Selective Preconcentration of Ultra Trace Copper (II) ion Using Square Wave Cathodic Adsorptive Stripping Voltammetry at Modified Carbon Past Electrode

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Ultra-trace copper determination in natural water and human hair samples was performed using stripping voltammetric based on Square wave cathodic adsorptive. The mechanism of Square wave cathodic Adsorptive Stripping was applied to increase the sensitivity of the proposed method. Copper (II) was preconcentrated on the surface of the carbon past electrode modified by pa(E)-2-(Mercapto-phenylamino-methylene)-3-oxo-N-p-tolyl-butanamide (MPMPB) through a surface coordination effect. To optimize the analysis of copper(II) ion, different parameters such as pH, accumulation potential and time, medium, scan rate, and ionic strength were investigated. By applying the optimal conditions, the adsorbed form is reduced irreversible viz; 0.1M Britton-Robinson at (pH ~ 6.00) with linear concentration ranges of 0.013 – 0.064 at 15, 30 and 0.012–0.076 ng/mL at 60 s. The common electroactive and metal ions interferences were tested. To increase the selectivity of the proposed method, common interferences of electroactive and metal ions were studied. This method is sensitive selective, and efficient, therefore it can determine the low levels of copper(II) in water and human hair samples successfully.

1. INTRODUCTION

Recently, current electroanalytical techniques, especially adsorptive cathodic stripping voltammetry (ACSV) modified with different chemical catalysis, have developed many electrochemical methods for low-levels analysis of many organic [1–4] and inorganic [5–12] analytes. Modification of adsorptive cathodic stripping voltammetry with different homogeneous chemical catalysis to exaggerate

the reduction current received great attention. [13–22]. The use of chemical catalysis with adsorptive cathodic stripping voltammetry improved the analysis in terms of selectivity, accuracy, sensitivity, precision, and low-cost instrumentation.

Over the last years, considerable improvement has been made in the electroanalysis of very low levels of different analytes in many samples based on the use of Catalytic-Adsorptive Stripping Voltammetry (CASV) [23–26]. A variety of organic and inorganic species can be analyzed at very low concentrations, which can be extremely useful for the environmental, industrial and clinic applications [27, 28].

Copper is a necessary element for many biological mechanisms, even at very low levels [29, 30]. For the mobilization and redox activity of copper, it plays an important rol in the production of reactive oxygen forms, such as O_2 and OH radicles. These radicals associated very rapidly with DNA and can breaking the DNA strands or modifying the bases and/or deoxyribose leading to some genetic mutations. Therefore, developed an efficient procedure for determining ultra-trace copper in natural samples are mandatory [31]. Adsorptive stripping analysis of Cu(II) in seawater samples was carried out using Catechol as a complexing agent [32, 33]. Volumetric analysis of trace levels of copper was performed using dimethylsulfinated bathophenanthroline as Polymer-modified electrode [34]. Moreover, a new Poly (pyrrole-N-carbodithioate) electrode was synthesized and used for stripping analyze of copper ions in natural samples [35]. The preconcentration and determination of copper in different samples was enhanced by the modification of Carbon paste electrode with 2,9-dimethyl-1,10-phenanthroline [36]. These modifications have maximized the sensitivity level of copper analysis to 10^{-10} mol/L. However, for copper content less than 10^{-10} mol/L, further development of electroanalytical methods is needed. For this purpose, a new modification of carbon paste electrode with pa(E)-2-(Mercapto-phenylamino-methylene)-3-oxo-N-p-tolyl-butanamide (MPMPB) was used to analyze the copper content in very low levels. MPMPB is a new derivative of acetoacetanilide Fig. (1):
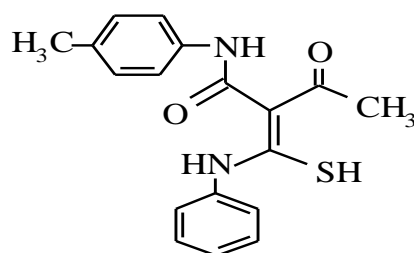

Figure 1. Structure of Pa(E)-2-(Mercapto-phenylamino-methylene)-3-oxo-N-p-tolyl-butanamide

2. EXPERIMENTAL

2.1 Apparatus

All voltammetric measurements were carried out using EG&G Princeton Applied Research (PAR Princeton, NJ, USA) - Model 273 A potentiostat, calculated by electrochemical software version

4.30- model 270/250. A three–electrode measuring cell was used, one of which was hand–make working carbon paste electrode that prepared previously [37], reference electrode of Ag/AgCl (saturated KCl) and counter electrode of platinum wire was used. The transfer of mass was done using a Teflon–coated bar (KIKA Labortechinik, Germany), at approximately 400 rpm magnetic stirrer rotation. All pH measurements were carried out using VWR scientific products model 2000, USA.

