

DETERMINATION OF SUB – PARTS PER BILLION LEVELS OF COPPER IN COMPLEX MATRICES BY ADSORPTIVE STRING VOLTAMMERY ON A MERCURY ELECTRODE

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Abstract

The voltammetric characteristics of Cu(II)-SSA complex at the mercury electrode were investigated. An analytical method that based on the adsorptive accumulation of Cu(II)-SSA complex followed by the reduction of the complexed copper was developed for copper determination in complex matrices in presence of the large amount of foreign ions. Adsorptive voltammetry determinations showed that the Cu(II)-SSA complex behaves irreversibly exchanging two electrons on the hanging mercury drop electrode (HMDE). Factor affecting on the complexation, accumulation, and stripping steps were studied and a procedure was developed. The instrumental parameters in the measurement step were also tested. The optimum conditions of pH, SSA concentration, accumulation potential and accumulation time were studied. Under optimal conditions (pH= 12.9 glycine Buffer, 7×10^{-3} M SSA and accumulation potential -100 mV vs. Ag/AgCl), a linear calibration graph in the range $1.25 \mu\text{g L}^{-1}$ to $42.5 \mu\text{g L}^{-1}$ and a detection limit of $0.8 \mu\text{g L}^{-1}$ were obtained. The average relative standard deviation (RSD) for seven determinations was calculated as 7%, 5.5% and 3% for the concentrations between 3, 15 and $23 \mu\text{g L}^{-1}$. The effect of foreign ions and surfactants on the peak height of Cu(II)-SSA complex was evaluated. The method was applied for the determination of the copper in different real samples such as crude oil, crude oil tank bottom sludge, wastewater and tap water samples. The accuracy of the results was checked by ICP.

Keywords: Copper, sulfosalicylic acid (SSA), adsorptive stripping voltammetry, sludge

Introduction

Copper is an essential element at trace level (i.e. catalytic action in heme synthesis) [1], but the intake of large quantities can be toxic. Sources of copper poisoning include beverages from vending machines, copper or brass vessels, and sometimes water supplies. The determination of copper is of special concern in both environmental and process monitoring. Monitoring Cu(II) concentration is also becoming important in microelectronics fabrication industry. Thus, the development of simple, reliable, and low-cost techniques for copper determination is essential.

Electrochemical methods were well known method for their simplicity and low-cost and their sensitivity in stripping mode [2]. The application of voltammetric techniques in determination of trace copper has been reviewed [3]. Several electrochemical methods have been worked out for the determination of Cu(II), most of them employing anodic stripping voltammetry (ASV) in which preconcentration proceeded by either electrodeposition on mercury electrode [2, 4-10]. The remarkable sensitivity of this technique is attributed to its effective in situ preconcentration of the metal of interest, generally into a mercury drop or film electrode and as it combines low maintenance costs with good accuracy and precision and excellent sensitivity that allows the determination of low levels of metals without prior treatment of the sample.

Like the majority of analytical techniques, stripping analysis is subject to interferences that affect the accuracy and precision of the measurement. Some of the difficulties, e.g. intermetallic compounds or overlapping peaks, are specific and relate to the nature of the stripping measurement [2]. For example to solve the problem in overlapping peaks case, two different standardization procedures have been applied in order to minimize the experimental effort necessary to determine copper in presence of iron by differential pulse anodic stripping voltammetry. The significant matrix interference caused by iron in the voltammetric determination of copper has been successfully solved by using partial least squares (PLS) regression [11]

To solve of the disadvantages an organic or inorganic ligand was used to complex with metal ions (in this case is Cu(II) or Cu(I)) with adsorptive property rather than an electrolytic accumulation on the surface of the electrode [2,12-14]. For Cu(II) ion, the ligands used include 8-hydroxyquinoline, thiourea, 1, 10-

phenanthroline, 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol, poly-L-histidine, imidazol, hetrocyclic azo-compound, Beryllon III, 1-(2-pyridylazo)-2,7-dihydroxynaphthalene (2,7-PADN), thiocyanate, iodides, 2-mercaptobenzothiazole, catechol, and pyrogallol red, adenine ([15] and its references) and 2-mercaptobenzimidazole [16].

These methods present advantages and disadvantages in relation to the detection limit, sensitivity, selectivity, time consume, interference and stability and they were compared [15, 16]. Most of the methods involve a pH adjustment of the sample to 8-10. At that pH level carbonate precipitation occurs, so difficulties in the Cu(II) determination arise therefore carbonate was registered as interference ions ([15] and its references).

The present paper deals with the development of adsorptive stripping voltammetry for the trace determination of copper in the complex matrices. Furthermore, it is intended that the suitability of the proposed method for the determination of copper at presence of large amount interference ions. In this method some ions such as carbonate and bromide or chromate did not have any interference effect on the cathodic peak. Because of the high pH nature in determination step, often cations are removed by precipitating in hydroxide form. Also the used of ligand, i.e. SSA, has had very strong stability constant for copper than other ions. For this reason copper was as complex form in this high alkaline solution. In other word, high pH and high complexing agent (SSA) are advantage for this method than other procedures and most heavy metals do not significantly interfere. The other important advantage is registered for this method is the oxidation state of adsorbed metal-ligand complex, i.e.Cu(II). Therefore, all of the anion that complex with Cu(I) is not interfere even in bulk concentration.

