Determination of Trace Copper in Water Samples by Anodic Stripping Voltammetry at Gold Microelectrode

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The applicability of gold microelectrode of 25 μm diameter for electrochemical determination of trace copper ions (Cu^{2+}) in water samples by anodic stripping voltammetry (ASV) has been demonstrated. The analysis of Cu^{2+} at gold microelectrode includes two steps. Cu^{2+} ions are firstly reduced and accumulated on the microelectrode surface during an accumulation step, then oxidized during the positive potential sweep. Due to the rapid mass transporting and low background current of gold microelectrode, low detection limit (0.3 nM) and wide linear range (1.0-90 nM) can be obtained. The practical application of gold microelectrode was verified by determination of trace level of Cu^{2+} in tap water, lake water and commercial drinking water samples.

1. INTRODUCTION

Determination of trace heavy metals is an important issue in both public health and environmental monitoring. As a typical heavy metal, copper (Cu^{2+}) plays an important role in human beings since it is an essential component of several enzymes and it can help the Fe transporting [1-3]. However, excessive absorption of Cu^{2+} can create health risks such as the blood and kidneys problems [4] and also make large influence on the growth of plants, such as the shortened root length, fewer leaves and decline in the plants biomass [5, 6]. Therefore, it is very important to efficiently detect the concentration of Cu^{2+} in environmental water samples.

Well-established measurements for determination of Cu^{2+} have been reported [7-11], including spectrophotometry, solid-phase extraction, atomic absorption spectroscopy, X-ray fluorescence and inductively coupled plasma mass spectrometry (ICP-MS), etc. However, most of these methods need not only expensive equipments but also time-consuming pretreatments [12]. Electrochemical analysis based on anodic stripping voltammetry (ASV) is a proper method for the trace analysis of heavy metals [13, 14]. ASV measurement is based on relatively cheap and portable equipment and the analysis time of it is much shorter than the other methods such as ICP-MS. ASV measurement also allows to monitor low concentration of metals by electrochemical accumulation of the metal on the electrode surface [15-17]. In the past, mercury hanging or dropping electrodes have been widely used for ASV due to their easy formation of amalgam with reduced metal, excellent reproducibility and easy surface renewal [18, 19]. However, because of its serious toxicity, the use of mercury can cause severe environmental and health problems [20]. Ordinary electrochemical solid electrodes have been developed for Cu^{2+} determination, such as modified carbon past electrodes [21], modified conducting copolymer electrodes [22], self-assembled monolayer modified gold electrodes [23]. But the detection limits of those chemically modified electrodes were not low enough to detect trace level of Cu^{2+} in water samples. Thus, new alternative electrodes are highly desired to meet the growing demands of determination of Cu^{2+} in environmental monitoring and water research.

In recent years, the development of microelectrodes has received considerable attention and the domain of their electrochemical applications has been widened. Microelectrodes are devices with a critical dimension smaller than the thickness of the Nernst diffusion layer. Accordingly, they possess several characters such as rapid mass transporting, enhancement of signal-noise ratio and low background current [24, 25]. Electrochemistry experiments can be performed at very small volumes when small size microelectrodes have been involved [26, 27]. Microelectrodes have been used to detect Cu^{2+} in human sweat and ethanol fuel samples [28, 29].

In this work, a gold microelectrode was employed to detect Cu^{2+} by differential pulse anodic stripping voltammetry (DPASV) in environmental water samples. Due to the excellent properties of microelectrode, low detection limit and wide linear range can be obtained. Additionally, experimental parameters, including the pH value of the supporting electrolyte, the accumulation potential and the accumulation time have been investigated in detail. The practical application of gold microelectrode has been carried out for determination of Cu^{2+} in tap water, lake water and commercial drinking water samples.