2.2 Synthesis of ligand

(E)-2-(Mercapto-phenylamino-methylene)-3-oxo-N-p-tolyl-butanamide L1(MPMPB) was synthesized as follows: 30mL of a suspension solution of potassium hydroxide in DMF (0.01 mole/l) and a solution of phenyl isothiocyanate 0.01 mole/l were added to the 0.01mole/mol of acetoacetanilide solution[38]. Then, the mixture was stirred magnetically for 5 h at 25 °C. The reaction mixture was placed in ice bath and then acidified with 0.2 ml of 10% v/v HCl. The formed solid product was filtered off, washed with water, dried from ethanol to give compound. Elemental analysis, IR, UV-Vis spectra and thermal analysis were used for the characterization of the produced compound.

2.3 Reagents and Solutions

All chemical used were either analytical or primary standard grade and were used directly without further purification. Bi-distilled water and Ethanol were used throughout Standard free sodium hydroxide solution 0.2 M; the sodium hydroxide solution was standardized against standard potassium hydrogen phthalate.

The solution of Cu(II) ion (Merck, BDH) as nitrate was prepared and titrated complexometrically by EDTA.

(MPMPB) ligand Stock standard solution (1×10^{-4} M) was prepared at 25°C in 50% ethanol.

2.4 Methods

2.4.1 Electrode Modification

Carbon paste electrode 15% was prepared by mixing with 4.25 gm of pure carbon with 0.75 gram paraffin oil. Carbon paste electrode was modified MPMPB by immersing it in 1×10^{-4} mol/L (MPMPB) solution for about 20 seconds. MPMPB was absorbed on the electrode surface. Then, the electrode is ready for the Copper preconcentration step.

2.4.2 Voltammetric Procedure for Cu(II) Determination

The preconcentration step was performed by immersing the modified carbon paste electrode in stirring 15 ml sample solution for 5 min. at potential rang from - 0.1 to - 0.6 V for (MPMPB) with Cu(II), then stop the stirring of the solution . After delay period of15 sec, the background current was decreased

and the square wave voltammogram was recorded in the potential direction. for each analysis, a renewed carbon paste surface was used.

For determination of Cu(II) ion 30 μL, 2×10^{-6} M (containing 127.09 ng/mL) of Cu(II) metal was added to 15 ml 0.1M Britton – Robinson buffer pH = 6.0. The solution was magnetically stirred at 400 ramps at open circuit conditions and the square wave voltammogram was recorded.

For determination of Cu(II) ion in real sample 30 μL of sample was added to 15 ml 0.1M Britton – Robinson universal buffer solution pH 6.0. After that different concentrations of Cu(II) were added by using Standard addition method. In all measurements the square wave voltammogram was reported in negative potential direction. The optimum practical parameters adjusted for the determination of Cu(II) by SWCASV using modified CPE illustrated in Table 1.

Table 1. The optimum practical parameters for the determination of Cu(II) by SWCASV at CPE.

Parameter	Selected value
Accumulation potential	-0.1 V
Accumulation time	Various
Scan increment	2 mV
Frequency	50 HZ
Modulation time	10 S.
Final potential	-0.6 V
Buffer type	0.1M Britton- Robinson universal buffer
pH	6.0

3. RESULTS AND DISCUSSION

3.1 Possible Mechanism and Voltammetric measurements

The possible mechanism for the formation of the Cu(II)-MPMPB compound on the electrode surface [39], the MPMPB compound can be strongly associated with a carbon paste electrode surface as a result of coordination to the copper ion producing a surface complex. Due to The metal ion coordination number of 6, the electrons spread over the whole of the ions forming the complex of Cu(II)-MPMPB and its reduction product Cu(I)-MPMPB Fig. (2).

As the copper ion forming 6 coordinate covalent bonds and the central ion is bonded to only two sites of the ligand molecule, four water molecules should bonded to the center of the ion. In addition, the voltammograms of the pure and coordinated ligand have similar waves to that for keto or Imine group, indicating that these groups may not participate in the coordination with the copper ion.
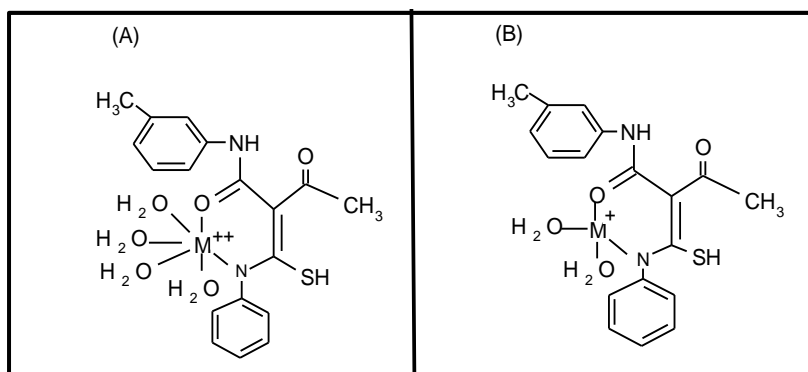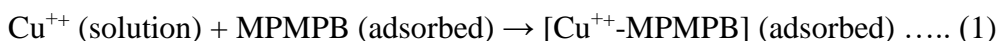
Figure 2. Proposed complexes structures of (A) Cu++ - MPMPB and (B) Cu+-MPMPB.