Experimental

Chemical and reagents

The stock standard solution of Cu(II) (0.1 M) was prepared by dissolving appropriate amount of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ in deionized water. A stock 0.154 M solution of SSA was prepared by dissolving of SSA analytical grade (Merck) in deionized water. It was more important that the pH was adjusted between 6 and 8 by adding of concentrated NaOH (3 M) before adjusting the solution in the volume. The glycin-NaOH buffer (pH 8.5-12.9) was prepared by dissolving of 7.507 g of glycin and 5.85 g of NaCl in one liter deionized water. Every wanted buffer was prepared by adjusting the pH of appropriate amount of this solution by NaOH 3M [17]. All reagents were of the highest grade available and used without further purification. All solutions were prepared using deionized water from a Millipore Milli-Q purification system.

Instrumentation

Voltammetric measurements were made with a Metrohm 694 (Herisau, Switzerland) VA Stand coupled with a Metrohm 693 VA Processor. Adsorptive and voltammetric experiments were carried out in a three-electrode arrangement with an Ag/AgCl, 3 M KCl reference electrode, platinum wire counter electrode and multi-mode mercury drop electrode. Dissolved oxygen was removed by argon. For pH measurements, a Metrohm 691 pH meter was used. All potentials are given vs. Ag/AgCl.

Procedure

General voltammetric procedure

The analysis was performed in a 10.00 ml aliquot containing 0.5 mL SSA and 2 mL buffer at suitable pH. The solution was first de-oxygenated by bubbling of argon through the solution for at list 10 minutes before the analysis and the procedure was repeated for at list 15 second before every standard or sample addition. The AdSV procedure consisted of the following steps and performed in an uninterrupted sequence. [a] The accumulation step: the accumulation potential (E_{acc}) was -100 mV and the accumulation time (t_{acc}) was 60 s with rotating the stirrer bar; [b] The rest step (as step (a), but without rotating the stirrer bar): for 3-5 s. [c] The stripping step was performed with differential pulse voltammetry or square wave voltammetry.

Procedure for acid digestion of sludge and crude oil (method 3050B)

The EPA method 3050B [18] was used for the digestion of samples for analysis. $1-2 \pm 0.001$ g of sample was weighed and put into digestion vessel i.e. a 50 ml erlenmeyer. 10 mL of 1:1 HNO_3 was add and mixed the slurry, and cover with a watch glass. The sample was heated to $95^\circ\text{C} \pm 5^\circ\text{C}$ and reflux for 10 to 15 minutes without boiling. The sample was allowed to cool and 5 mL of concentrated HNO_3 was added and the reflux was continued for 30 minutes. If a brown fume was generated, indicating oxidation of the sample by HNO_3 and the digestion was repeated this step (addition of 5 mL of conc. HNO_3) over and over until no brown fumes was

given off by the sample indicating the complete reaction with HNO_3 . By removing watch glass, the solution was evaporated to approximately 5 mL without boiling or heat at $95^\circ\text{C} \pm 5^\circ\text{C}$ without boiling for two hours. After this step has been completed and the sample was cooled and 2 mL of water and 3 mL of 30% H_2O_2 was added. The vessel was covered with a watch glass and the digestion was continued until effervescence was subsided and the sample was cooled and again the digestion (heating the acid-peroxide digestate) was continued until the volume has been reduced to approximately 5 mL. After cooling, the solution was diluted to 100 mL with deionized water. Particulates in the digestate should then be removed by filtration, by centrifugation, or by allowing the sample to settle.

Procedure for extraction of copper as ammonia complex to minimize interference effect of some cations

By using extraction with concentrated ammonia copper was extracted as ammonia complex in which often cations were precipitated as hydroxide. This method minimizes the possible interferences from often cation even in the high concentrations.

Procedure for minimizing the effect of the surfactants

To avoid surface active interference a separation step was performed as follows. Extract 2 mL of sample solution with 1 mL of dichloromethane. After vigorous shaking, the solution was allowed to form the two phases. The aqueous solution was saved as the analyte.

Results and discussion

Adsorptive and voltammetric characteristics of Cu(II)-SSA complex

Preliminary experiments were carried out to identify the general features, which characterize the behavior of the Cu(II)-SSA system at a mercury electrode. No peak was found on the linear potential scan voltammogram in a solution containing 0.01M SSA in glycine buffer solution at pH 12.9.

In Fig. 1, the adsorption voltammograms of the solutions of glycine buffer solution at pH 12.9 containing SSA (curve A) and after adding Cu(II) ion (curve B-I) were reproduced. The peak potential of the reduction of adsorbed Cu(II)-SSA in the glycine buffer is -350 mV and unchanged with increasing the Cu(II) concentration that shows the reversibility of electrochemical reaction. The peak was very stable and after even 10 hours it was changed as 4 % at the concentration 22 ppb of Cu(II).

Cyclic voltammetry (CV) was used to investigate the electrode reaction. The scan was preceded by 60 s adsorption at -100 mV. The single reversible system of peaks, corresponding to the Cu(II)/Cu(Hg) couple is unchanged after adding SSA as it was illustrated in Fig. 2 and it is not converted to two irreversible peaks on the cyclic curve like Cu(II)-Adenine system [15].

The plot of the scan rates versus the linear sweep voltammetric peak current of Cu(II)-SSA is linear. The peak height increases with increasing deposition time at first but eventually becomes constant as a result of saturation. Subsequent repetitive scans in cyclic voltammetry (CV) yield significantly smaller (but stable) cathodic peaks. (Fig. 3) The difference in the peak potentials and peak heights in CV is caused by the irreversibility of reduction at this high scan rate 2400 mV s^{-1} . The above features are characteristic of a reaction in which the reactant is adsorbed on the surface. The apparent transfer coefficient, αn , can be estimated from the peak half-width, $W_{1/2}$, according to the Laviron [19] equation:

$$\alpha n = \frac{2.44RT}{W_{1/2}F} = \frac{62.5}{W_{1/2}}$$

The peak half-widths at different conditions in determination of copper were equal 58 mV (for more than 35 measurements). From, this value, an αn value of 1.07 was obtained. If the α value was 0.5 (regarding to α value is smaller than 1) a n value of 2 can be obtained therefore, Cu(II) was the present in the structure of complex. This result, could be expected, because of the redox peak potential of Cu(II)-SSA and Cu(II) were the same (Fig. 2).

