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PAGES: 11-16

Gazi University Journal of Science
GU J Sci
24(1):11-16 (2011)

GUJS
www.gujs.org

# Preconcentration and electroanalysis of copper at glassy carbon electrode modified with poly(2-aminothiazole)

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*Received: 11/03/2010 Revised: 09/06/2010 Accepted: 10/06/2010*

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## ABSTRACT

Conducting poly(2-aminothiazole), PAT, was synthesized in acetonitrile with tetrabutylammonium tetrafluoroborate, TBAFB, as supporting electrolyte via constant potential electrolysis, CPE. Glassy carbon, GC, electrode was modified by immersing the electrode in a DMSO solution of PAT. Preconcentration of copper on polymer matrix was carried out at –0.7 V. The effects of preconcentration time and pH and Cu(II) concentration of the preconcentration solution on the stripping peak current of copper were studied.

**Keywords**: *Poly(2-aminothiazole), conducting polymer, modified electrode, copper determination, stripping voltammetry*

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## 1. INTRODUCTION

Copper is an essential trace element in biological systems. However, it has an important role in water as pollutant. Therefore, developing sensitive and selective methods for the determination of copper are required. Several analytical techniques have been employed in copper ion analysis, such as atomic absorption spectrometry (AAS) [1, 2], UV-spectrophotometry [3, 4], atomic fluorescence spectrometry (AFS) [5], X-ray fluorescence [6] and inductively coupled plasma spectrometry (ICP) [7-9]. These techniques commonly are used for trace measurement of heavy metal ions in the laboratory and usually are not suitable for the task of in situ testing and monitoring. Expensive instrumentation and complicated sample preparation processes are also required. Electrochemical techniques are in the most favorable techniques for the determination of heavy metal ions because of their low cost and high sensitivity [6]. Modification of the working electrode surface with an appropriate reagent offers analytical methods with enhanced selectivity and sensitivity [10, 11]. Modification can be achieved by electrochemical, chemical, and physical methods. The modifiers used include organic chelating groups [12], polymers [13, 14], and nanoparticles [15].

2-Aminothiazole, AT, modified silica gel has been used for the removal of several metal ions from aqueous solutions [16, 17]. Electroanalytical application of AT-modified silica gel for the stripping analyses of several metal ions has also been reported [11, 18, 19]. To our knowledge, no electroanalytical application of PAT has been reported. In this work, we present results of measuring Cu(II) in aqueous solutions with a GC disk electrode modified with PAT.

## 2. EXPERIMENTAL

### *2.1. Materials*

The monomer AT (Aldrich Chemical Co., 90%) was purified by recrystallization from methanol. TBAFB (Aldrich Chemical Co.) was used without further purification as supporting electrolyte for constant potential electrolysis. $Cu(NO_3)_2$, $Ni(NO_3)_2$, $Co(NO_3)_2$

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Corresponding author, e-mail: zoktem@kku.edu.tr and $Zn(NO_3)_2$ (Merck A.G.) were used as received. All other chemicals (Merck A.G.) were analytical reagent grade and were used as received. The solutions buffered with standard aqueous buffer solutions (50%, V/V) of 0.2 M KCl/0.2 M HCl (pH=1-2), 0.1 M potassium hydrogen phthalate/0.1 M HCl (pH=3-4) and 0.1 M potassium hydrogen phthalate/0.1 M NaOH (pH=5) [20]. Cu(II) solutions in 0.1 M NaCl(aq) and all other aqueous solutions were prepared with deionized water. Electrodes were cleaned with deionized water, also.

### *2.2. Instrumentation*

Electrochemical measurements were performed with a potentiostat, Wenking POS 88, Bank Electronics, Germany, in a conventional three-electrode arrangement, equipped with a GC (3.0 mm diameter) working electrode, a platinum wire counter electrode, and a Ag/AgCl reference electrode. GC electrode was polished with 1.0 and 0.1 µm alumina powder. Electrochemical measurements were conducted at room temperature.

### *2.3. Preparation of poly(2-aminothiazole)-modified GC electrode*

PAT was synthesized on a Pt electrode by constant potential electrolysis of 0.2 M AT in acetonitrile containing 0.1 M TBABF, as supporting electrolyte, at +2.5 V. Details of CPE of AT and characterization of PAT is presented elsewhere [21]. Modified GC disk electrode was prepared by immersing the electrode in a DMSO solution of PAT (0.01 g polymer/mL), followed by evaporation of the solvent and washing the electrode with deionized water. The electrode coated with a yellow PAT film, PAT-GC electrode, was used in Cu(II) measurements.