2. EXPERIMENTAL

2.1. Reagents

The National Standard 1.0 g L^{-1} copper solution was used as the stock solution and then diluted to various concentrations of working solutions. Otherwise, 0.01 M HNO$_3$ (pH 2) was used as the supporting electrolyte for Cu^{2+} determination. All other chemicals were analytical reagents and used

without further purification. Deionized water (18.2 MΩ cm specific resistance) obtained with a Pall Cascada laboratory water system was used throughout.

2.2. Apparatus

All electrochemical measurements were performed with a LK2006 electrochemical workstation (LK Chemical Electronic High Technology Co., Ltd, China). The measurements were performed in a 10 mL electrochemical cell.

A gold microelectrode of 25 μm diameter (CH Instruments Inc., China) was used as the working electrode. A platinum electrode and an Ag/AgCl (3 M KCl) electrode were used as the counter electrode and reference electrode, respectively. All potential values given below refer to reference electrode. All the electrochemical experiments were carried out at room temperature. The UV digestion was performed using a 705 UV digestor (Metrohm AG, Switzerland). ICP-MS measurements were performed using an Elan Drc II inductively coupled plasma mass spectrometer (PerkinElmer, USA).

2.3. Sample preparation

The tap water, lake water and drinking water samples were collected from local. The tap water and drinking water were acidified to pH 2 using HNO_3.

The lake water was fist filtered through a standard 0.45 μm filter and acidified to pH 2. Subsequently, the lake water was UV digested in 10 ml quartz tube for 30 min in the presence of H_2O_2 to destroy the natural organic matter. All water samples were stored at -4°C in acid-cleaned HDPE sample bottles.

2.4. Analytical procedure

Before each measurement, the surface of the microelectrode was mechanically polished with alumina powder (0.3 and 0.05 μm) on a microcloth polishing pad and then rinsed by ethanol and deionized water thoroughly. After that, the microelectrode was activated in 0.5 M H_2SO_4 by cyclic voltammetric sweeping from -0.15 V to 1.5 V at a scan rate of 50 mV s^{-1}.
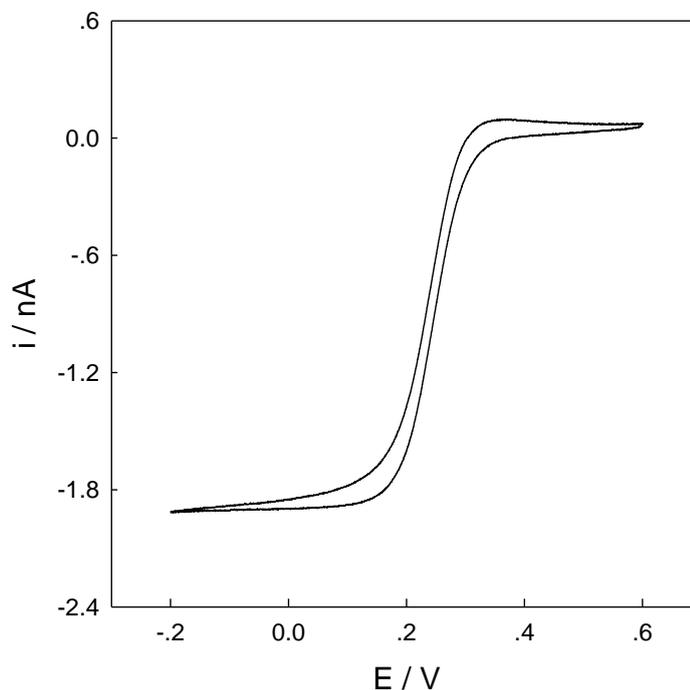
The stripping analysis of Cu^{2+} has two main steps including accumulation and stripping out. Cu^{2+} ions were first reduced to Cu under −0.4 V for a desired time onto the gold microelectrode. In the following step, the reduced Cu was oxidized at 0.28 V during the potential sweeping from 0 to 0.6 V. The stripping peak current was measured for Cu^{2+} quantification. Prior to the next measurements, the microelectrode was activated at 0.6 V for 30s in the supporting electrolyte to remove the previous deposit completely.