The surface stripping voltammograms recorded after electrolyte preconcentration step in an aqueous solution with a concentration of 2×10^{-10} mol/L Cu(II) ion. The broad peak current observed at Emax=-0.23V is corresponding to the surface electrochemical response of MPMTB ligand. The keto or imino group contribute in a two-electron reversible redox reaction. The stripping peak near Emax= -0.23V can be interpreted as the catalytic-adsorptive current to the preconcentrated Cu(I) - MPMPB complex.

The possible mechanism for the whole electrochemical reactions may be proposed as follows for Cu(II)–MPMPB Complex.

Preconcentration:

Cu^{++} (solution) + MPMPB (adsorbed) $\rightarrow$ [Cu^{++}-MPMPB] (adsorbed) ….. (1)

Reduction:

[Cu^{++}- MPMPB] (Adsorbed) + e^- $\rightarrow$ [Cu^+ - MPMPB] (Adsorbed) ………. (2)

3.2 Effect of Supporting Electrolyte and pH

The influence of supporting electrolyte on peak current response of Cu(II) ion with ligand (MPMPB) was examined using different supporting electrolytes such as Potassium Chloride, Sodium nitrate, sodium Perchlorate Acetate buffer, Phosphate buffer and Britton – Robinson universal buffer. The type of buffer was selected based on the Both the peak shape and height.

The Britton – Robinson (universal buffer) solution was selected for determination of these trace Cu(II) ions as optimum conditions. The effect of pH of universal buffer solution on square wave stripping voltammetry of trace ions Cu (II) metal ions 2×10^{-6} M (127.09 ng/mL) in 0.1 M Britton – Robinson (universal buffer) at different pH range (3–12) was studied respectively, as shown in Fig. (3).

Firstly, very small current was observed at (pH = 4) which then increased steadily up to pH = 6 and there is no improvement was observed after that value, and therefore (pH 6) was used in all measurements. Moreover, by increasing the pH over than 6, less negative values of the cathodic potential curve of the Cu(II) with ligand (MPMPB) were observed. The best medium used for studying the stripping analysis of Cu (II) with ligand (MPMPB) is 0.1M Britton – Robinson universal buffer (pH = 6.0).
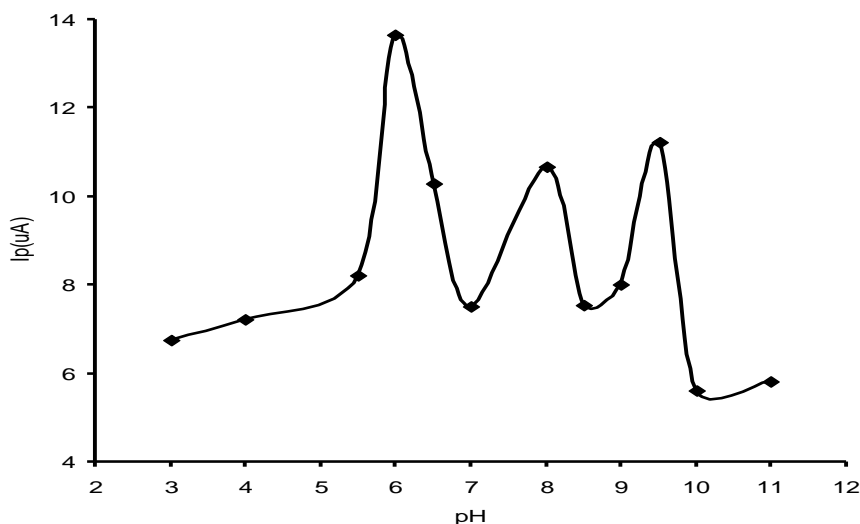
Figure 3. Plot of Ip versus pH using Britton–Robinson buffer solution in presence of 127.09 ng/mL of Cu(II) ion at -0.1V accumulation potential and 15s accumulation time.

3.3 Effect of Buffer Concentration

The effect of buffer concentration of universal buffer of pH 6.0 on the square wave stripping voltammetry of trace Cu(II) ions was investigated. The study utilizing (127.09 ng/mL) Cu(II) using different ionic strength from 0.02-0.6 M of Britton– Robinson universal buffer. Figure (4) illustrate the plot of peak current versus buffer concentration, the study raveled that the best medium used for studying the stripping analysis of Cu(II) ion is 0.1 M Britton – Robinson universal buffer (pH= 6.0).
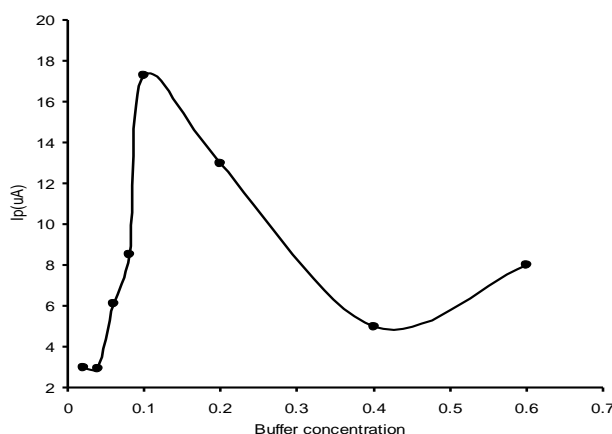

Figure 4. Plot of Ip versus buffer concentration in presence (127.09) ng/mL of Cu(II) ion at (pH=6.0), -0.1V accumulation potential and 15 s accumulation time.