The peak height a of Cu(II)-SSA was found to depend on the SSA as well as on the copper concentration, the solution pH, the collection potential, the collection period. These parameters were therefore optimized to achieve maximum sensitivity in our analytical measurements.

Effects of operational parameters

Effect of Analytical Parameters

Effect of variation of pH

The influence of pH on the stripping peak current was studied in the range of pH 1–14 and it was found that the most peak current is in the range pH 12–14. When the pH value was lower than 10, there was no peak and when the pH value exceeds 13, the peak current began to decrease (Fig. 4). For pH values lower than 10 no cathodic signal was observed, indicating a weak acid behavior of the ligand on the electrode surface. For pH greater than the indicated, a voltammetric response of complex was observed. The peak potential was shifted to negative value with increasing the pH as result of formation of complex and adsorbed to the electrode.

Extraction steps

The extraction procedure had two steps. The first includes extraction of Cu(II) from real samples as copper complex and precipitation of other cation as hydroxide and the second is removal of surface active substances if present.

Because of the other cations have had the effects on adsorptive peak, this step is more important in determination of copper in real sample, especially when the low concentration of copper is present in bulk concentration of other cations. Concentrated ammonia solution was selected to remove other cations from the analyte solution in this step and copper was remained as copper complex with ammonia and other cation was precipitated as hydroxide.

The surface active agent, if present, could interfere in voltammetric determination procedure. The extraction with organic solvent has shown a powerful effect to remove surfactant and other organic materials from analyte solution [20]. The extraction could be performed by organic solvents such as hexane, dichloromethane, chloroform or carbon tetrachloride. Dichloromethane was the best solvent for removal of the surface active substances.

Effect of Instrumental Parameters

Effect of variation of SSA concentration

The effect of SSA concentration on peak height was shown in Fig. 5. As it can be seen the peak current increases with increasing SSA concentration and reaches a maximum at $\sim 5-10 \times 10^{-3}$ M of SSA and then decreases slightly. Thus, 7×10^{-3} M of SSA was chosen for further analysis.

Effect of variation of accumulation potential (E_{acc})

Fig. 6 shows the plots of the peak current of the complex changing with accumulation potential. As it was shown, a maximum peak height value is reached at an accumulation potential of -100 mV. At more negative potentials the signal reduces slowly due to reduction of complex and at the potential more positive potential the peak high is decreased as result of oxidation mercury electrode. An accumulation potential of -100 mV was therefore, chosen for obtaining high sensitivity in determination step.

Effect of variation of accumulation time (t_{acc})

The effect of accumulation time on peak current was illustrated in Fig. 7. At first, the peak current increased with accumulation time, indicating that before adsorption equilibrium is reached, the longer the accumulation time, the more Cu(II)-SSA was adsorbed and the peak current became larger. However, after a specific accumulation period, the peak current tended to level off, illustrating that adsorption equilibrium is achieved. An accumulation time of 60 s is used for further studies.

Effect of variation of scan rate and scanning wave forms and its parameters

It was found that the peak current, I_p , of the complex varies with potential scan rate v (Fig. 8). There is linear relation between $\log I_p$ and $\log v$ in range from 200 to 1000 mV s^{-1} , with slope of 0.913 ($r = 0.995$) indicates the target in electrochemical process was adsorbed on the electrode surface. As it was mention the electrochemical process was irreversible at very high scan rate.

The effect of applied waveform in determination step was examined. Different wave form including alternative current and differential pulse and square wave voltammetry was applied to get better result in stripping step (Fig. 9). The square wave mode showed the better sensitivity and was chosen in determination step. Alternative current mode at phase angle = 90° caused the background signal was increased and cancelled out any analytical advantage of the greater peak heights. As result of electrochemical adsorbed target, the higher scan rate showed the higher sensitivity but because of limitation of square wave mode in applying scan rate the maximum scan rate that could be applied was 120 mV s^{-1} , therefore, it was selected to optimum condition.

Another parameter that had effect on sensitivity was pulse height, the effect of which was studied in the range of 10 to 50 mV. A pulse amplitude of 50 mV which gave the best sensitivity was chosen as an optimum value. At higher modulation frequency than 60 HZ, the peak became broadened, therefore the modulation frequency of 60 HZ was selected.

Analytical applications

Analytical figures of merit: Reproducibility, linear range and detection limit of the method

Under the optimum experimental conditions, the calibration curve was linear over the range of $1.25 \mu\text{g L}^{-1}$ to $42.5 \mu\text{g L}^{-1}$, i.e. pH= 12.9 glycine Buffer, $7 \times 10^{-3} \text{ M}$ SSA, accumulation potential of -100 mV and accumulation time of 60 s, square wave mode; $v = 120 \text{ mV s}^{-1}$; pulse height = 50 mV modulation frequency = 60 Hz. The correlation coefficient (r) and the equation for calibration graph were 0.9982 and $Y_{\text{na}} = 9.04 X_{[\text{Cu(II)}]} \mu\text{g L}^{-1} + 30$, respectively. The detection limit ($Y_{\text{DL}} = \bar{X}_B + 3 S_B$, where Y_{DL} is the signal for detection limit, \bar{X}_B is the mean of blank signal and S_B is the standard deviation of blank signal, [22]) was obtained as $0.8 \mu\text{g L}^{-1}$ for an accumulation time of 60 s. The average relative standard deviation (RSD) for seven determinations was calculated as 7%, 5.5% and 3% for the concentrations between 3, 15 and $23 \mu\text{g L}^{-1}$.

