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Electrochemical Determination of Trace Copper Ions in Drinking Water Source

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Abstract: Aiming at the on-site and quick safety evaluation of the dissolved trace copper ions (Cu^{2+}) in drinking water source, an electrochemical detection platform was developed on the basis of the square wave anodic stripping voltammetry using the gold nanoparticles (Au NPs) modified glassy carbon electrode, where Au NPs were deposited via electrochemical cyclic voltammetry. The proposed method displayed the limit of detection as low as $1.3 \mu\text{g} \cdot \text{L}^{-1}$ in the linear range of $2 \sim 50 \mu\text{g} \cdot \text{L}^{-1}$. The proposed method was applied to the determination of Cu^{2+} in the midstream of Minjiang River, one of the most important drinking water sources in Fujian province, China. The results were nearly identical to that obtained by the standard method quantitatively with a deviation less than 20%. Furthermore, the proposed electrochemical method is simple, economical and fast, and has the potential for the field determination of trace dissolved Cu^{2+} in various drinking water sources facilitated with the portable potentiostat.

Key words: electrochemical determination; square wave anodic stripping voltammetry; gold nanoparticles; trace copper ion; drinking water

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As an essential trace metallic element for human health, copper is indispensable to the functioning of organs and metabolic processes. Copper ion (Cu^{2+}) combines with certain proteins to produce enzymes that act as catalysts to help a number of body functions, such as antioxidant, energy supplying, and immune function. Copper deficiency is one of the factors leading to an increased risk of developing coronary heart disease^[1-2]. However, too much nutritional ingestion of copper can result in the genetic or non-genetic disease^[3], especially we are nowadays facing various copper contamination sources^[4] from the effluent discharge of the copper mine^[5], the daily civilian use^[6] and the improper handling of municipal waste^[7]. With the evaluation of the human health risk towards the copper exposure, the World Health Organization (WHO) suggests the daily dietary standard intake of copper should not exceed $10 \text{ mg} \cdot \text{day}^{-1}$ for

adult.

For the human health risk control, the qualitative and quantitative analyses of Cu^{2+} concentration in the drinking water source are essential, where the Cu^{2+} concentrations are averagely 3 and $0.25 \mu\text{g} \cdot \text{L}^{-1}$ for the natural surface water and seawater, respectively^[8]. Up to now, various techniques have been involved for the detection of Cu^{2+} in the aquatic environment. For instance, the Cu^{2+} concentrations in tap water, river, spring or well water were measured by inductively coupled plasma atomic emission spectrometry (ICP-AES)^[9], while the Cu^{2+} concentration in seawater was evaluated by inductively coupled plasma-mass spectrometry (ICP-MS) and atomic absorption spectrometry (AAS)^[10-11].

Although these techniques displayed high sensitivity, selectivity and accuracy, the expensive laboratory based facilities, tedious pretreatment and cum-

bersome instrument operation restrict their field application, which brought great chance for the development of other optical and electrochemical techniques. The optical techniques including UV-Vis absorption, fluorescence and surface-enhanced Raman spectroscopy (SERS) have been successfully applied for the measurement of Cu^{2+} in various aqueous environments with good selectivity and sensitivity. It should be noted that due to the lack of optical signal from Cu^{2+} itself, the measured optical signals indirectly reflected the Cu^{2+} concentration, which is based on either the catalytic ability of Cu^{2+} or the interaction between Cu^{2+} and various ligands^[12-16]. In contrast, the electrochemical methods, such as Anodic Stripping Voltammetry (ASV), monitoring the electrochemical signal directly from Cu^{2+} itself, is becoming a promising on-site detection technique for Cu^{2+} in various environments^[17-19].

Typically, the detection of ASV towards Cu^{2+} includes two steps: the cathodic deposition of Cu^{2+} to enrich the trace Cu^{2+} in solution, and then the anodic stripping of the Cu layer on the working electrode surface. Therefore, the Cu^{2+} concentration in solution could be measured by its quantitative relationship with the electrochemical stripping peak intensity of Cu layer on the surface^[20-23]. Among the typical working electrode materials used for Cu^{2+} detection, Au electrode outstands itself due to the underpotential deposition (UPD) of Cu^{2+} on the surface^[24]. Although the electrochemical detection has the advantages of fast detection, high selectivity & sensitivity, easy operation, low cost and measuring multi-metal ions simultaneously, the ultrahigh sensitivity at the $\text{ng}\cdot\text{L}^{-1}$ or even high level normally demands expensive facilities such as the rotating disk working electrode^[21-22], specific surface^[25] and complicated surface modification^[19-20, 26-27]. It is well-known that the safety point of the Cu^{2+} concentration in drinking water is at the $\mu\text{g}\cdot\text{L}^{-1}$ level, therefore, the higher sensitivity is less important for the quality control of the drinking water, but a cheaper and easier to be operated protocol with reliable accuracy, which could be applied for the on-site detection, is highly demanded.