Quantitative determinations of Cu^{2+} were performed with differential pulse anodic stripping voltammetry. The optimal conditions were as follows: accumulation potential of −0.4 V; accumulation time of 210 s; amplitude of 0.05 V; pulse width of 0.1 s; pulse interval of 0.1 s; quiet time of 10 s.

3. RESULTS AND DISCUSSION

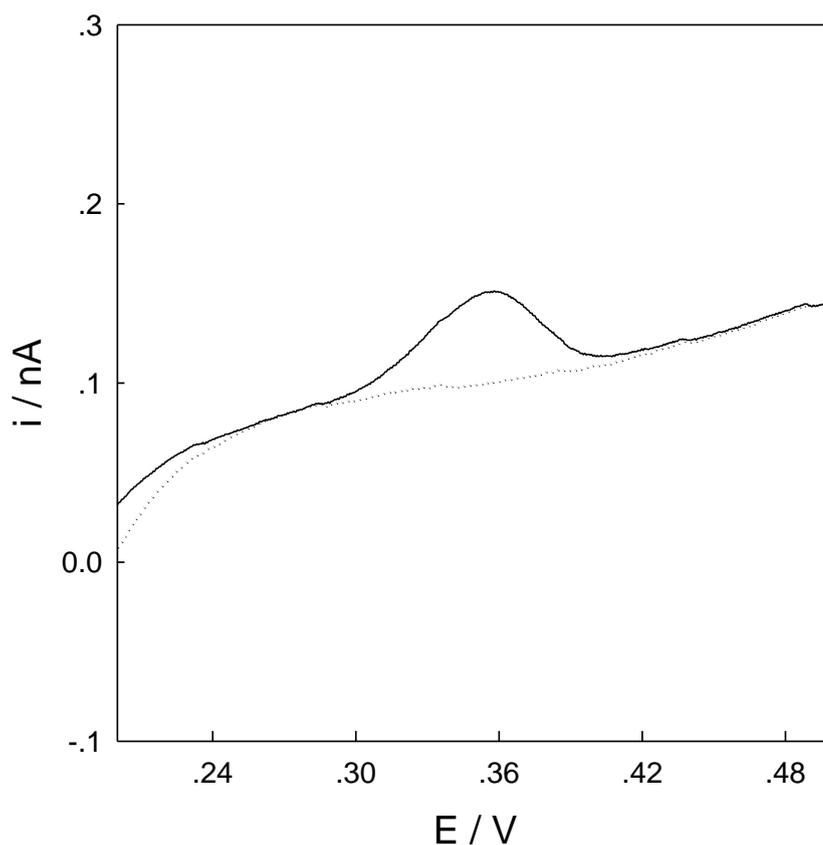### 3.1. Voltammetric behaviors of Cu^{2+} at the gold microelectrode

Figure 1 shows the cyclic voltammograms recorded at the gold microelectrode from -0.2 to 0.6 V in 0.2 M KNO_3 solution containing 1.0 mM potassium ferricyanide.

Figure 1. Cyclic voltammograms recorded at the gold microelectrode in 0.2 M KNO_3 containing 1.0 mM $K_3[Fe(CN)_6]$. Scan rate, 50 mV s^{-1}.

The voltammogram of the gold microelectrode exhibits the typical sigmoid shape, indicating the predominance of radial diffusion to electrode surface [30]. Due to the micro-size effect, an enhanced mass transport can be obtained at microelectrode rather than traditional electrode, which results in the improved signal-to-noise ratio and low analytical detection limit [31-33]. Accordingly, the microelectrode has great potential for determination of trace heavy metals.