Effect of interfering substances

The effect of interfering substances on the analysis of $12 \mu\text{g L}^{-1}$ Cu(II) were studied using the proposed method (Table 1). All of the substances were added to the voltammetric cell directly. But any substances in Table 1 that were signed as "a" or "c" superscript, were added to initial sample solution and one of the extraction applied them. Because of SSA ligand was complexed strongly with Cu(II), the interference from most substance is lower than other methods. The study of the effect of interfering substances was categorized in three parts as follows.

Effect of interfering anions

The EPA extraction method (method 3050B) used hot concentrated HNO_3 to extract Cu(II) from real sample. In this condition often anions (CO_3^{2-} , HCO_3^- , SCN^- , $\text{S}_2\text{O}_3^{2-}$, SO_3^{2-} , CN^- , Br^- , I^- , ...) that were registered as interference substances were decomposed even in bulk concentration. Also because of determination has been based on the adsorptive of Cu(II)-SSA on to mercury electrode and not Cu(I), the anion such as (CO_3^{2-} , SCN^- , $\text{S}_2\text{O}_3^{2-}$, SO_3^{2-} , CN^- , Br^- , I^- , ...) could not interfere in determination step in higher concentration than other methods if the EPA extraction method was not applied.

Effect of interfering cations

The alkaline characteristic of the method (pH > 12.9) has caused the interference removal of cations by means of precipitating them as hydroxide. The extraction with concentrated ammonia procedure could be used to help this effect and as it was shown in the Table 1.

Effect of interfering surfactants and ionic strength

The effect of the ionic strength of the medium on the signal, in potassium nitrate solutions in concentrations between 0.1 and 10^{-2} M was studied. The cathodic adsorptive stripping peak of Cu-Ade remained constant in this range.

The serious interference in electrochemistry, especially in adsorptive stripping voltammetry, is the presence of surface active substances, i.e. surfactants. They can be adsorbed onto the electrode and decreases the available electrode surface for adsorption of the copper complex. As it was illustrated in Table 1, surfactant even at low concentration had much effect on the cathodic peak. For example, Triton X-305 had no effect on the signal at

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the concentration of 30 ppb. But at the higher concentration this effect was decreased the signal sharply. In here, we used the solvent extraction method to remove the effect of surfactants. As it is shown (the labeled substances as "c" Table 1), the solvent extraction step minimizes the interfering effect of surfactants to a great extent [20]. It should be mentioned that if the concentration of surfactant was high, the extraction step must be repeated.

Table 1. The effects of various possible interfering ions on the analysis of [Cu(II)] = 12 µg L⁻¹; [SSA] = 7×10⁻³ M; pH 12.9; E_{acc} = -100 mV; t_{acc} = 60 s; v = 80 mV s⁻¹; differential pulse mode; pulse height = 100 mV

Ion	Amount of Ion (M)	Recovery	Ion	Amount of Ion (M)	Recovery
I ⁻	1×10 ⁻⁴	94	H ₂ O ₂	5×10 ⁻³	98
Br ⁻	3×10 ⁻³	95	As (III)	8×10 ⁻⁴	98
Cl ⁻	9×10 ⁻³	96	Se(VI)	6×10 ⁻⁴	95
F ⁻	5.3×10 ⁻⁴	96	Ti	1×10 ⁻⁶	85
Citrate	1×10 ⁻⁴	96	Ti	1×10 ^{-5b}	96
Acetate	Bulk	100	Ti	1×10 ^{-4b}	75
Borate	Bulk	100	Mn(II)	1×10 ^{-4b}	96.5
SO ₄ ²⁻	Bulk	100	Mn(II)	1×10 ⁻⁴	40
PO ₄ ³⁻	Bulk	100	Ni(II)	3×10 ⁻⁴	95
NO ₃ ⁻	Bulk	100	In(III)	1×10 ⁻⁴	100
NO ₂ ⁻	2×10 ⁻²	100	Co(II)	6×10 ⁻⁵	104
HCO ₃ ⁻	6×10 ⁻⁴	96	Zn(II)	2.1×10 ⁻⁴	96
CO ₃ ²⁻	5×10 ⁻⁴	98	Cd(II)	2×10 ⁻⁴	102
SCN ⁻	7.2×10 ⁻⁴	96	Fe(III)	5×10 ^{-3b}	98
SO ₃ ²⁻	2×10 ⁻⁴	94	Fe(III)	5×10 ⁻⁵	85
S ₂ O ₃ ²⁻	1×10 ⁻⁵	98	Al(III)	5×10 ^{-4b}	98
S ₂ O ₃ ²⁻	2×10 ⁻⁴	92	Al(III)	1×10 ⁻³	90
SCN ⁻	1.5×10 ⁻³	93	Cr(III)	1×10 ⁻⁴	95
CN ⁻	6×10 ⁻⁵	96	Cr(III)	8×10 ⁻⁵	99
CN ⁻	6×10 ⁻⁴	92	Cr(VI)	5×10 ⁻³	91
Tartrate	5×10 ⁻⁴	95	Pb(II)	1×10 ⁻⁵	80
EDTA	1×10 ⁻⁵	94	Pb(II)	5×10 ^{-4b}	98
Triton X-305	30 ^a	99	Ca(II)	Bulk	100
Triton X-305	100 ^a	90	K(I)	Bulk	100
Triton X-305	1000 ^a	60	Na(I)	Bulk	100
Triton X-305	1000 ^{a, c}	93	Mg(II)	Bulk	100

(a) Concentration is in ppb.

(b) The extraction with concentrated ammonia was applied.