Therefore, in this work, we developed an electrochemical platform for the trace Cu^{2+} detection in drinking water source using square wave anodic stripping voltammetry (SWASV). Au nanoparticles (NPs) with ~ 70 nm in diameter were electrochemically deposited on the glassy carbon (GC) electrode simply by cyclic voltammetry to form Au NPs-GCE. The SWASV was used for the determination of Cu^{2+} in the midstream of Fujian Minjiang River in China. The result which is in good agreement with those obtained with the traditional technique, providing a simple, inexpensive and fast way.

1 Experimental

1.1 Chemicals

All chemicals used were of analytical grade or the highest purity available, unless stated specifically. All solutions were prepared in purified water (resistivity $\geq 18.2 \text{ M}\Omega\cdot\text{cm}$, Merck Millipore, USA). Hydrochloric acid (HCl, 36% \sim 38%, *w/w*) was from Kunshan Jincheng Reagent Co. (China). Chloroauric acid (HAuCl_4), potassium chloride (KCl, $\geq 99.5\%$, guaranteed), sodium nitrate (NaNO_3 , $\geq 99\%$), sodium acetate trihydrate ($\text{C}_2\text{H}_3\text{O}_2\text{Na}\cdot 3\text{H}_2\text{O}$, $> 99\%$), and acetic acid ($\text{C}_2\text{H}_4\text{O}_2$, $> 99.5\%$) were obtained from Sinopharm Chemical Reagent Co. (China). Nitric acid (HNO_3 , 65%, *w/w*) and sulfuric acid (H_2SO_4 , 95% \sim 98%) were from Xilong Chemical Co. (China). Copper standard solution ($1000 \text{ mg}\cdot\text{L}^{-1}$ Cu^{2+} in 2% nitric acid) was from Sigma-Aldrich Co. (USA). Standard solutions of $1000 \text{ mg}\cdot\text{L}^{-1}$ Fe^{3+} , Mn^{2+} , Co^{2+} , Ni^{2+} , Zn^{2+} , Pb^{2+} , Ba^{2+} , Cd^{2+} , Bi^{3+} , Sb^{2+} , As^{3+} , Hg^{2+} , and Cr^{3+} (spectroscopic grade) were purchased from Thermo Fisher Scientific (USA).

1.2 Materials and Instruments

All electrochemical experiments were carried on the QJ2000 Potentiostat (Qunji Instrument Ltd., Xiamen). Glassy carbon electrode ($\phi = 3$ mm) was used as the working electrode, which was polished by $0.3 \mu\text{m}$ and then $0.05 \mu\text{m}$ α -alumina powders, and cleaned in water by sonication before electrochemical treatments. The Ag/AgCl electrode and platinum wire were used as the reference and counter electrodes, respectively.

S-4800 Scanning Electron Microscope (Hitachi Co., Japan) was used for the surface morphologic characterization of the working electrode. The Cu^{2+} concentrations in drinking water were measured by the NOVAA400P Graphite Furnace Atomic Absorption Spectrometer (GFAAS, Analytik Jena Co., Germany) to evaluate the accuracy of the proposed method.

1.3 Au NPs-GCE Preparation

The Au NPs-GCE was obtained by electrochemical deposition of Au NPs onto GC electrode by cyclic voltammetry (CV) in the range of 0 ~ 900 mV with a scanning rate of $50 \text{ mV} \cdot \text{s}^{-1}$ for 12 times in $0.2 \text{ mol} \cdot \text{L}^{-1} \text{ NaNO}_3$ solution containing $1.0 \text{ mmol} \cdot \text{L}^{-1} \text{ HAuCl}_4$. The Au NPs-GCE was further electrochemically swept in $0.5 \text{ mol} \cdot \text{L}^{-1} \text{ H}_2\text{SO}_4$ solution in the range of 0.3 ~ 1.5 mV with a scanning rate of $100 \text{ mV} \cdot \text{s}^{-1}$ to obtain a stable electrochemical feature.

