Bismuth Coated Carbon Fiber Microelectrode with Gallic Acid n-Propyl Ester for Trace Copper Analysis

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A bismuth-coated carbon fiber microelectrode was prepared using cyclic voltammetry (CV). An analytical application was performed for the copper analysis with Square Wave Stripping Voltammetry (SWSV). Gallic acid n-propyl ester (PG) was used for the complex formation with a copper ion, and electrochemical measurements were performed with a pre-amplifier of a low-current module for nano amper detection. The effects of various parameters on the response were optimized. Analytical working ranges of 0.03-25.9 μgl^{-1} and 0-25 mgl^{-1} Cu(II) were obtained. The relative standard deviation at 13 mgl^{-1} Cu was 0.9% (n = 12) in optimum conditions. The detection limit was found to have been 0.019 μgl^{-1}, with a 30-sec accumulation time. The developed methods were applied to a copper assay in water samples.

Key Words : Stripping voltammetry, Bismuth coating, Carbon fiber microelectrode, Gallic acid n-propyl ester

1. Introduction

In human science, tracing in the blood, food, and drinking water of copper toxicosis, or copper salt poisoning, which affects the liver, the central nervous system, the eyes, and the kidneys, is very important. The various analytical methods used for this purpose are based on atomic absorption spectrometry, inductively coupled plasma spectrometry, neutron activation analysis, and other instrumentals[1,2]. In analytical science, trace (ppb) assay of electrochemical stripping methods has always been recognized as a powerful technique[3~7]. The accumulation and stripping step is very sensitive, and inexpensively compact systems and numerable working electrode sensors are valuable. Recently, a number of investigators have described various types of electrodes. For example, mercury electrodes[8,9], glassy carbon electrodes[10~12], metal-type electrodes[13], and several other modified electrodes[14~18] have been developed. All the working systems arrived at had very sensitive and specific properties, and variations among the micro- and nanoelectrodes were increased for low-range detection systems and real-time

human body analysis. The first goal of this study is the preparation of a carbon fiber microelectrode[19~23]. Optimum experimental conditions for trace copper analysis were searched for in in vivo and in vitro biological conditions.

On the other hand, with regard to the more sensitive coated electrode techniques developed such as those that involved mercury-coated electrodes[24~27], bismuth-coated electrodes[28~32], chitosan-modified electrodes[33], cysteine-modified mercury film electrodes[33], and nafion/8 quinolinol mercury film-modified electrodes[35], all the coated modifications were very sensitive and had several advantages, whereas commonly used mercury films are environmentally toxic, bismuth-coating methods are environmentally friendly[28], and bismuth powders are used in pharmaceutical treatment. Thus, the second goal of this study refers to the bismuth-coated carbon fiber micro methods, and the sensitivity was increased to ppb levels.

Also in electrochemical voltammetry, sensitive methods are used for various forms of ligand complex formation. For example, uranium determination methods are used for the complex reagent of pyrocatechol oxine, cupferron chloranilic -acid, SALEN propyl-gallate, etc.[36~38]. Moreover, the molybdenum antimony vanadium and uranium detection methods are used for

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the chloranilic acid complex[39]; the copper determination methods, for the copper-adenine complex on mercury drop electrodes[40]; the chromiun and uranium simultaneous analysis methods, for the mixed ligand of propyl-gallate and diethylenetriaminepentaacetic acid[41]. All these methods arrive at very sensitive detection ranges. Thus, the last goal of this study is to examine the propyl-gallate copper complex. The complex signals were sensitivity increased to the ppb-ppt levels. The developed methods are valuable for low-range trace analysis in in vivo or in vitro assays and several other analytical fields.