3.4 Effect of Accumulation Potential

The influence of accumulation potential on stripping current for 2×10^{-6} M (127.09 ng/mL) of Cu(II) at pH = 6.0 in potential range from +0.2 to (-0.6)V at 15 s. For Cu(II)-(MPMPB) complex preconcentration, the peak current of stripping signal complex increase in range from +0.2 to (-0.1) V

potential, however, by shifting the accumulation potential negatively from (-0.1) to (-0.6)V stripping peak current decrease sharply. The maximum peak current value was recorded at initial potential (-0.1) V, which was selected in the subsequent experiment. Plot of peak current against initial potential is shown in Fig.5.
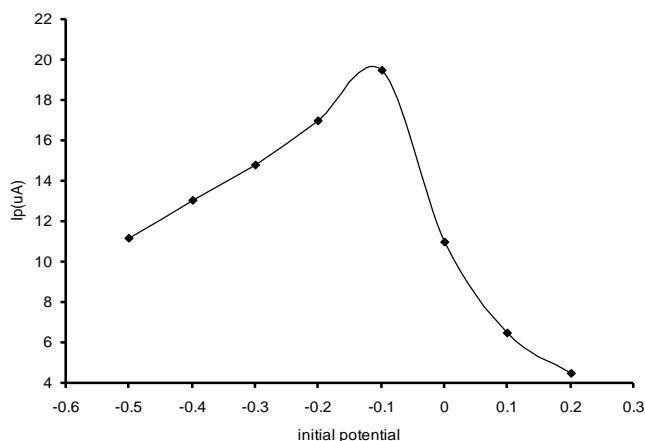

Figure 5. Plot of Ip versus different initial potentials (V) in presence of (127.09 ng/mL) of Cu(II) ion at (pH = 6.0).

3.5 Effect of Accumulation Time and Reproducibility

The relation of the peak current with accumulation time was investigated for a concentration of 2×10^{-6} (127.09 ng/mL) of Cu(II) at 0.1M Britton – Robinson buffer (pH = 6.0). The stripping wave increases linearly with increasing accumulation time up to 105 s after that occur a decrease in the stripping signal. Figure 6 show plot of peak current versus different of accumulation times.
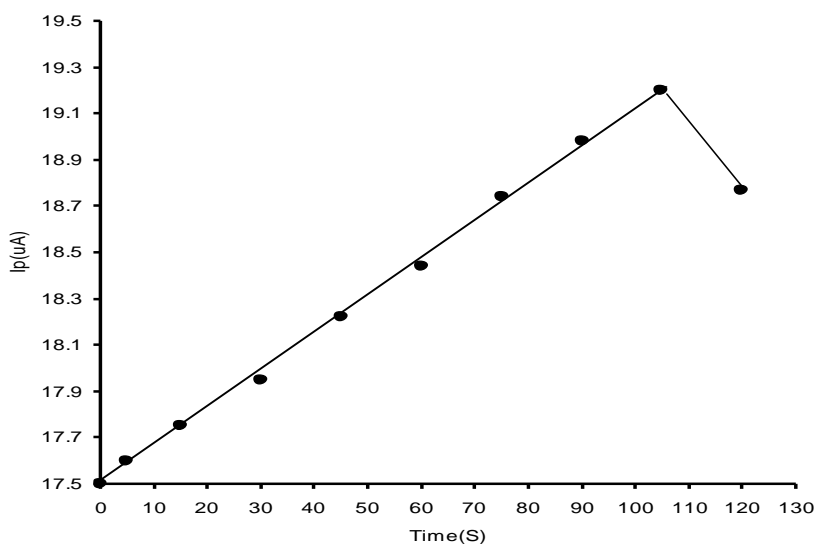

Figure 6. Plot of the peak current versus different pre-concentration times in presence of 127.09 ng/mL of Cu(II) ion and 652.8 ng/mL of (MPMTB) at optimum conditions.

3.6 Effect of Concentration and Quantitative Detection Limit

A well–defined concentration of Cu(II) ion with (MPMPB) complex was yielded using Square Wave Cathodic Adsorptive Stripping Voltammetry (SWCASV) method. The range of the concentration of Cu(II) - (MPMPB) complex with different preconcentration times was investigated.

For Cu(II) the quantitative evaluation is based on the dependence of the peak current on Cu (II) concentration. A well–defined peak was observed with the stirring at (-0.23V) of Cu(II) ion is shown in Fig. 7, at 15 s. A linear concentration ranges were (2×10^{-10} - 10×10^{-10} M) 0.013-0.064 ng /mL at 15, 30 s and (2×10^{-10} - 12×10^{-10}M) 0.013 – 0.076 ng/mL at 60 s, respectively. A deviation from linearity is observed over the concentration of Cu(II) ion above 0.076 ng/mL. The Calibration plot of the peak current versus different concentrations is shown in Fig. 8. In addition, Table (2) shows different ranges of linearity at different times, the detection limits calculated as 3σ/b [40–42], where σ = standard deviation (SD) of the intercept and b is the slope, limits of quantitative (LOQ) was computed as 10σ/ b. The lower detection limit of Cu(II) ion using the proposed method was 1.2 pg/L (1.88×10^{-14} M) with relative standard deviation ± 0.155 %, Correlation coefficient r = 0.9986 (n = 5) at accumulation time 60 s . In comparison with other reported method [44] we can concluded that our method is good because the deposition time in our work is 60 sec (SD= ± 0.155) but in the reported method is 10 min(SD= ± 3.2 %). However, the comparison between the proposed electrode and reported electrodes are shown in table 3.