1.4 Determination of Cu^{2+} in Aquatic Environment with SWASV

The $0.1 \text{ mol} \cdot \text{L}^{-1} \text{ HNO}_3$ aqueous solution was prepared. The SWASV measurement was proceeded as follows: stepping to -0.5 V (the deposition potential) for 300 s, then linear scanning to 0.6 V with the square wave of 25 mV, the potential step of $5 \text{ mV} \cdot \text{s}^{-1}$

and the square wave frequency of 200 Hz. In order to avoid the interference from the current disturbance of the Au NPs-GCE itself, the ASV curve obtained with a deposition time of 30 s was used as the reference for the subtraction^[28-30]. The obtained peak current Δi_o ($= i_o(300\text{s}) - i_o(30\text{s})$) is used for the quantitative analysis of Cu^{2+} in the sample in the system measured.

1.5 Sample Collection and Pretreatment

Drinking water source samples were collected on Feb. 27th, 2017, from the 11 sampling sites distributed along the midstream Minjiang river from Nanping city to Minqing city (Fujian Province, China) as shown in Fig.1. The samples being static precipitated were filtered by a filter membrane with the pore size of $0.45 \mu\text{m}$ to remove all the suspended particulate substance, and then acidified in $0.1 \text{ mol} \cdot \text{L}^{-1} \text{ HNO}_3$ solution for 12 h to transfer all copper speciation including organic ones to inorganic Cu^{2+} as much as possible.

2 Results and Discussion

2.1 Electrochemical Deposition of Au NPs on Glassy Carbon Electrode

Fig. 2(A) shows the cyclic voltammograms of GC electrode in the solution ($\text{pH} = 3$) containing $0.2 \text{ mol} \cdot \text{L}^{-1} \text{ NaNO}_3$ and $1.0 \text{ mmol} \cdot \text{L}^{-1} \text{ HAuCl}_4$ with a

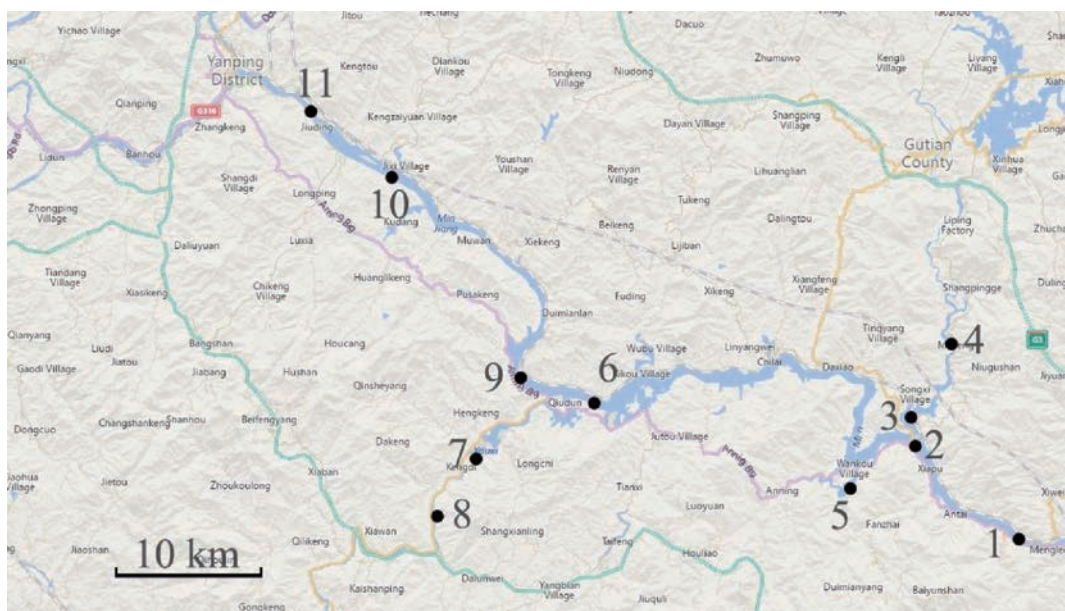


Fig. 1 Map of 11 sampling sites along the Midstream Fujian Minjiang River in China

scanning rate of $50 \text{ mV} \cdot \text{s}^{-1}$. For the first scan from 900 mV to 0 mV, a broad reduction peak current was observed at ca. 710 mV, indicating the electrochemical nucleation and growth of Au species on the GC surface. The broad reduction peak is a result of the surface morphology sensitive electrochemical deposition of Au on GC surface. The dominated reduction peak is in good agreement with the previous result that the electrochemical formation of Au(0) by AuCl_4^- on the GC surface was realized directly with the one step reduction process in aqueous solution^[31].