### *2.4. Voltammetric measurements*

PAT-GC electrode was used as the working electrode in voltammetric measurements. Prior to measurements, the electrode was preconcentrated with copper. Preconcentrations were performed in 0.1 M NaCl(aq) solutions with definite Cu(II) concentrations. After washing the modified electrode enriched with copper, it was used in stripping voltammetric measurements. The measurements were carried out in 0.1 M NaCl(aq) solutions in the potential range of –0.7 to 0.6 V at a scan rate of 50 $mVs^{-1}$.

## 3. RESULTS AND DISCUSSION

### *3.1. Cyclic voltammetry*

The efficiency of PAT-GC electrode in Cu(II) measurement was studied by stripping voltammetry in 0.1 M NaCl(aq) solution. The polymer obtained from the electrochemical polymerization of AT, carried out in acetonitrile on Pt electrode was used for the modification of GC disk electrode. The conductivity of PAT was measured to be about $10^{-6}$ S $cm^{-1}$ by four-probe technique [21]. PAT-GC electrode did not indicate any electroactivity in the range of –0.7 to 0.6 V. Cyclic voltammograms, CV, measurements carried out with GC electrode in 0.2 mmol $L^{-1}$ Cu(II) showed the oxidation of copper at –0.030 V. Preconcentration of copper on PAT-GC electrode was conducted at –0.7 V in aqueous solution of $1.0 \times 10^{-3}$ M Cu(II) and 0.10 M NaCl for 5 min. CV's recorded between –0.7 to 0.6 V in 0.10 M NaCl(aq) showed stripping of reduced copper at –0.13 V (Fig. 1). The obtained oxidation behavior of copper indicated that PAT-GC electrode could be used in Cu(II) measurements in aqueous solutions.

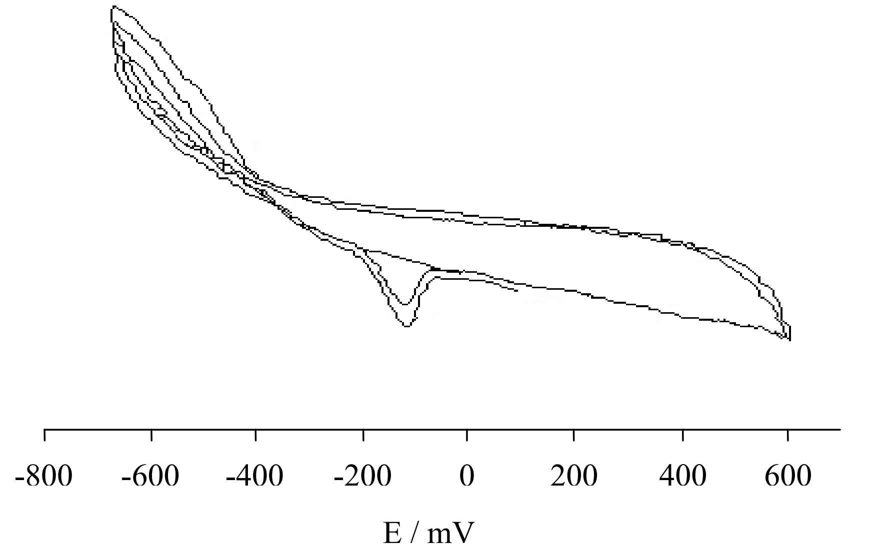

Figure 1. CV of copper on PAT-GC electrode in 0.1 M NaCl(aq)

### 3.2. EDX measurements

Accumulation of copper on polymeric matrix was confirmed on an IXRF, EDS2000 microanalysis system. Obtained spectrum indicated the presence of copper on PAT film (Fig. 2).