Table 2. Aspect of linear correlation of calibration curve for Cu(II) ion in presence of 0.1 M Britton–Robinson buffer (pH= 6.0) using SWCASV at different deposition times.

Deposition time (s)	Detection limit (ng/L)	Linearity range (ng/mL)	Correlation Coefficient (r)	Slope (uA/ngmL) ±SD	Intercept (µA)±SD
15	0.002	0.012 – 0.064	0.9996	323.2 ± 15.90	4.55 ± 2.22
30	0.0051	0.012 – 0.064	0.9996	343.6 ± 13.58	5.40± 0.574
60	0.0012	0.012 – 0.076	0.9998	242.3± 3.14	2.65 ± 0.155

Table 3. Comparison between the proposed electrode and reported electrode.

Ref. No.	Electrode	Detection limit	Method
This work	Carbon Past Electrode (CPE)	1.2 pg L^{-1} (1.88×10^{-14} mL^{-1}) at 60 sec deposition time	adsorptive Square wave stripping voltammetry
43	carbon nanotubes paste electrode modified with crosslinked chitosan	1×10^{-8} mL^{-1}	linear scan anodic stripping voltammetry (LSASV)

| 44	gold electrode modified	1.8×10^{-14} m L^{-1} at 10 min deposition time	Cyclic voltammetry
45	carbon paste electrode	5.0×10^{-10} M	Differential pulse stripping voltammetry
46	glassy carbon electrode (GCE)	1.7×10^{-9} ML^{-1}	Square wave stripping voltammetry
47	glassy carbon electrode (GCE)	4.9 ± 0.2 nM	Differential pulse voltammetry
48	carbon paste electrode	$0.01 \mu g$ L^{-1}	Stripping voltammetry
49	Polypyrrole (PPy/Nitroso-R films)	0.7 ng mL^{-1}	Stripping voltammetry
50	Nafion-modified glassy carbon electrode	3.0×10^{-9}	Differential pulse stripping voltammetry
51	BiF modified glassy carbon electrode (GCE)	9.6×1^{-10} mL^{-1}	Square wave stripping voltammetry
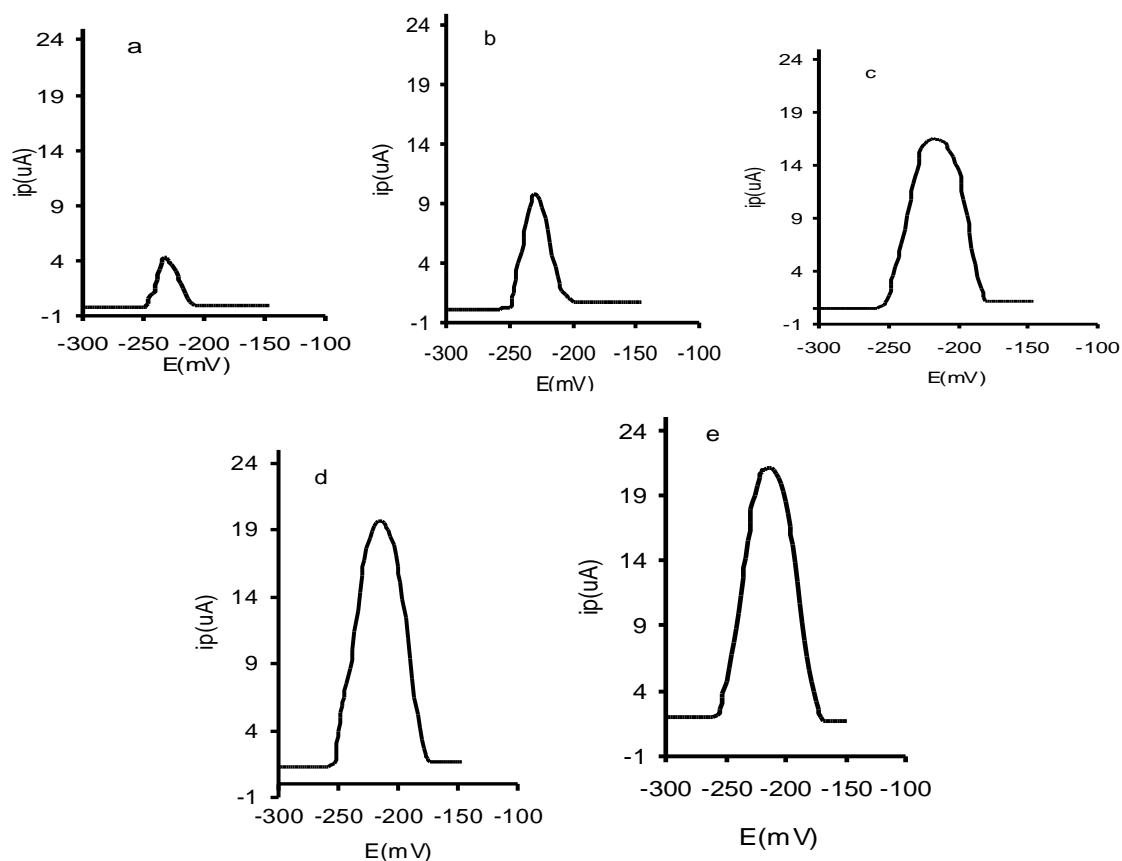
Figure 7. Typical SWCAS voltammograms at different concentrations of Cu(II) ion in presence 0.1M Britton–Robinson buffer (pH= 6.0) and15s accumulation time,(a):0.013 ng/mL,(b):0.025 ng/mL, (c):0.038 ng/mL, (d) 0.051 ng/mL, (e): 0.064 ng/mL.
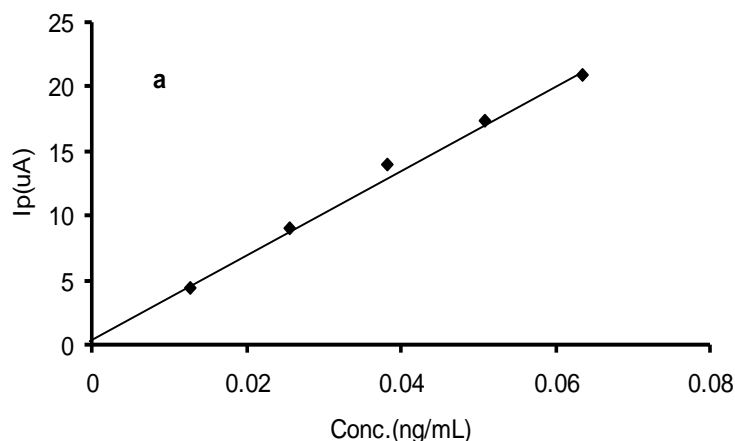
Figure 8. Plot Ip versus concentration of Cu(II) ion 0.1M Britton– Robinson buffer (pH=6.0)at accumulation time 15s