Starting from the second cycle, the reduction peak was significantly shrunk with a positive shift of 90 mV to ~ 800 mV, and the reduction current continuously decreased slightly with the increasing scan cycle. The positive shift of the reduction peak is due to the less energy demanded for the preferable electrochemical deposition of Au atom on the Au surface, i.e., the competitive deposition of Au atom on GC or Au NPs surfaces, considering the much stronger interaction between Au-Au than that of Au-C^[32]. The decreased current might be a result of the two processes: 1) the drastic consumption of AuCl_4^- near the GC electrode during the first negative shift scan, and 2) the diffusion of AuCl_4^- from the bulk to the diffusion layer could not keep up with the electrochemical reduction consumption, which could be overcome by the solution agitation^[29].

The obtained Au NPs-GCE was electrochemi-

cally treated in the $0.5 \text{ mol} \cdot \text{L}^{-1} \text{ H}_2\text{SO}_4$ solution by CV in the range from 300 mV to 1500 mV as shown in Fig. 2(B) which displays the typical redox behavior of Au^[33-34] and the interference from the broad double layer of GC electrode has been subtracted in advance. The positive peaks at ~ 1160 and 1310 mV were assigned to the two-step oxidation of surface Au, which were then reduced with the potential negatively shifted to ~ 1000 mV. The coulombic charge for the reduction or oxidation peak was 18.8 or $19.0 \mu\text{C}$, respectively. The almost identical values further confirmed that these two peaks are one redox pair originating from the redox process of the surface Au atoms on the Au NPs-GCE surface. Therefore, we used the current of this reduction peak to evaluate the reproducibility of the prepared Au NPs-GCE. The RSD (standard deviation of mean) of the peak current was $\sim 4\%$ for seven parallel experiments as shown in the right insert of Fig. 2(B), demonstrating that the prepared substrate was suitable for the forthcoming quantitative measurement.

Furthermore, the surface morphology of the prepared substrate, characterized by SEM with the image given in the left inset of Fig. 2(B)), revealed that most of the Au NPs deposited on GC surface were spherical accompanied with a few dumbbell shapes, which might be formed by the coalescence among neighboring NPs. The electrochemical deposition and growth process of Au NPs were relatively random

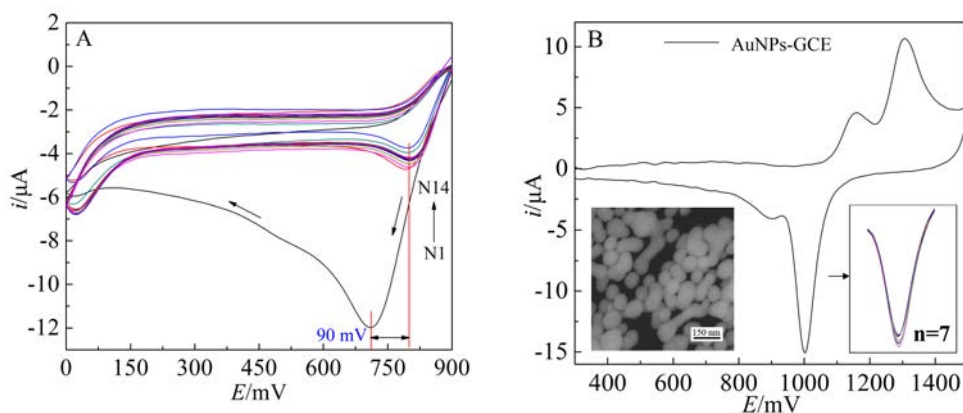


Fig. 2 (A) CV curves of GC electrode in $0.2 \text{ mol} \cdot \text{L}^{-1} \text{ NaNO}_3$ solution containing $1.0 \text{ mmol} \cdot \text{L}^{-1} \text{ HAuCl}_4$ ($\text{pH} = 3$). (B) CV curve of AuNPs-GCE in $0.5 \text{ mol} \cdot \text{L}^{-1} \text{ H}_2\text{SO}_4$ solution. The left and right insets show the SEM image and the peaks for seven parallel experiments of AuNPs-GCE, respectively.

due to the non-uniformity of the GC surface at the nanometer scale. Therefore, surface diffusion of Au atoms on these closely packed Au NPs would happen and induce Au NPs to coalesce together forming a neck to reduce their surface energy. Averagely, the size distribution of Au NPs (spherical & semi-spherical) is 70 ± 18 nm with the surface coverage of ca. $41 \pm 5 \text{ N} \cdot \mu\text{m}^{-2}$.