(c) The extraction of 2 mL of sample solution with 1 mL of dichloromethane was applied.

Practical application, recovery and accuracy of the method

The suggested method was applied to the determination of copper in real samples such as crude oil, crude oil tank bottom sludge, wastewater and tap water. The result was summarized in Table2. The method could be applied successfully to the determination of trace amounts of Cu(II) in real samples. For testing the accuracy of the method, Cu(II) has also been determined by ICP after digestion using the EPA method.

Table 2. Results of analysis of real samples.

Sample	Added ^a	Found ^a	Recovery	Concentration ^b	Relative Error%
Crude Oil Sludge (New)		18		4.5	6
	15	28.4	86		
Crude Oil Sludge (Old)		30		11.5	8
	15	37.4	83		
Tap Water		18		0.06	3
	10	26.9	96		
River Water		33		0.5	5
	10	38.3	89		
Waste Water		27		66	8
	10	31.5	85		

(a) $\mu\text{g L}^{-1}$
(b) mg L^{-1}

Conclusion

In this work, a voltammetric method for Cu(II) determination has been used based on the adsorptive of Cu(II)-SSA on to mercury electrode (NOT Cu(I)-Ligand) and the advantage on this method on other references is this point. For this reason the anion such as (CO_3^{2-} , SCN^- , $\text{S}_2\text{O}_3^{2-}$, SO_3^{2-} , CN^- , Br^- , I^- ,...) could not interfere in determination step even in higher concentration than other methods (base on adsorbed Cu(I)-Ligand) without considering the EPA extraction method. The primary benefit of this method is high pH value (>12) in determination step was caused the remove often the cation as hydroxide precipitation and the strong complex of Cu(II)-SSA helped to eliminate the interference effect of often cations. Also the use of EPA method increased the sensitivity and selectivity in this procedure.

Acknowledgments

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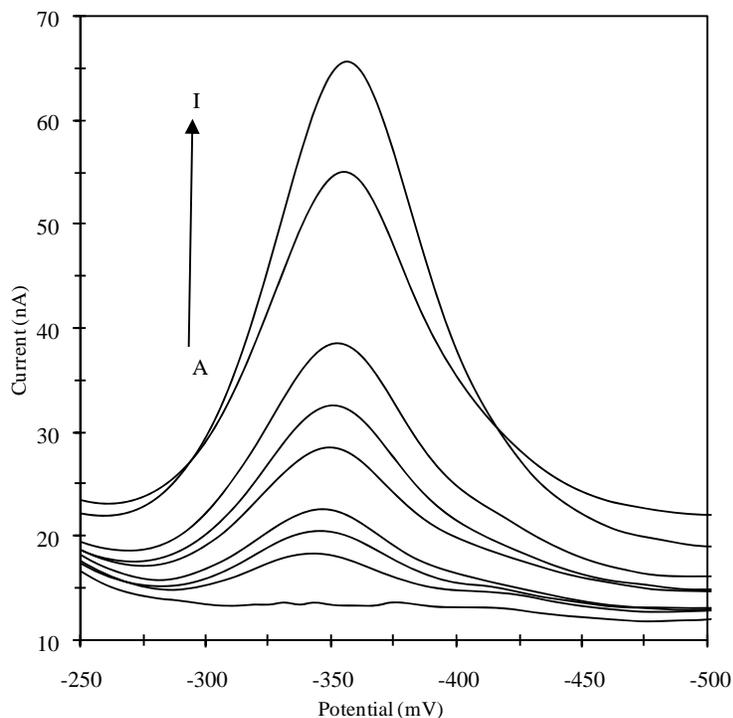


Fig. 1 Effect of Cu (II) concentration on the glycine-NaOH buffer solution, pH=12.9 containing: $[SSA] = 5 \times 10^{-3}$ M; $E_{acc} = -100$ mV; $t_{acc} = 60$ s; square wave mode; $\nu = 120$ mV s^{-1} ; pulse height = 50 mV modulation frequency = 60 Hz.; I_p was recorded after adding: [Cu(II)] = A, blank; B, $0.24 \mu g L^{-1}$; C, $0.48 \mu g L^{-1}$; D, $0.72 \mu g L^{-1}$; E, $1.19 \mu g L^{-1}$; F, $1.67 \mu g L^{-1}$; G, $2.14 \mu g L^{-1}$; H, $3.33 \mu g L^{-1}$; I, $4.52 \mu g L^{-1}$.