3.7 Effect of Interferences

The efficiency and selectivity of the proposed method for the analysis of Cu(II) - MPMPB complexes was investigated. A solution containing 2×10^{-6} M of Cu(II) ion was spiked with excess amount of some common interfering species (10:1) the interfering species Glycine, DL- argnine, DL - Valine (amino acids), Ascorbic acid, Urea, Glucose, Fe(III), pb(II), Na(I) and Cd (II). These interfering species were added directly to voltammetric cell under the optimum experimental conditions.

3.7.1 Effect of Some Amino Acids

Different concentrations Glycine, DL- argnine and DL - Valine ranged 2×10^{-6} - 2×10^{-5} M were added to 2×10^{-6} M of Cu(II) -(MPMPB) complex then the currents were recorded. The results illustrated that the addition of 2×10^{-6} - 2×10^{-5} M of Glycine, DL- argnine and DL-Valine increase in the current peak by approximately 12.16 - 13.63%, 61.28 -79.08% and 63.49 -76.19 % for Glycine, DL- argnine and DL-Valine, respectively.

3.7.2 Effect of Ascorbic Acid, Urea and Glucose:

Also, different concentrations of Ascorbic acid, urea and Glucose ranged from 2×10^{-6}- 2×10^{-5} M were added to 2×10^{-6} Cu(II)-(MPMPB) complex, and then the peaks responses were recorded. A significant interference was observed. The addition of 2×10^{-6} - 2×10^{-5} M from Ascorbic acid, urea and Glucose to Cu(II)-(MPMPB) complex, showed the peak current increase by about 10.71–26.5 %, 12.19–53.04 % and 10.97–13.04 % for Ascorbic acid, urea and Glucose, respectively.

3.7.3 Effects of Some Metal Ions

The influence of some metal ions such as Pb (II), Fe (III), Cd (II), and Na (I) on the voltammogram of 2×10^{-6} M of Cu(II)-(MPMPB) was investigated. Various concentrations of these

metal ions ranged from 2×10^{-6} - 2×10^{-5} M were spiked. In the case of Fe (III),the current was decreased by (-30.58-(- 21.49) %. However, by adding Pb(II), the current peak response was decreased by about 23.56–27.48 %. For Cd(II) and Na (I) the peak current response increase by about 11.30–31.5 % and 25.43-30.43 %, respectively.