2. Materials and Methods

2.1. Apparatus and Reagent Solution

Voltammetry measurements were performed with a Bas 100 BW equipped with a faraday cage (Model C2) and a pre-amplifier of a low-current detection module. A three-electrode system was used to monitor the square wave stripping voltmeter (SWSV) signals. The working electrode was a 7 μm diameter carbon fiber. The reference electrode was an Ag/AgCl electrode (saturated KCl), and the auxiliary electrode was a platinum wire. All the solutions were prepared from double-distilled water (-18 M ohm cm). The standard bismuth solution used for the deposition of the bismuth film electrodes was prepared by diluting the corresponding standard stock atomic absorption (1,000 mgl^{-1}). The 0.1M acetic acid buffer solution (pH 4.5) served as the supporting electrolyte.

2.2. Preparation of the Bismuth-plated Carbon Fiber Microelectrode and Procedure

The working electrode was constructed from a 7-microdiameter carbon fiber. About 15 mm of its length was attached to a copper wire via silver paint. Then this fiber was inserted into a 0.3 mm-diameter polyethylene tube. The electrode was sealed via heating. The electrode was then cleaned via sonication for 10 min, first in acetone, then in nitric acid (1:1), and finally, in double-distilled water[20]. The three electrodes systems were immersed in a 15 mL cell, the cell of which contained a 400 mgl^{-1} bismuth plating solution. The plating potential of -1.1 V was applied for 3 min while the solution was being stirred[29]. Then the three electrode systems were moved to a new cell, which contained a 0.1 M acetic buffer sol-

ution of pH 4.5. After the preconcentration step in which 30 S is commonly used. The deposition condition (initial potential: 1.0 V; final potential: -0.6 V; deposition time: 30 s; quiet time: 2 s) was applied to the three electrode systems. The voltammogram was recorded with an SWSV scan at a 20 Hz frequency, 150 mv amplitude, and 5mv potential step for each time-removed target, and cleaned with 400 mV bismuth in 30 s. The entire experiment was performed in dissolved oxygen.

3. Results and Discussion

3.1. Cyclic Voltammetry, Supporting Electrolyte, and Bismuth Plating Effects

First, the cyclic voltammogram was recorded to determine the electrode behavior of copper ions in a 0.1 M acetic acid solution at a bismuth-plated carbon fiber microelectrode with 2×10^{-4} M PG. The CV effects were recorded for each continued spiking in (a) an electrolyte and a PG that contained a 10ml blank solution, (b) 100 mgl^{-1} Cu(II), (c) 200 mgl^{-1} Cu(II), and (d) 300 mgl^{-1} Cu(II), in turn, over the 0.4 to -1.0 V potential range at a scan rate of 100 mVs^{-1}. As seen in Fig. 1, the CV, on the forward positive scan, shows a sharp peak current that continues to increase at 0.01 V. This was exactly due to the oxidation peak current of the copper. Then on the backward scan, an increasing peak current was observed at -1.0 V. In the square wave voltammetric study, the forward increasing current of 0.01 was used to determine the
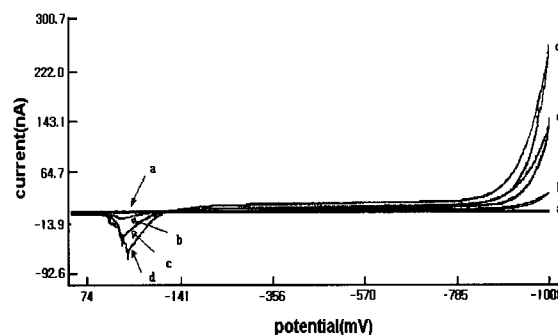

Fig. 1. Cyclic voltammograms at the bismuth-plated carbon fiber microelectrode in (a) a 0.1M acetic acid solution of 2×10^{-4} M PG, to which was added (b) 100 mgl^{-1} Cu(II), (c) 20 mg L^{-1} Cu(II), and (d) 300 mgl^{-1} Cu(II). The pH was 4.5 at a scan rate of 100 mVs^{-1} and a scan range of 0.07 to -1.0 V.

copper ion. Then the effect of the acetic acid supporting electrolyte concentrations was studied in the range of 0.01-0.5 M at fixed copper concentrations, the valuable factors and various diluted activities were tested, the highest peak current was determined for a 0.1 M acetic acid concentration, and electrolyte solutions of various other acids and bases were tested. For example, sulphuric, hydrochloric, phosphoric acid and other base solutions were tested, but no signal was produced. Various square wave voltammetric stripping studies were also tested. For this study, cathodic wave voltammetric stripping was used.

