the literature, it has been pointed out which similar ions, including cobalt and nickel, could be strongly complexed with oximes in alkaline pH. We assume that the reaction to form this desired complex could have competed against hydroxide precipitation at higher pH (basic solution $pH > 7$) and ligand protonation at lower pH, which both lead to reduce in sensitivity. If applicable pH range may be larger than 7, expectable hydroxo complexes of PPKO : copper ion: OH could be formed, but in this work due to the high stability constant of $Cu(PPKO)_2$ complex and low hydroxide ion concentration c , hydroxide ion could not compete with PPKO for substitution.

Thus, we decided to examine its capability as a suitable reagent for sensitized spectrophotometric or cathodic adsorptive stripping voltammetry determination of copper ions and comparing the characteristic performances of both methods with each other.

The influence of effective parameters such as pH, type and amount of surfactant, amount of ligand in spectrophotometric method and potential and time of accumulation, pH, amount of ligand on adsorptive stripping for determination of copper content has been investigated.

Absorption spectra of $Cu(PPKO)_2$ in SDS

Some preliminary experiments were undertaken in order to investigate the effectiveness and utility of the SDS as a sensitizer for bathochromic agent and promoting method sensitivity. Therefore, a set of similar experiments at pH 7.0, 0.1mM PPKO, $1.0\mu g mL^{-1}$ copper ion in the presence and absence of 0.1mM SDS were carried out. The absorption spectra of $Cu(PPKO)_2$ in the presence and absence of surfactant SDS was obtained, which is shown in figure 3. As it can be seen, the experiment in surfactant media has higher sensitivity without the need to extraction of complex into

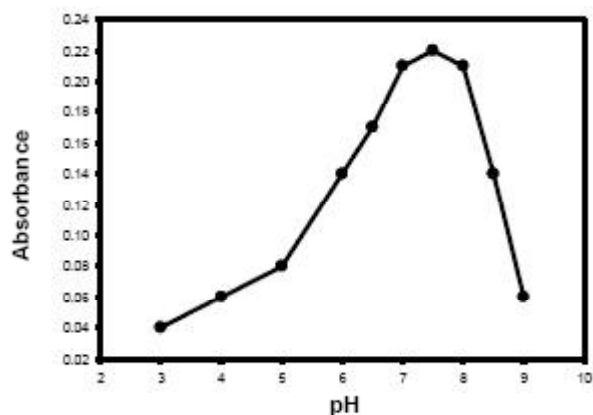


Figure 4: Effect of pH on sensitivity conditions: 0.1mM PPKO, 0.1mM SDS and $1.0\mu\text{g mL}^{-1}$ copper ion at various pH

TABLE 2 : Effect of type of surfactant on spectra and sensitivity for $0.1\mu\text{g mL}^{-1}$ of copper ion

Surfactant	pH	Absorbance	Maximum wavelength (nm)
Triton X-100	7.0	0.51	423
CTAB	5.7	0.53	415
DTAB	5.8	0.54	416
SDS	7.0	0.62	452
Triton X-114	7.0	0.56	443
In the absence of surfactant	7.0	0.34	420

organic harmful organic solvent. On the other hand, the method is fast, simple, low cost and powerful alternative tool for replacement of conventional expensive AAS or electrochemical method. This higher sensitivity may be attributed to the fact that, hydrophobic chelating agents could easily be introduced into the micelles for the separation and preconcentration of trace elements. The studies focused on investigation of complexation between copper ion and PPKO in surfactant media and evaluating optimum conditions for sensitized spectrophotometric determination of copper ion using PPKO. The stability and decomposition rate of complex seriously depend on pH and time. The low sensitivity and omitting spectra in acidic media is an indication.

Effect of pH on sensitivity

Most chelating ligands are conjugate bases of weak acid groups and accordingly have a very strong affinity for hydrogen ions. Therefore, the pH will be a very important factor in the complexation of metal ions by chelation and will determine the values of the conditional stability constants of the metal complexes on the

surface of the ligand. Due to the presence of an oxime group on the PPKO structure, it is expected that the extent of its complexation is sensitive to pH. Thus, the effect of pH on the complexation of copper ions with PPKO was studied. In order to investigate the effect of pH on the sensitivity of copper ion determination, a set of experiments containing 0.1mM PPKO, $1.0\mu\text{g mL}^{-1}$ copper ion and 0.1mM SDS at various pH were undertaken and results are shown in figure 4. It is immediately obvious that the Cu (PPKO)_2 complex showed the maximum absorption at pH 7.0-8.0. From this experimental fact, we determined that Cu (PPKO)_2 complex was quantitatively formed and well dissolved in SDS media at this pH range. We assume that the reaction to form this complex could have competed against hydroxide precipitation at higher pH (basic solution) and ligand protonation at lower pH that lead to reduce in sensitivity. Hence, subsequent spectrophotometric experiments were carried out at pH 7.0.