3.8 Application to real sample

The applicability of the developed method was investigated by the determination of Cu(II) in natural waters [52–56] and human hair. For human hair analysis, the study was approved by the local ethical committee of Umm Al-Qura University, Medical Faculty, Saudi Arabia, Prior to conduct of the study, each human was informed about the purpose of the analysis and signed an informed consent. Human hair was prepared using wet ashing procedure described previously [57]. The hair sample was dried at 50 °C for 2 h and rinsed with acetone. 4.20 g of the dried sample was precisely weighed and ashed in a furnace at 700°C. 2 g of the ashed sample was dissolved in 2 mL of concentrated nitric acid. The solution was boiled untill brown fumes formed, then cooled and diluted with double distilled water to 20 mL. 30 µL of the diluted solution were added to 15 mL 0.1M Britton–Robinson buffer (pH 6), and the proposed procedure was applied to the resultant solution. For natural waters, real water samples were taken instead of distilled water for the preparation of Britton–Robinson buffer (pH 6), the resultant solutions were analysed using and the proposed procedure. To minimize the analysis errors, the standard addition method was applied for the determinations of copper ions. To investigate the accuracy and precision of the proposed method, the obtained results were compared statistically with Inductive Coupled Plasma method (ICP). The results were summarized in Table 4. Statistical comparison at the 95% confidence level demonstrated no significant difference between the results obtained with the proposed procedure and those of the ICP standard method. Also, the concentration of Cu found in human hair sample using the proposed procedure (13.55 µg/g) is comparable with that reported (12.41µg/g), (13.90µg/g), (14.89–15.29 µg/g) and (4.90–22.54 µg/g) [58–61].

Table 4. Comparison of Cu(II) Levels of in real water and human hair samples obtained with the proposed method and ICP standard method.

Sample	Present method, ng/mL or µg/g for hair	ICP method ng/mL or µg/g for hair	Recovery of ICP, %	Spiked Cu2+, ng/mL	Found Cu2+, ng/mL	Recovery of ICP, %
Red Sea Water	0.14± 0.07	0.15 ± 0.06	93.33	100	99.84 ± 1,53	99.76
River Water	10.33 ± 0.15	10.55 ± 0.04	97.91	100	103 ± 0.08	99. 83
Human Hair	13.55 ± 0,65	14.01 ± 0,07	96.71	-	-	-

4. CONCLUSIONS

A novel method based on Square wave cathodic adsorptive stripping voltammetry was successfully developed for preconcentration and determination of Cu(II) in natural waters and human hair samples. The performance of the proposed method was evaluated and optimaized for

preconcentration of ultra coper traces from real water and hair samples. Under the optimaized condition, a convenient operation, rapid, sensitive, and effective method for determining Cu(II) in water and human hair samples. Statistical comparison of the results obtains using the proposed method with ICP standard method showed good recoveries and precision. The LOD was 1.2 pg/L (1.88×10^{-14} M) with relative standard deviation ± 0.155 %.

CONFLICTS OF INTEREST
The authors declare that there is no conflict of interest.

References

1. A. Arranz, S.F. de Betoño, J. M. Moreda, A. Cid , J. F. Arranz, *Analyst,* 122 (1997) 849.
2. X. Tan, J. Hu,Q. Li, *Analyst*, 122 (1997) 991.
3. A.C. Le Gall, C.M.G. Van den Berg, *Anal Chim Acta,* 282 (1993) 459.
4. M. Khodari, M. Ghandour and A. M. Taha. Talanta, 44 (1997) 305–310.
5. A. Safavi and E. Shams, *Anal. Chim. Acta*, 396 (1999) 215.
6. G. Mattson, L. Nyholm, A. Olin, *J. Electroanal Chem.,* 379 (1994) 49.
7. J. Wang, J. Lu, C. Yarnitzky*, Anal. Chim. Acta,* 280 (1993) 61.
8. C.M.G. Van den Berg, *Anal. Chem.,* 57 (1985)1532.
9. J. Pelzer, F. Scholz, G. Henrionand, P. Heininger, *Fresen. Zeitsch. Analyti. Chemie*, 334 (1989) 331.
10. K. Torrance, C. Gatford, *Talanta*, 32 (1985) 273.
11. J. Wang, P. A. M. Farias, J.S. Mahmoud, *Anal. Chim. Acta,* 171 (1985) 215.
12. C.M.G. Van den Berg, *J. Electro. Chem. Interfa. Electrochem.,* 215 (1986) 111.
13. K. Jiao, W. Jin, H. Metzner, *Anal. Chim. Acta,* 260 (1992) 35.
14. J. Wang, J. Lu, K. Olsen, *Analyst,* 117 (1992) 1913.
15. K. Yokoi, C. M.G. Van den Berg, *Anal. Chim. Acta,* 257 (1992) 293.
16. Z. Gao, K.S. Siow, *Talanta,* 43 (1996) 255.
17. J. Wang, B. Tian, J. Lu, *Talanta,* 39 (1992) 1273.
18. M. Vega, C.M.G. Van den Berg, *Anal. Chem.,* 69 (1997) 874.
19. A. Bobrowski, A.M. Bond, *Electroanalysis*, 3 (1991) 157.
20. B. Godlewska, J. Golimowski, A. Hulanicki, C.M.G. Van den Berg, *Analyst*, 120 (1995) 143.
21. A. Bobrowski, *Anal. Lett.,* 23 (1990) 1487.
22. J.R. Donat, K.W. Bruland, *Anal. Chem.,* 60 (1988) 240.
23. J. Wang, Z. Myung, M. Jianmin, M. Vuki, *Microchem J*, 62 (1999) 121.
24. J. Wang, J. Zadeii, M. S. Lin, *J. Electro. Chem. Interf. Electrochem.,* 237 (1987) 281.
25. M. Z. Czae, J. Wang, *Talanta*, 50 (1999) 921.
26. M.A. Cousino, T.B. Jarbawi, H.B. Halsall, W. R. Heineman, Anal. Chem., 69 (1997) 544A.
27. H.G. Valery, T.R. Ngono, H. Saâdane, M. Ennachete, M. Khouili, A. Hafid, L. Benoît, A.