The square wave cathodic stripping effect of the 3-10 pH range was examined using a 0.1 M acetic acid buffer solution at a 30s preconcentration time, in which other parameters were used for the optimized conditions shown in Fig. 6. As shown in Fig. 2, the peak current increased quickly with the increase in the pH up to 4.5, and then remained constant at the pH range of 4.5-5. This was due to the increasing current for the PG complex formation of copper with bismuth at the electrode surface with the increasing pH of up to 5. At the range of 6-7 pH, the peak current decreased quickly with the increase in the pH, and in the range above pH 7-10, the copper signal disappeared. The decreasing peak current was due to the stable complex formation of copper with OH at

the electrode surface with the increase in the pH.

The effects of bismuth coating on a carbon fiber microelectrode were also compared. Fig. 3 shows very different signals. Curve (b) represents a non-spiking carbon fiber blank signal. It is stable and linear, with no noise detected. Thus, the copper ion was spiked with 1 mgl⁻¹ Cu(II) (a), a bare carbon fiber electrode, for the 1mgl⁻¹ Cu(II) spiked peak signal. A very small and poor peak was obtained, and no completed high signal of copper ion was detected even at the more spiked conditions. The high peak calibrations were also very difficult.

The other bismuth-coated electrode was tested, with curve (C) representing the 1 mgl⁻¹ Cu(II) spiking. A considerably increased sharp signal was obtained. Although this study did not use oxygen exclusion, very sensitive signals were obtained using a bismuth-coated electrode. Likewise, the two carbon fiber electrodes had the same geometric shape and similar optimized conditions. The bismuth plating peak ratio was found to have been six times better in the bismuth-coated electrode than in the bare electrode at low concentrations of a 3 mgl⁻¹ copper ion. In addition, the bare electrode was tested using low-range
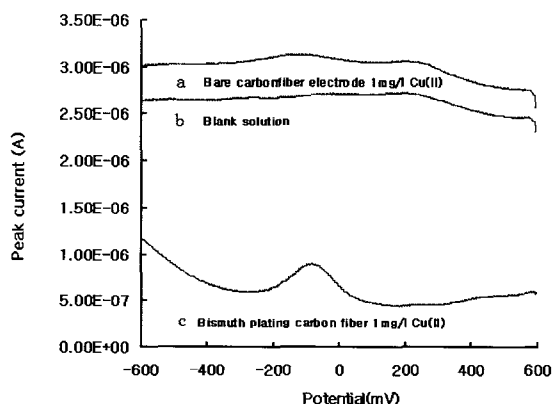
Fig. 3. Comparison of the effects of the bismuth coating of a carbon fiber microelectrode. (a) 1.0 mgl⁻¹ Cu(II) spiking of a bare carbon fiber electrode; (b) bare carbon fiber blank; and (c) 1.0 mgl⁻¹ Cu(II) spiking of the bismuth-coated electrode. The electrolyte solutions of the 0.1 M acetate buffer contained a 2x10⁻⁴ M PG concentration, and the deposition took place for 30 s at 1.0 V (cleaning for 30 s at 0.4 V, square wave voltammetric stripping scan with a frequency step of 20 Hz, a potential step of 5 mV, and an amplitude of 150 mVs⁻¹. Other parameters considered optimum conditions.
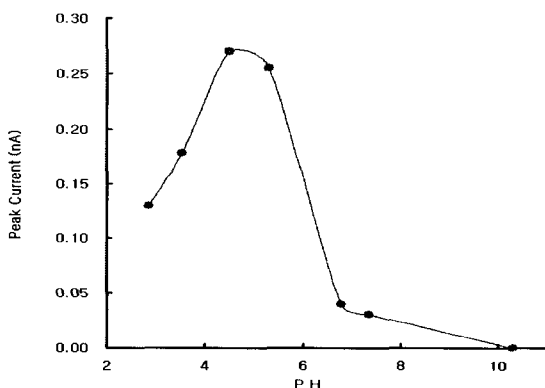
Fig. 2. Dependence of the square wave cathodic stripping voltammetric peak current on various pH values of copper with a bismuth-plated carbon fiber microelectrode at a copper concentration of 5 mgl⁻¹, an initial potential of 1.0 V, a final potential of - 0.6 V, a potential step of 5 mVs⁻¹, a supporting electrolyte of 0.1M acetic acid buffer solution, a deposition time of 30 s, a frequency of 20 Hz and a 2x10⁻⁴ M PG in dissolved oxygen.