Effect of surfactant on sensitivity

In order to choose the most effective types of surfactants for increasing the sensitivity of spectrophotometric method for determination of copper ion, a set of similar experiments at 0.1 mM PPKO, $1.0\mu\text{g mL}^{-1}$ copper ion and 0.1 mM of various surfactants such as Triton X-100 and Triton X-114 as non-ionic and sodium dodecyl sulfate as anionic surfactant and cetyltrimethyl ammonium bromide and n-dodecyltrimethyl ammonium bromide as cationic surfactant were carried out and results are summarized in TABLE 2. For 0.1mM SDS media, the calibration curve with high sensitivity and red shift could be constructed and its slope was about 2 times more than other surfactant. In nonionic surfactant a mentionable spectra for complexes could not be obtained. In CTAB and DTAB media spectra can be obtained with lower sensitivity, so SDS was selected for further studies. This observation that in the presence of anionic surfactant, method had high sensitivity is an indication that surfactant only lead to aggregation of complexes and increase in sensitivity.

Effect of SDS concentration

A set of similar experiments at various concentration of SDS was prepared by addition of several aliquots of 10mM SDS surfactant to a 25mL volumet-

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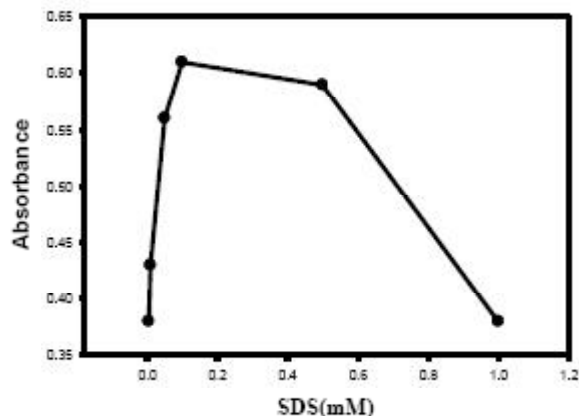


Figure 5 : Effect of SDS concentration on sensitivity of method, conditions: different concentration of SDS, 0.1 mM PPKO and $1.0\mu\text{g mL}^{-1}$ copper ion at pH 7.0

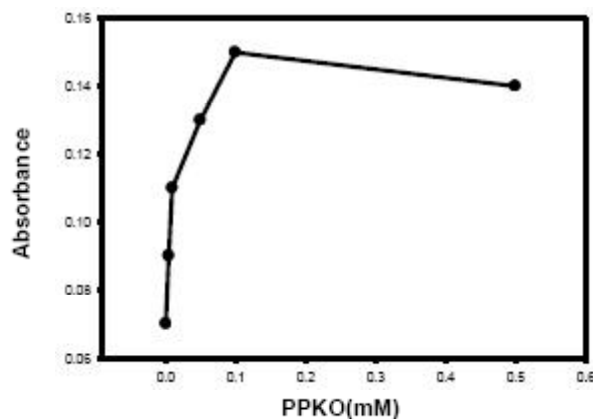


Figure 6: Effect of PPKO concentration on sensitivity of method, Conditions: different concentration of PPKO, 0.1mM SDS and $1.0\mu\text{g mL}^{-1}$ copper ion at pH 7.0

ric flask containing 0.1mM PPKO and $1.0\mu\text{g mL}^{-1}$ copper ion at pH 7.0 and their absorbance were evaluated using UV-Vis spectrometer. Results are shown in figure 5. When the concentration of SDS surfactant exceeds its critical micelle concentration, the homogeneous micelle solution is formed at a point where $\text{Cu}(\text{PPKO})_2$ complex can be well dissolved. With the concentration of SDS varying from 0.005 mM to 5 mM at pH 7.0 for PPKO the absorbance of desired complexes at concentration of $0.13\mu\text{g mL}^{-1}$ Copper was investigated. The maximum absorbance was obtained when the concentration of SDS was 0.1mM.