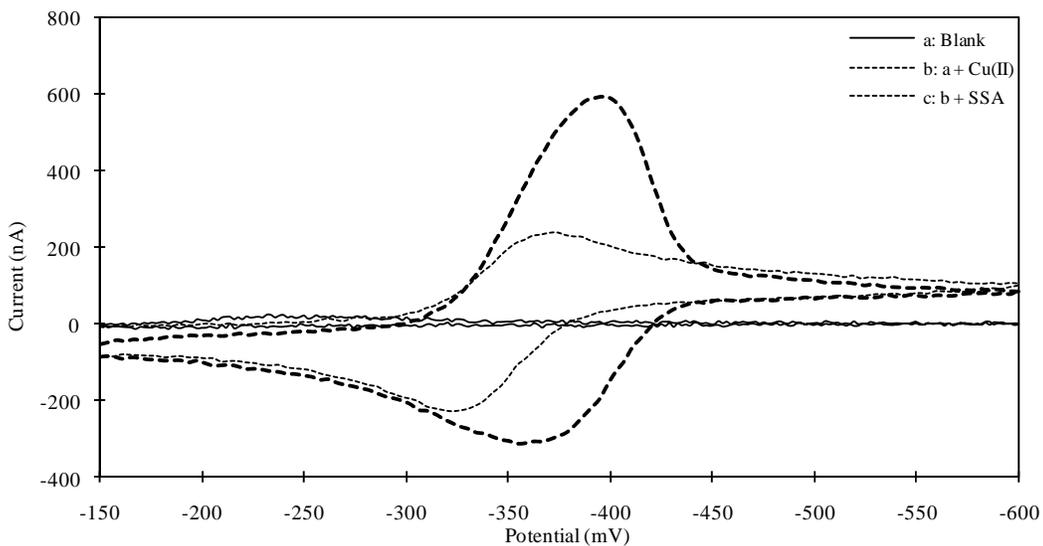


Fig. 2 Cyclic voltammograms of glycine buffer solution pH=12.9 containing: $E_{acc} = -100$ mV; $t_{acc} = 60$ s; cyclic mode; $\nu = 100$ mV s^{-1}
 a) The buffer solution (denoted as blank)
 b) After adding 3 mg L^{-1} of Cu(II) (denote as Cu(II) Only)
 c) After adding the $[SSA] = 7.7 \times 10^{-3}$ M (denoted as Cu(II)-SSA)

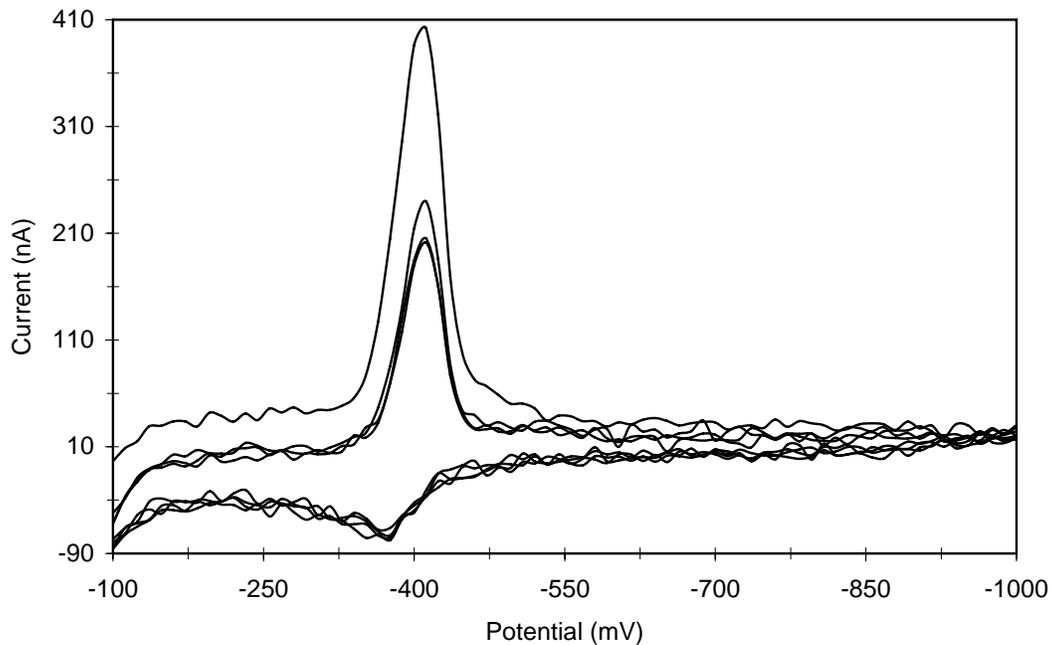


Fig. 3 Repetitive cyclic voltamperograms: $[SSA] = 7.33 \times 10^{-3} \text{ M}$; $[Cu(II)] = 47.6 \mu\text{g L}^{-1}$; $E_{acc} = -100 \text{ mV}$; $t_{acc} = 60 \text{ s}$; $v = 2400 \text{ mV s}^{-1}$; cyclic mode.

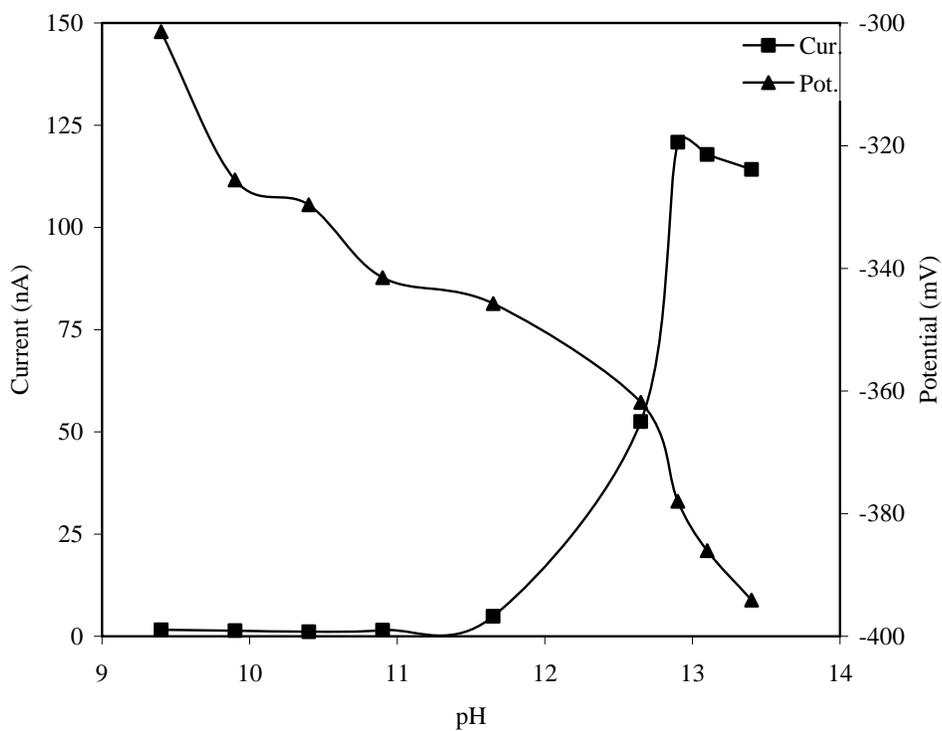


Fig. 4 Effect of pH on peak current and peak potential: $[SSA] = 1.4 \times 10^{-2} \text{ M}$; $E_{acc} = -100 \text{ mV}$; $t_{acc} = 60 \text{ s}$; $v = 80 \text{ mV s}^{-1}$; differential pulse mode; pulse height = 50 mV ; I_p was recorded after adding $[Cu(II)] = 22 \mu\text{g L}^{-1}$