On the other hand, the voltammetric behaviors of Cu^{2+} at the gold microelectrode was recorded by linear sweeping voltammetry in 0.01 M HNO_3 (pH 2) solution containing 1.0 μM Cu^{2+} at a scan rate of 50 mV/s and the corresponding results were shown in Figure 2. Compared to the voltammetric curve of the gold microelectrode in electrolyte without Cu^{2+} (dotted line in Figure 2), a large anodic peak at 0.35 V can be observed at the same electrode in electrolyte containing 1.0 μM Cu^{2+} (solid line in Figure 2). Since no electro-deposition was applied during the linear sweeping step, the rapid chemical redox of Cu^{2+} at the gold microelectrode is the logical explanation of this result. These indicate the gold microelectrode can be used to sensitively detect Cu^{2+}.

Figure 2. Linear sweeping voltammograms recorded at the gold microelectrode in HNO_3 (pH 2) solution with (solid line) and without (dashed line) 1.0 μM Cu^{2+}. Scan rate, 50 mV s^{-1}.

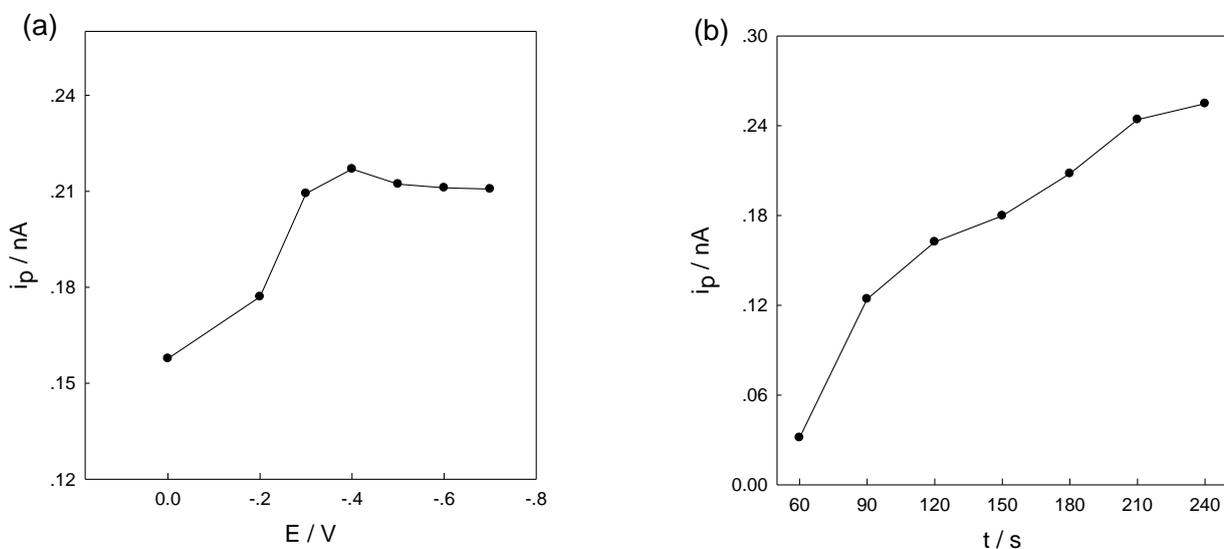### 3.2. Optimization for determination of Cu^{2+} at the gold microelectrode

In order to establish the most suitable experimental conditions for the anodic stripping voltammetric determination of Cu^{2+} at the gold microelectrode, optimization studies about the pH value of the supporting electrolyte, the accumulation potential and the accumulation time were investigated in detail.

3.2.1. Effect of pH value of the supporting electrolyte

The effect of the pH values of the supporting electrolyte on the stripping peak current of 30 nM Cu^{2+} was examined in the range of 1 to 3. At the pH value of 2, the stable stripping peak and largest peak current can be obtained. Additionally, in order to detect the total dissolved Cu^{2+} in the lake water, the digestion measurement was used to destroy the natural organic matter. Previous studies had consistently suggested that acidification of samples to less than pH 2 would have positive effect on disintegration of metal complex [34]. Accordingly, pH 2 was selected as the working pH value of the supporting electrolyte.

3.2.2. Effect of accumulation potential

The effect of the accumulation potential on the stripping peak current of 30 nM Cu^{2+} was examined over the potential range of -0.7 to 0 V.