Effect of PPKO concentration on sensitivity

The analytical sensitivity and the reproducibility in the complex spectra were good in surfactant media. It is known that copper interact stoichiometrically with

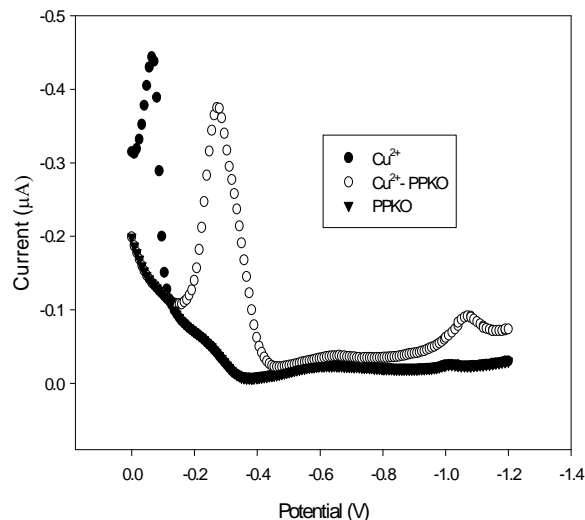


Figure 7: differential pulse voltammogram of the Cu^{2+} -PPKO complex, conditions: DP mode, 60 s accumulation of 33 ng mL^{-1} Cu^{2+} at -0.5V in the presence of $60\mu\text{M}$ PPKO at pH=6.0, scan rate 80.0mV/s

PPKO to form a 1: 2 complexes that its pH dependency were investigated and confirmed with potentiometrically and spectrophotometry. For evaluating and investigating the effect of the chelating agent concentration various amount of ligand was added to similar solution at optimum conditions. Respective results which are shown in figure 6 display that ligand concentration must be exceed of copper ion concentration to reach high sensitivity. Therefore, PPKO was added more than 10 times copper concentration to reduce fluctuation in measurement of absorbance.

Adsorptive stripping voltammetry conditions

Various experiments were carried out to identify the general features that characterize the behavior of the $\text{Cu}(\text{II})$ -PPKO system at mercury electrode. In order to obtain some information on the reactant and products, several measurement were carried out as following: (1) the DP mode of the blank solution did not show any peak at about -0.30V; (2) no peak was observed upon addition of PPKO to the above solution; (3) addition of a small amount of Cu^{2+} results in appearance of a peak at about -0.30V (Figure 7). These experiment indicate that electro active species at about -0.30V is $\text{Cu}(\text{II})$ - $(\text{PPKO})_2$ complex. The peak was highly diminished upon addition of surfactants such as Triton X-100, which can be taken as an indication for the presence of adsorptive current. According to the fact that

Cu²⁺ is the only electro-active species in the adsorbed complex, it can be concluded that the peak current is proportional to copper(II) ion content

Effect of pH and electrolyte

The influence of pH on the stripping peak current of Cu²⁺ complex was studied in the pH range 2.0-8.4. It was found that in the pH range 5.8 to 7.0 the peak current is approximately independent of pH and has maximum value that was expectable and confirmed by results of spectrophotometry. Among various electrolytes examined for adsorptive stripping study, the best results were obtained in acetate buffer solution, which used it for further studies. Variation of PPKO concentration showed that the peak current for copper increased with increasing PPKO concentration up to 60 μM, whereas greater amounts of the ligand does not significantly affect the peak current and cause leveling off. The increase in peak current was accompanied by a negative shift in peak potential for the reduction of complex. An optimum PPKO concentration of 60 μM was selected for future experiments.

The choice of deposition potential may affect the efficiency of the adsorption step as a result of coulombic effects and competitive adsorption. The effect of accumulation potential on the stripping peak current of the complex was examined over the potential range of 0.0 to -0.8V. As was seen the peak current increased with changing potential from 0.0 to -0.5V. This can be attributed to the accumulation of Cu (PPKO)₂ as layer on the HMDE then reduced when the potential is stepped to -0.8V at the start of stripping scan.

The choice of suitable accumulation time requires a trade-off between sensitivity, speed and selectivity. The effect of accumulation time on the peak current was also studied. Variation of the adsorption time between 0 and 100s at an adsorption potential of -0.5V, indicate that the peak current increases upon extending accumulation time to 60s and then starts to level off, that this is due to saturation of electrode surface. Thus 60s was selected for further studies as compromise between sensitivity and speed.