ppb levels. No peak signal in the ppb range was detected. For the bismuth-coated electrode, a linearly sensitive curve was obtained at the ppb levels.

3.2. Effect of Varying the Accumulation Potential, PG, and Times

In this study, various final potentials were tested, and sensitive final potentials were found to have had no effect. Fig. 4 illustrates the effect of the stripping voltammetric peak current on the accumulation potentials of copper. The preconcentration potential was examined over the range of 0.4-2.0 V. The peak intensity was found to have decreased as the initial potential increased. At potentials in the range of 1.0-1.4 V, there was little change in the peak current height. In the potential range of 1.4-1.9 V, the background peak height gradually decreased, and in the 2.0V potential, the signals significantly decreased. For this reason, a deposition potential of 1.0 V was selected as the optimum stripping condition for the quantification of copper. In this condition, the PG complex effect was examined using an optimal concentration. As shown in Fig. 4 (b), the PG concentration was varied from 0 to 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, and 11 x 10^{-4} moll^{-1}, in the presence of 5 mgl^{-1} Cu(II). The accumulation potential was set at 1.0 V, and the solution was stirred within a 30 s deposition time. Within this time, the peak current sharply increased with the increase in the PG concentration at 2x10^{-4} M PG. Later, the peak current slowly increased with a further increase in the PG. The variations of the complex for-

mation depended on the PG concentration. The optimum point of 2x10^{-4} M PG was also obtained. This corresponds to the mole ratio of the metal Cu and the PG ligand at the electrode surface.

3.3. Effect of Varying the Accumulation Time, Square Wave Frequency, and Square Wave Amplitude

Fig. 5 shows the dependence of the peak current on the accumulation times of 30, 60, 120, 150, 180, and 210 s. As the accumulation time increased, the response rose slowly, an increasing current of 5x10^{-3} A was obtained, and the copper chelate on the electrode generally depended on the short period and not the accumulation time. It was also found that only 30 s was enough to attain the equilibrium condition, after which the copper variation was studied. Each time, very short adsorption times were detected. The accumulation time chosen was 30 s. In this condition, the SW frequency was examined. Fig. 5 (b) shows the frequency variations from 5 to 10, 15, 25, 35, 45, 65, 85, and 105 Hz in the 5 mgl^{-1} Cu(II) spike. In the same conditions as those shown in Fig. 4, well-defined sharp peaks were observed following the 30s deposition, and no measurements were used for electrode cleaning. The peak current strongly depended on the accumulation frequency, and at high frequencies, the peak width increased and the peak sharp broadly interfered. Therefore, 20 Hz was chosen as the optimum condition.