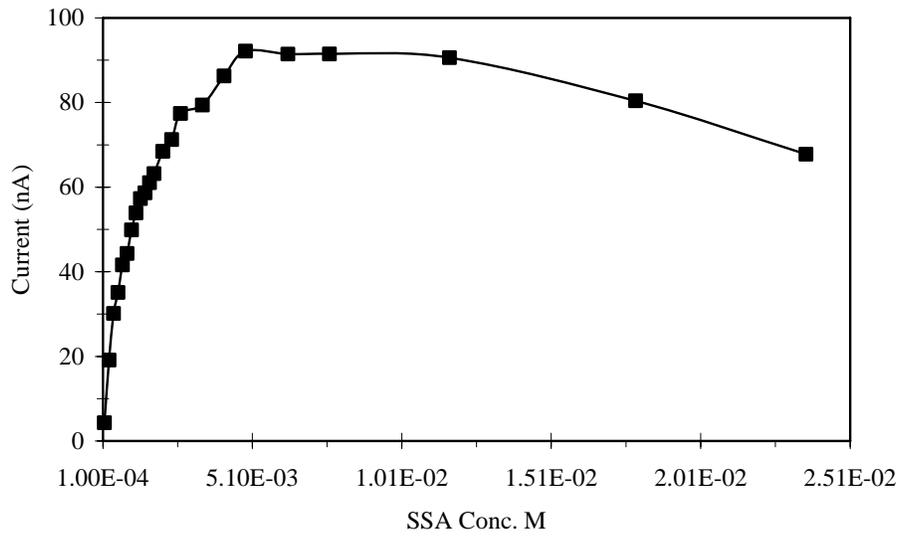


Fig. 5 Effect of concentration of SSA on the response: pH= 12.9; $E_{acc} = -100$ mV; $t_{acc} = 60$ s; $v = 80$ mV s⁻¹; differential pulse mode; pulse height = 50 mV; [Cu(II)]= 25 μ g L⁻¹.

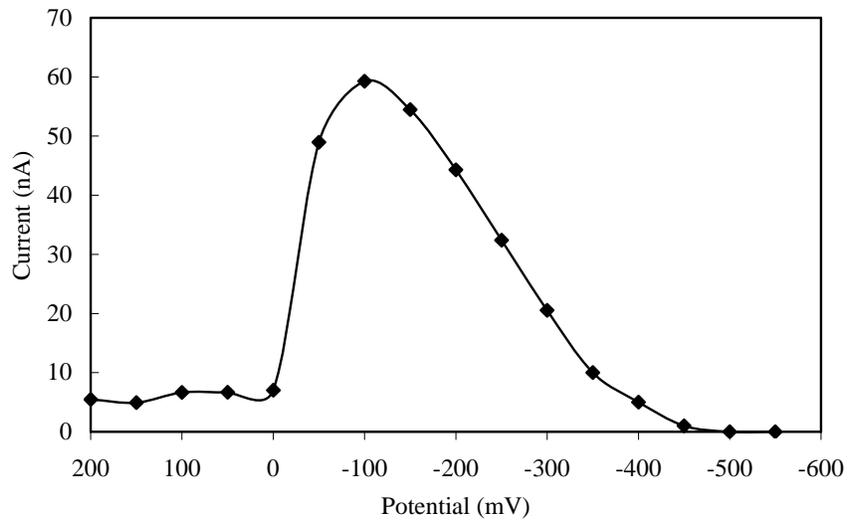


Fig. 6 Effect of accumulation potential on peak current: [Cu(II)]= 12 μ g L⁻¹; [SSA] = 4.8 $\times 10^{-3}$ M; pH= 12.9; $t_{acc} = 60$ s; $v = 80$ mV s⁻¹; differential pulse mode; pulse height = 50 mV.