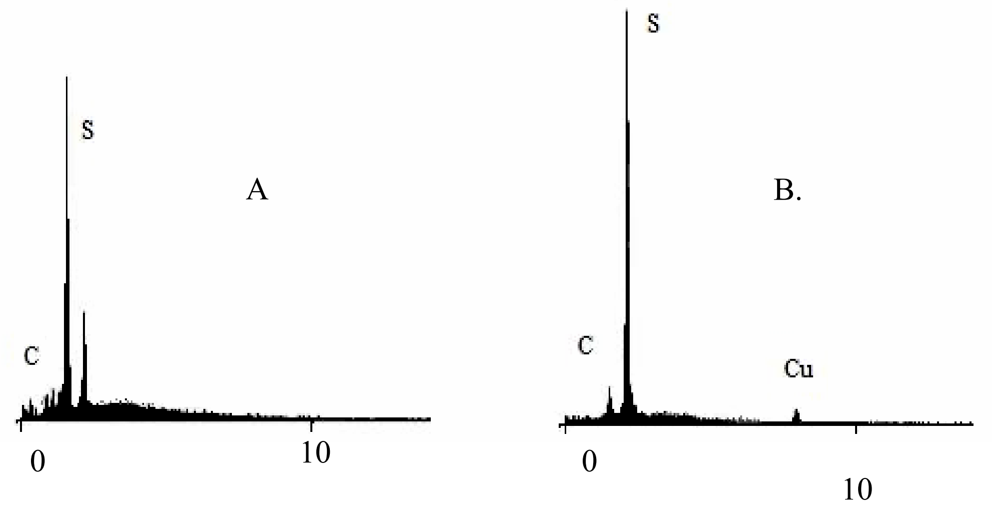

Figure 2. EDX spectrum of a) PAT, b) PAT preconcentrated with copper

### 3.3. Influence of pH

The influence of pH of Cu(II) solution on the preconcentration of copper on PAT-GC electrode was studied with Cu(II) solutions buffered to different pHs. Preconcentration of the polymeric matrix was performed in aqueous 0.20 mmol $L^{-1}$ Cu(II) solution at –0.7 V for 5 min and then the electrode used in the stripping voltammetric measurement of Cu(II). The plot of maximum oxidation peak current versus pH of the preconcentration solution indicated the maximum sensitivity of PAT-GC electrode at pH=1.0. Sensitivity of the modified electrode decreased continuously with the increase in solution pH (Fig. 3). Therefore, further studies were conducted with Cu(II) solutions buffered to pH=1.0.

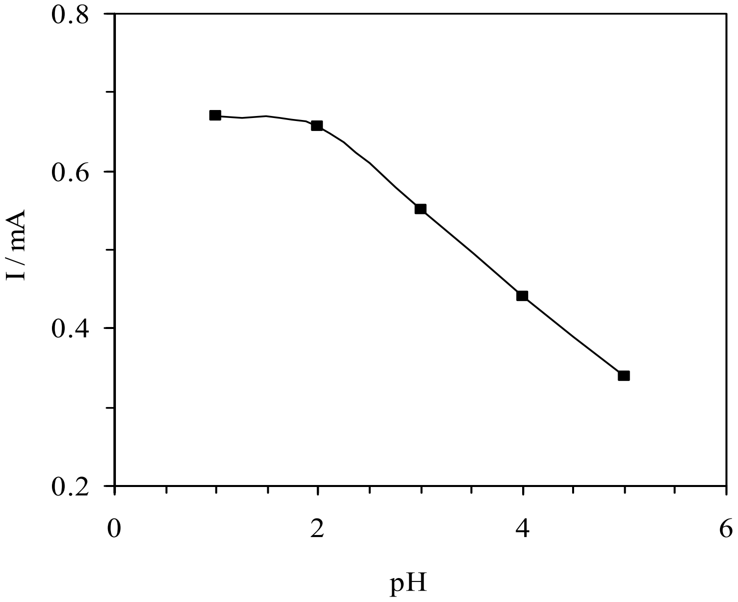

Figure 3. Variation in stripping peak current with pH. $C_{Cu(II)}$= 0.20 mmol $L^{-1}$, $E_d$= –0.70 V and $t_d$= 5 min

### *3.4. Effect of time*

Variation in the stripping peak current with preconcentration time was studied at –0.7 V with aqueous solutions having 0.020 mmol $L^{-1}$ Cu(II) concentrations in 0.10 M NaCl(aq). The solutions were buffered to pH=1.0. The plot of maximum oxidation peak current against time indicated the increase in stripping peak current up to 20 min (Fig. 4).