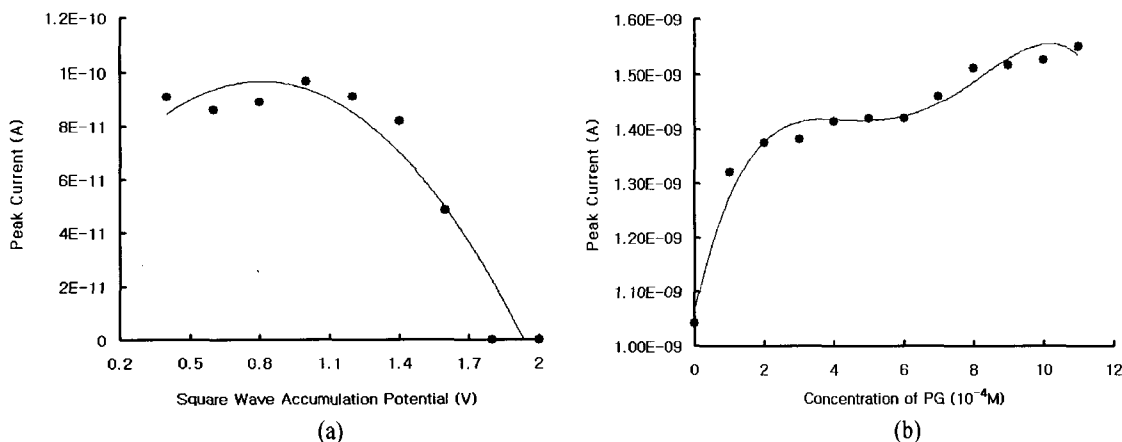Fig. 5(c) illustrates the peak current as a function

(a)

(b)

Fig. 4. Dependence of the peak current on the accumulation potentials of (a) 0.4, 0.6, 0.8, 1, 1.2, 1.4, 1.6, 1.8, and 2 V, and the PG concentration effects of (b) 0, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, and 11 x 10^{-4} molL^{-1} PG, and 5 mgl^{-1} Cu(II). Other experimental parameters were as shown in Fig. 2.
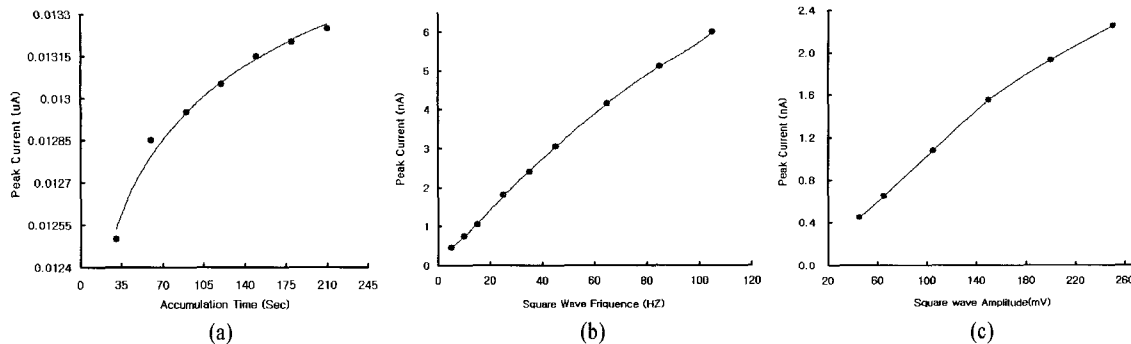
Fig. 5. Responses at the accumulation times of (a) 30, 60, 120, 150, 180, and 210 s; the square wave frequencies of (b) 5, 10, 15, 25, 35, 45, 65, 85, and 105 Hz; and the square wave amplitudes of (c) 40, 65, 105, 150, 200, and 250 mVs^{-1}; at the 0.1 M acetic acid buffer (pH 4.5) of the 5 mgl^{-1} Cu concentration. Other conditions were as those in Fig. 5.

of the amplitude for a 5 mgl^{-1} copper spike at a 30s preconcentration time. The pulse amplitude studied ranged from 40 to 250 mVs^{-1}. The results showed a linear increase in the stripping peak current when the amplitude was increased, despite an extremely low concentration and a short accumulation time. These parameters affected the peak shape and the peak high of the copper response. The peak current increased rapidly with the increase in the amplitude, and the peak width widely increased. Therefore, 150 mVs^{-1} was chosen as the optimum pulse height.