Figure 3. Effect of (a) accumulation potential and (b) accumulation time on the stripping peak current of 30 nM Cu^{2+}. Amplitude, 0.05 V; pulse width, 0.1 s; pulse interval, 0.1 s; quiet time, 10 s.
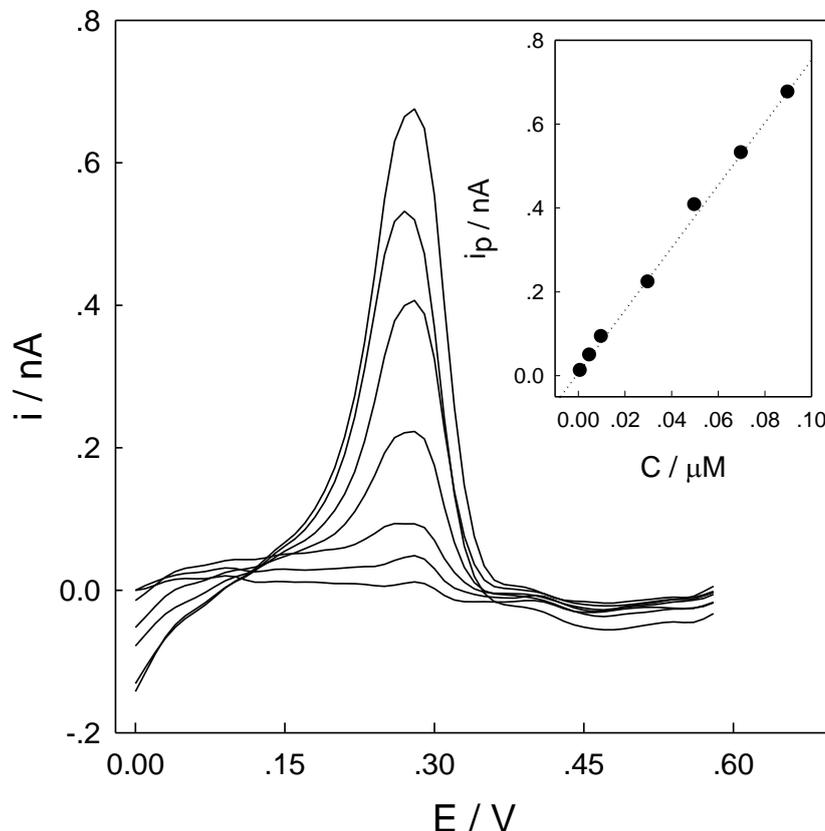
As shown in Figure 3 (a), the stripping peak current increased sharply with changing potential from 0 to -0.4 V, probably due to the fact that Cu^{2+} can be reduced more efficiently at more negative accumulation potentials. The stripping peak current did not change significantly at a potential more negative than -0.4 V, which is mainly attributed to the complete reduction of Cu^{2+} in the solution to the gold microelectrode during the certain accumulation time. So, -0.4 V was chose as the optimum accumulation potential in the following measurements.

3.2.3. Effect of accumulation time

The effect of the accumulation time on the stripping peak current of Cu^{2+} at the gold microelectrode was also discussed. Undoubtedly, the sensitivity of the proposed method for determination of Cu^{2+} was promoted with the increase of the accumulation time because of the increased amount of Cu on the gold microelectrode. However, this tendency would not be prolonged all through due to the limited active sites for Cu accumulation. As shown in Figure 3 (b), the response of the gold microelectrode to 30 nM Cu^{2+} increased rapidly with the accumulation time up to 210 s, and then tended to increase slowly. Therefore, 210 s was used as the accumulation time in the following measurements.

3.3. Calibration curve

The calibration curve for determination of Cu^{2+} was derived from the differential pulse stripping voltammetric curve obtained at the gold microelectrode and the corresponding results are shown in Figure 4.