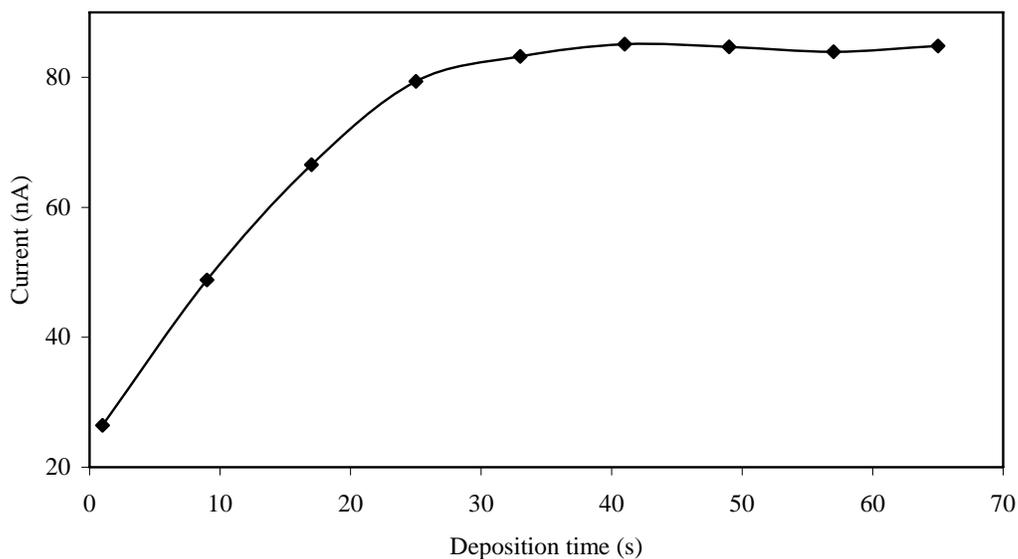


Fig. 7 Effect of accumulation time on peak current: $[Cu] = 24 \mu g L^{-1}$; $[SSA] = 7 \times 10^{-3} M$; $pH = 12.9$; $v = 80 mV s^{-1}$; differential pulse mode; pulse height = 50 mV.

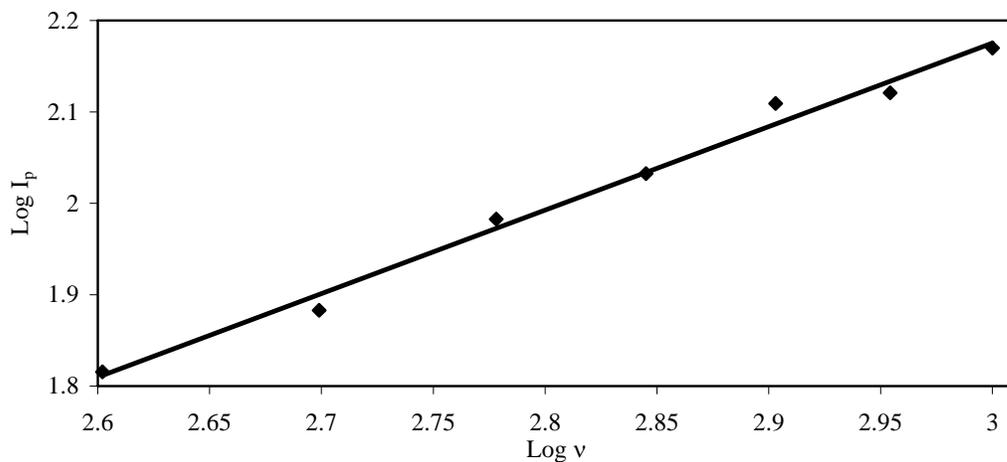


Fig. 8 Effect of scan rate on peak current: $[Cu] = 47.5 \mu g L^{-1}$; $[SSA] = 7 \times 10^{-3} M$; $pH = 12.9$; $E_{acc} = -100 mV$; $t_{acc} = 60 s$; linear sweep mode.

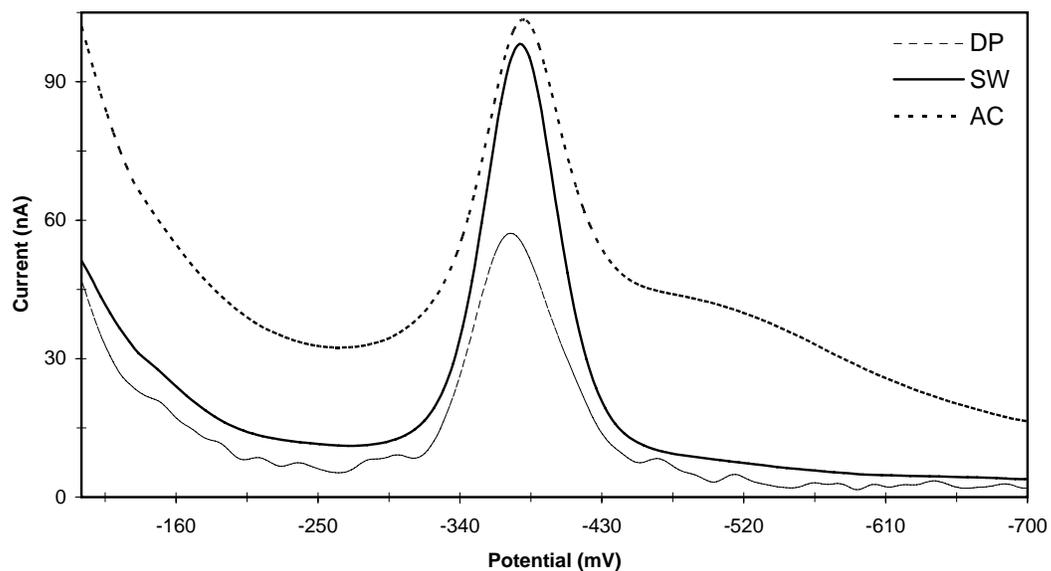


Fig. 9 Effect of scanning wave forms in stripping step: $[\text{Cu}] = 47.5 \mu\text{g L}^{-1}$; $[\text{SSA}] = 7 \times 10^{-3} \text{ M}$; $\text{pH} = 12.9$; $E_{\text{acc}} = -100 \text{ mV}$; $t_{\text{acc}} = 60 \text{ s}$; scanning wave forms were as follows:
DP) Differential pulse mode; $\nu = 40 \text{ mV s}^{-1}$; pulse height = 50 mV
SQ) Square wave mode; $\nu = 40 \text{ mV s}^{-1}$; pulse height = 20 mV modulation frequency = 60 Hz.
AC) Alternative current mode; $\nu = 40 \text{ mV s}^{-1}$; pulse height = 20 mV modulation frequency = 60 Hz; phase angle = 0° .