3.4. Effect of Varying the Concentration of Copper, the Linear Range, the Interference, the Detection Limits, and the Application

The adsorptive stripping peak current for Cu-PG complexes yields a well-defined concentration. Measurement of Cu(II) peaks is commonly carried out at -32 mV. At the optimized conditions, tests were conducted for low and high range concentrations. A very low range of 0.3-1.8 ppt was obtained, and the linear equations were uncertain and not exact. Therefore, the values were ignored, and higher ranges (ppb) were examined. Fig. 6 (a) shows the concentration effects for the sharp and exact peak current. The experimental raw voltammograms show the values of 0.03, 0.07, 0.17, 0.37, 0.71, 1.97, 3.97, 5.97, 7.97, 9.97, 13.97, 17.97, 21.97, and 25.97 Cu(II) µgl^{-1}, and the linear range of 0.03-9.97 ppb with 9 points was fixed. The equation used was y = 0.3374 x + 3.9436, the correlation coefficient was 0.9961, y is the peak current of 1x10^{-10} amperes, and x is the Cu(II) concentration of µgl^{-1}. High ppm levels were

obtained. Fig. 6 (b) shows the narrow-width raw voltammograms for 0, 1, 3, 5, 7, 9, 11, 13, 15, 17, 19, 21, 23, and 25 mgl^{-1} Cu(II) in the dissolved oxygen. The Cu(II) peaks were well-defined following the 30s deposition. For the abovementioned values, the statistical linear point was set at 0-19 mgl^{-1}, the linear plot gave a regression equation of y = 0.06 x + 4 (correlation coefficient: 0.9932; 11 points; y = current, nA; and x = copper concentration, mgL^{-1}). At the range of 19-25 mgl^{-1} Cu(II), the calibration curve non-linearly increased, and then decreased. All the stripping responses were highly reproducible, and 12 successive measurements of 13 mgl^{-1} Cu yielded a relative standard deviation of 0.9%. The detection limit of 0.019 µgl^{-1} at a 30s preconcentration time was estimated based on the signal-to-noise characteristics of these data (S/N = 3).

Moreover, several other selected metal ions were tested for their possible interference in copper determination. The criterion used for ascertaining the existence of interference was a 5% or greater change in the peak current of copper. Thus, for the detection of 0.1 mgl^{-1} copper with 30s accumulation, the existence of 0.1 mgl^{-1} Ag(I), Ca(II), Cr(III), and Ni(II) did not interfere. Also, at the same interfering level, Ba(II), Fe(II), Hg(I), and Cd(II) depressed the copper peak by 47.0, 35, 100, and 100%, and probably prevented the complex formation of bismuth and PG at the electrode surface, and the determination of 0.1mgl^{-1} copper with the same accumulation. The existence of 0.5 mgl^{-1} Ba(II), Ni(II) and Cd(II) increased the copper current by 125, 50, and 57%. Several oth-

(a)

$y = 0.3374x + 3.9436$
$R^2 = 0.9961$

(b)