Characteristics of the methods

The calibration curve was obtained by using sample solutions at the optimum conditions of two methods

TABLE 3 : Optimum parameters of proposed two methods

Parameter	Spectrophotometric	Adsorptive stripping voltammetry
pH	7.0 -8	5.8-7
PPKO concentration (mM)	0.1	0.06
SDS (mM)	0.1	-
accumulation time(sec)	-	60
adsorption potential (mV)	-	-0.5
scan rate (mV/s)	-	80

TABLE 4 : Specification of two methods at optimum conditions for copper

Parameter	Spectrophotometric	Adsorptive stripping voltammetry
Linear Range (μg mL ⁻¹)	0.1-25	0.3-65
Regression equation	A=0.1084C _{Cu} +0.0143	ΔIp(μA)=0.0053C _{Cu} +0.0118
correlation coefficient	0.997	0.994
Detection Limit (ng mL ⁻¹)	1.3	0.1
RSD %	2.1	2.4

TABLE 5 : Investigation of tolerance limit of interfering ions on proposed methods

Interfering ions	[Interfering Ion] / [Copper ion]	
	Spectrophotometric	Adsorptive stripping voltammetry
K ⁺ , Na ⁺ , Cl ⁻ , Br ⁻	1200	1000
Ba ²⁺ , SO ₄ ²⁻ , NO ₃ ⁻	850	1000
Ca ²⁺ , Mn ²⁺	1000	1000
Zn ²⁺ , Mg ²⁺ ,	750	1000
Cr ³⁺ , Cd ²⁺	550	1000
Co ²⁺	150	50
Ni ²⁺	100	50
Hg ²⁺ , Ag ⁺	400	250
Pb ²⁺	250	250

(TABLE 3). A calibration curve was constructed at optimum conditions according to calibration curve procedure in experimental section. TABLE 4 gives the characteristic performance of the proposed method of standard solutions subjected to the entire procedure. Limits of detection and quantification according to IUPAC are also included. The limit of detection and the linear range of the proposed method are comparable to other methods that also employed FAAS. The characteristics of the proposed method are shown in TABLE 4.

Interference effect

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TABLE 6 : Investigation of accuracy and precision of proposed methods for real sample analysis

Sample ^a	Added Cu ²⁺	Spectrophotometric			Adsorptive stripping voltammetry			
		Found	Recovery %	RSD%	Found	Recovery %	RSD%	AAS
River water	0	0.32	-	0.9	0.36	-	0.7	-
	1	1.29	97	0.6	1.32	96	1.3	1.26
	0	0.44	-	1.5	0.39	-	1.4	-
Tap water	1	1.39	95	1.2	1.41	102	1.5	1.37
Tap water	0	0.67	-	1.5	0.74	-	1.8	-
Blood	1	1.69	102	1.0	1.69	95	1.4	1.73

^aall value are $\mu\text{g mL}^{-1}$

A study of potential interferences in the determination of copper was performed. An error of $\pm 5\%$ in signal reading was considered tolerable. Solutions containing copper $0.1 \mu\text{g mL}^{-1}$ for spectrophotometric method and 20ng mL^{-1} for adsorptive stripping voltammetry method with other ions were prepared and the developed procedure was applied. The tolerance limits of various foreign ions are given in TABLE 5. These results demonstrate that the effects of other ions at given concentrations are negligible. Also, the presence of large amounts of alkali and alkaline earth metals have no significant effect on the determination of copper.

Analytical application in real samples

We have explored the feasibility of the methodologies using them for the determination of copper ion in different matrices. The procedures were applied to the determination of copper ion in different samples, including tap water, river water and blood sample. Spiking experiments and independent analysis checked reliability. To ensure that the method is valid and has reasonable accuracy and precision, recovery of the copper ions in the river water, the tap water and blood sample were determined by these proposed techniques and the results are shown in TABLE 6 has a good agree with reference AAS method. The low relative standard deviations represent the high reproducibility in these measurements. Therefore, this proposed technique could be applied to the determination of ng mL^{-1} level of Copper in real samples.

CONCLUSION

Most of the Analysis method for copper ion as its colored complex with the reagents, suffer from drawbacks including reagent cost, instability and regeneration of the reagent for re-use, low sensitivity and selec-

tivity. In order to cope with these difficulty, the proposed methods due to advantages such as high reliability, reproducibility, sensitivity, selectivity and high tolerance limit and high selectivity and sensitivity and wide linear range in addition to low detection limit are powerful tools for rapid and sensitive determination of copper ion in various media. Due to the mention advantages these proposed methods have been successfully applied to the determination of copper at trace level. The low RSD of real sample analysis is an indication of methods versatility for real sample analysis. The characteristic performance of both methods is compared with each other and results are shown in TABLE 4. These characteristics and the typical applications presented in this paper, make the methods suitable for measuring the copper content in a wide variety of samples.

The present study demonstrates that adsorptive stripping voltammetry method and spectrophotometric method determination of copper in presence Interfering ions is excellent for determination of ng mL^{-1} concentrations in real samples, of copper because of high sensitivity, very large dynamic range, simplicity and speed, a combination very better from previously reported systems.

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