Figure 4. Anodic stripping differential pulse voltammograms of gold microelectrode in HNO_3 (pH 2) containing various concentration of Cu^{2+}. The values for the curves are 1, 5, 10, 30, 50, 70, 90 nM from bottom to top, which are in the linear rang. Accumulation potential, −0.4 V; accumulation time, 210 s and other conditions are the same as in Fig. 3. The inset is the calibration plot calibration curve of Cu^{2+} obtained at the gold microelectrode.

From Figure 4, for 210 s accumulation, a proportional relationship between the stripping peak current and the concentration of Cu^{2+} was obtained in the range of 1.0 to 90 nM ($i_p = 7.5C + 0.01$, i_p in nA, C in μM) with a linear correlation coefficient of 0.9976. The sensitivity was found to be 7.5 nA/μM. The detection limit calculated at $S/N = 3$ was 0.3 nM, which was lower than those obtained at carbon paste electrode [35], poly(vinyl) chloride membrane copper-selective electrode [36], 4-carboxyphenyl-grafted screen printed electrode [37].

On the other hand, the reproducibility of three gold microelectrodes and the same gold microelectrode with three measurements for 30 nM of Cu^{2+} were estimated and the results reveal the gold microelectrode has satisfactory reproducibility and repeatability with a relative standard deviation

of 5.1% and 3.2%, respectively. Low detection limit, wide linear dynamic range and excellent reproducibility and repeatability may attribute to the excellent and unique properties of the gold microelectrode.

3.4. Determination of copper in real water samples

In order to verify the accuracy of the proposed method, the gold microelectrode was used to detect Cu^{2+} in China National Standard Substance (GBW080080, trace heavy metals containing Cu^{2+}, Pb^{2+}, Zn^{2+}, Cd^{2+}, Ni^{2+} in water). The National Standard Substance was diluted to 1000 multiples and acidified to pH 2 using HNO_3. The concentration of Cu^{2+} was detected to be 15.2±0.1 nM (*n*=3), which agreed well with the nominal value of Cu^{2+} in GBW080080 (15.6 nM). These indicated the gold microelectrode has good anti-interference and can be used in determination of Cu^{2+} in real samples.

On the other hand, to illustrate the application of gold microelectrode in real practical analysis, the trace concentration of Cu^{2+} was detected at the gold microelectrode in tap water and lake water samples by the standard addition method and the results were shown in Table 1.

Table 1. Comparison of the gold microelectrode and ICP-MS for determination of Cu^{2+} in real water samples

Sample	Detected by gold microelectrode (nM)[*]	Detected by ICP-MS (nM)
Tap water	12.7±0.4	13.8
Lake water	21.8±1.0	22.3

Note: [*]Average value of three determinations ± standard deviation.

From Table 1, the results obtained at the gold microelectrode showed good agreement with those obtained by ICP-MS measurements. Additionally, the gold microelectrode was also employed to detect Cu^{2+} in the commercial drinking water. But the concentration of Cu^{2+} in the commercial drinking water can not be detected due to the rather low concentration of Cu^{2+}. The recovery experiments were carried out and the results were varied between 93.4% and 95.7%, indicating the potential application of this microelectrode in real water sample analysis with a high accuracy and good reliability.

4. CONCLUSIONS

The results obtained in this work have demonstrated that the gold microelectrode can be successfully employed for Cu^{2+} determination in water samples. The use of microelectrode implies a series of advantages with respect to conventional bulk electrodes, which can be resulted in the improvement of the electroanalytical responses of the corresponding analytes, especially concerning

the signal-to-noise ratio and the precision of the measurements. The practical analytical utility of the gold microelectrode was assessed by measurements of tap water and lake water samples and the results were in agreement with the results from ICP-MS. Due to its cheap cost, easy fabrication and excellent electrochemical properties, the microelectrode has great potential in rapid, on-site voltammetric determinaton of Cu^{2+} or other heavy metals in environmental monitoring. Our following work is to detect heavy metals in sea water by using modified microelectrode.

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