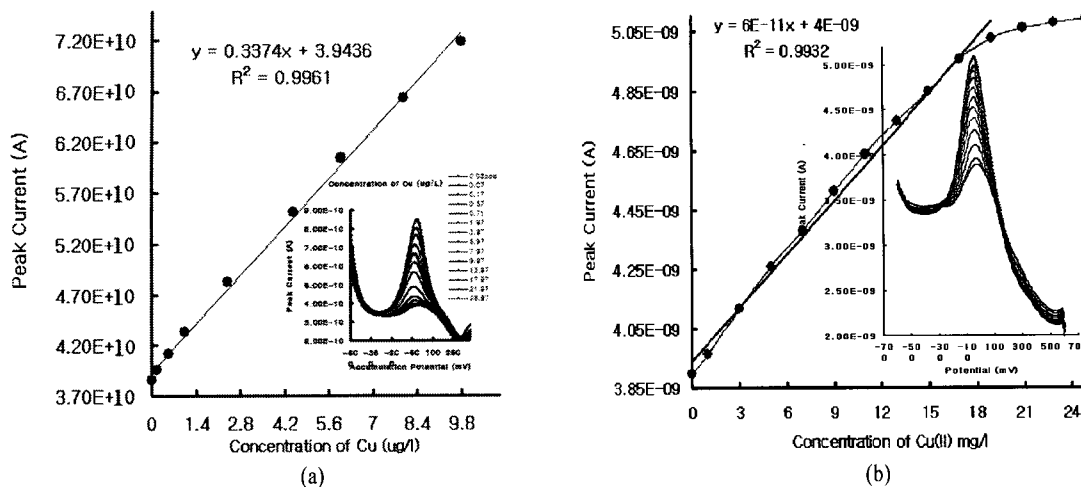$y = 6E-11x + 4E-09$
$R^2 = 0.9932$

Fig. 6. Stripping voltammograms of Cu(II) at carbon fiber microelectrodes coated with bismuth films. Solutions of 0.1 M acetate buffer containing (a) 0.03 ~ 25.9 μgl^{-1} Cu(II), and (b) 0 ~ 25 mgl^{-1} Cu(II), 2×10^{-4} M PG concentration, deposition for 30s at 1.0 V, cleaning for 30s at 0.4 V, square wave voltammetric stripping scan with a frequency step of 20 HZ, potential step of 5 mV, amplitude of 150 mVs^{-1}.

er weakly interfering ions could be eliminated by applying the standard addition method for the determination of the copper ion.

The developed method was used to determine the amount of copper in the pond water samples via the standard addition method with known concentrations. Fig. 7 shows the voltammogram of the tested pond waters. The first scanning was for the blank solution, after which a 1ml sample solution was spiked. At this time, a small peak was detected, and then suitable 3-6
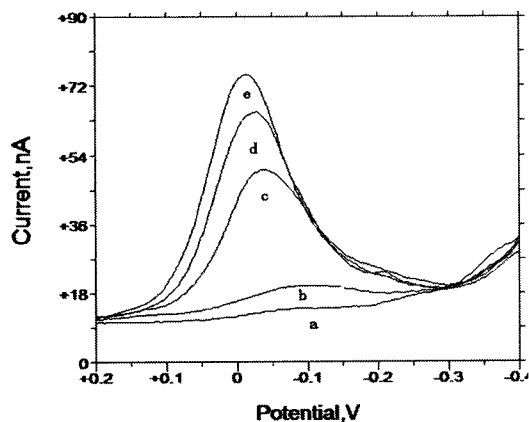

Fig. 7. Stripping voltammetric real sample test of (a) a blank solution (0.1M acetic acetate buffed to 10 mL) and (b) a 1ml pond water sample, and spiking of (c) 3, (d) 6, and (e) 9 μgl^{-1} Cu(II) standard solutions. Other conditions were as those shown in Fig. 6.

ppb aliquots of the known standard copper solution were spiked into four different cells that contained 10 ml of the supporting electrolyte cell. Afterwards, the least square equations of the standard addition plot yielded a slop of 0.1 $nA/10^{-3}$ mgl^{-1} with a correlation coefficient of 0.9777. The average concentration of the copper ions was 0.48 ugl^{-1}.

4. Conclusions

Using this modified method, this study demonstrated that non-mercury film electrodes with sensitive response characteristics and bismuth films are suitable for the detection of several metals in biological voltammetry. The said method makes it possible to measure low concentrations of copper ions in aqueous solutions, and showed good accuracy under optimum conditions. This film, which can be reproducibly plated, is stable and can be used in any voltammetric measurement of long times. The developed methods are usable in in vivo or in vitro biological analysis and real-time copper detection.

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