Chtaini,   *Pharm. Anal. Acta*, 4 (2013) 2153.
28. X. Wang, Y. Zhang, *Guangzhou Chem Ind,* 23 (2015) 161.
29. D. A. Phipps, Oxford University Press, (1976) London, UK.
30. T. Theophanides, J. Anastassopoulou, *Crit Rev Oncol Hematol*, 42 (2002) 57.
31. J. Wang, S.P. Chen, M. S. Lin, *J. Electro. Chem. Interf. Electrochem.,* 273 (1989) 231.
32. C.M.G. Van den Berg, *Anal. Chim. Acta, 16* (1984) 195.
33. C.M.G. Van den Berg, Mar Chem., 5 (1984) 1.
34. L.M. Wierl, A. R. Guadalupe, H. D. Abruna, *Anal. Chem.,* 57 (1985) 2009.
35. D.M.T. O'Riordan, G.G. Wallace, *Anal. Chem.,* 58 (1986) 128.
36. S.V. Prabhu, R. P. Baldwin, L. Kryger, *Anal. Chem.*, 59 (1987) 1074.
37. O.A. Farghaly, *Talanta*, 63 (2004) 497.
38. A.A. Gahlan, A.Y. El-Sayed, M.A. Marouf, M.M. Tawfik, *Int.J.Adv. Res.,* 3 (1) (2015) 630.
39. C.R.B. Cordeiro, A. L. B. Marques, E. P. Marques, W. S. Cardoso and J. Zhang, Int. J. Electrochem Sci.,1   (2006) 343.
40. O.A. Farghaly, *Microchem J*, 75 (2003) 119.
41. A.M.M. Ali, O. A. Farghaly and M. A. Ghandour, *Anal. Chim. Acta, 412* (2000) 99.
42. O.A. Farghaly, H.M.A. El-Wadood, M.A. Ghandour, *J. Pharm. Biomed. Anal.,* 21 (1999) 233.
43. B.C. Janegitz,L.H. Marcolino-Junior, S.P. Campana-Filhoc, R.C. Faria, O.Fatibello- Filho, *Sensors   and Actuators B* 142 (2009) 260.
44. R.S. Freire, L.T. Kubota, *Electrochimica Acta*, 49 (2004) 3795.
45. H. Alemu, B.S. Chandravanshi, *Anal. Chim. Acta*, 368(1998) 165.
46. C.E. Cardoso, W.F. Pacheco, R. Sarubi. M.L.N. Ribeiro, Pércio A.M. Farias, R.Q. Aucelio, *Anal.   Sci.*, 23(9) (2007)1065.
47. H. Wei, D. Pan, X. Hu, M. Liu, H. Han, *Microchimica Acta,* (2018) 185.
48. V. Izadkhah, A. Farmany, S.S. Mortazavi, *J. Indus. Engin. Chem.*, 21(25) (2015) 994.
49. A. Mohadesi, A. Salmanipou, S.Z. Mohammadi, A. Pourhatami, M.A. Taher, *J. Braz. Chem.   Soc.*, 19 (5) (2008) 956.
50. D. Stankovic, G. Roglic, J. Mutic, I. Andjelkovic, M. Markovic, D. Manojlovic, *Int. J. Electrochem. Sci.,* 6 (2011) 5617.
51. E.A. Al-Harbi, M.S. El-Shahawi, *Electroanalysis,* 30 (8) (2018) 1837.
52. G. Scarano, E. Morelli, A. Seritti, A. Zirino, Anal Chem., 62 (1990) 943.
53. M. A. Shriadah, M. A. Okbah, M.S. El-Deek, *Water Air Soil Pollut*., 153 (2004) 115.
54. A. Bobrowski, K. Agnieszka, M. Mariola, K. Aneta, *Insights Anal Electrochem.,* 1 (2015).
55. A.S. Amin, M.A. Kassem, Anal. Chem. Lett., 6 (2016) 820.
56. M. Majidian, J.B. Raoof, S.R. Hosseini, R. Ojani, *J. Iran Chem. Soc.,* 14 (2017) 1263.
57. A. Mohadesi, M. A. Taher, F. Majidi, J. Anal. Chem., 66 (2011) 207.
58. A. Mohadesi, M.A. Taher, *Talanta,* 72 (2007) 95.
59. V.V. Ramakrishna, V. Singh, A.N. Greg, *Sci. Total Environ.,* 192 (1996) 259.
60. A. Bertazzo, C. Carlo, M. Biasiolo, G. Allegri, G. Cirrincione ,G. Presti, *Biol. Trace Elem. Res.,* 52 (1996) 37.
61. K.S. Rao, T. Balaji, T. P. Rao, Y. Babu, G.R.K. Naidu, *Spectrochim Acta B,* 57 (2002) 1247.