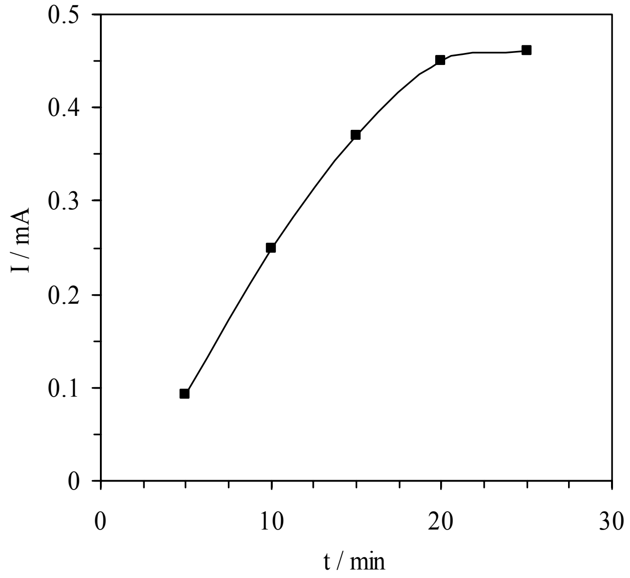

Figure 4. Variation in stripping peak current with time. $C_{Cu(II)}$= 0.020 mmol $L^{-1}$, $E_d$= –0.70 V

### *3.5. Influence of Cu(II) concentration*

Influence of the amount of Cu(II) in the preconcentration solution on the sensitivity of PAT-GC electrode in measuring Cu(II), were carried out with solutions buffered to pH=1.0. The electrode was preconcentrated in solutions with different Cu(II) concentrations at –0.7 V for 20 min. Results showed that PAT-GC electrode could not measure a Cu(II) concentration less than 0.020 mmol $L^{-1}$. The graph of maximum peak current versus Cu(II) concentration indicated an increase in the sensitivity of the electrode with the increase in Cu(II) concentration. However, the linear correlation between stripping peak current and Cu(II) concentration was obtained in the concentration range of 0.040 – 0.10 mmol $L^{-1}$ with a regression equation of I (mA)=22.6C (mmol $L^{-1}$) - 0.607 and a correlation coefficient, $R^2$, of 0.990 (Fig. 5).

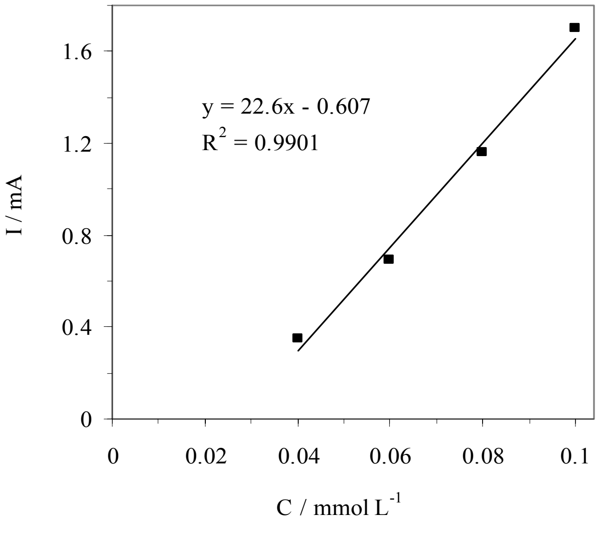

Figure 5. Variation in stripping peak current with Cu(II) concentration at pH=1.0. $E_d$= –0.70 V and $t_d$= 20 min

### *3.6. Interferences*

Effects of Ni(II), Co(II) and Zn(II) ions on the stripping peak current of copper were also studied. Solutions containing 0.2 mmol $L^{-1}$ Cu(II) and 0.3 mmol $L^{-1}$ interfering metal ion were used in CV measurements in the range of −0.7 to 0.6 V. No effect on the stripping peak current and oxidation potential of copper were observed. Voltammograms did not indicate any oxidation or reduction peak due to interfering ions, also. Obtained results showed the insensitivity of PAT-GC electrode to Ni(II), Co(II) and Zn(II) ions.

## 4. CONCLUSION

In this study, GC electrode was modified with PAT by immersing the electrode into DMSO solution of the polymer. CV measurements indicated that the modified electrode could be used in the measurement of Cu(II) in aqueous solutions. The maximum sensitivity of PAT-GC electrode was obtained from the preconcentrations conducted in solutions with pH=1.0 for 20 min. However, concentrations studies showed that the electrode is not sensitive to Cu(II) concentrations less than 0.020 mmol $L^{-1}$ and has a linear stripping peak current – concentration response over ca. 0.040 mmol $L^{-1}$ Cu(II) concentrations.

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