It should be noted that the above condition for the electrochemical preparation of Au NPs-GCE was optimized by adjusting the concentrations of HAuCl_4 and NaNO_3 , as well as pH and cycle number of deposition, with the reduction peak current shown in Fig. 2(B) as the standard. Detailed optimization results and the related discussion were referred to Fig. S1.

2.2 Quantitative Characterization of Cu^{2+} by SWASV

Fig. 3 (A) depicts the SWASV curves of the Au NPs-GCE in $0.1 \text{ mol} \cdot \text{L}^{-1} \text{ HNO}_3$ solution containing different Cu^{2+} concentrations after the electrochemical deposition at -500 mV for 300 s . The electrolyte of $0.1 \text{ mol} \cdot \text{L}^{-1} \text{ HNO}_3$ was selected owing to the two advantages (Fig. S2(A)). 1) HNO_3 was the typical solvent used for the acidification of environmental aquatic samples. 2) The better shape and reproducibility in the stripping peak of Cu^{2+} were observed in $0.1 \text{ mol} \cdot \text{L}^{-1} \text{ HNO}_3$ than those in $0.1 \text{ mol} \cdot \text{L}^{-1} \text{ HCl}$ solution, accompanied with the larger oxidation peak current difference between the spiked and the blank (controlled) samples ($\Delta i (\Delta i = i_{\text{Cu}^{2+}} - i_{\text{Blank}})$). Thus, the pre-stripping electrochemical deposition potential of Cu^{2+} was set at -500 mV for 300 s in order to reach the optimized sensitivity with good signal-to-noise ratio under a suitable time interval, which is free of the interference from hydrogen evolution (Fig. S2(B) & (C)).

Compared to the control experiment free of Cu^{2+} , the electrochemical signal from Cu^{2+} oxidation at ca. 400 mV significantly overlapped with a broad oxidation peak located at ca. 350 mV , which has been reported and discussed tentatively^[29,35]. Although the complicated surface oxidation process has been suggested to be responsible for this oxidation peak^[30],

the conclusive explanation towards the detailed mechanism deserved further endeavor. Furthermore, it was found that this broad background peak current fluctuated with different Cu^{2+} concentrations, which would bring the uncertainty for the quantitative measurement of Δi and then the concentration of Cu^{2+} .

Therefore, by borrowing the background subtraction strategy from the electrochemical measurement of Hg^{2+} concentrations on Au NPs-GCE^[29-30,35] to remove the interference of this broad peak, the SWASV curve measured upon the deposition at the same concentration for 30 s , i.e., $\Delta i_o = i_o(300 \text{ s}) - i_o(30 \text{ s})$, was subtracted, with the other parameters remaining unchanged. The obtained results are shown in Fig. 3 (B).

Obviously, comparing to Fig. 3(A), the difference between two Cu^{2+} concentrations was relatively amplified with the removal of the background. For example, the curves at $5 \mu\text{g} \cdot \text{L}^{-1}$ and $10 \mu\text{g} \cdot \text{L}^{-1}$ cases were overlapped each other in Fig. 3(A), while were clearly discrete in Fig. 3(B), where the blank curve free of Cu^{2+} displayed a featureless line in the range of 300 mV to 500 mV . The variation of Δi_o with Cu^{2+} concentration is plotted in the insert of Fig. 3(B), showing a linear range of $2 \sim 50 \mu\text{g} \cdot \text{L}^{-1}$ with the linearity parameter (R^2) of 0.996 . Furthermore, the standard deviation of mean was $\sim 7\%$ or $\sim 4\%$ (based on 5 times measurements) for the standard samples with a concentration of $10 \mu\text{g} \cdot \text{L}^{-1}$ or $30 \mu\text{g} \cdot \text{L}^{-1}$, respectively, indicating a reliable repeatability.

The limit of detection (LOD), which was obtained by the standard deviation (3 times measurements) of the averaged blank (7 measured values) divided by the slope of the working curve, was $\sim 1.3 \mu\text{g} \cdot \text{L}^{-1}$, which is comparable or even better than other ASV strategies (Tab. S1), whereas, the linear range ($2 \sim 50 \mu\text{g} \cdot \text{L}^{-1}$) was relatively narrower. For the measurement at high Cu^{2+} concentration, a short deposition time for trace Cu^{2+} enrichment, such as 60 s or 180 s , could be applied (not shown) to avoid the saturated stripping at low concentrations. Nevertheless, considering the Cu^{2+} concentration in drinking water source should be less than $10 \mu\text{g} \cdot \text{L}^{-1}$, therefore, the

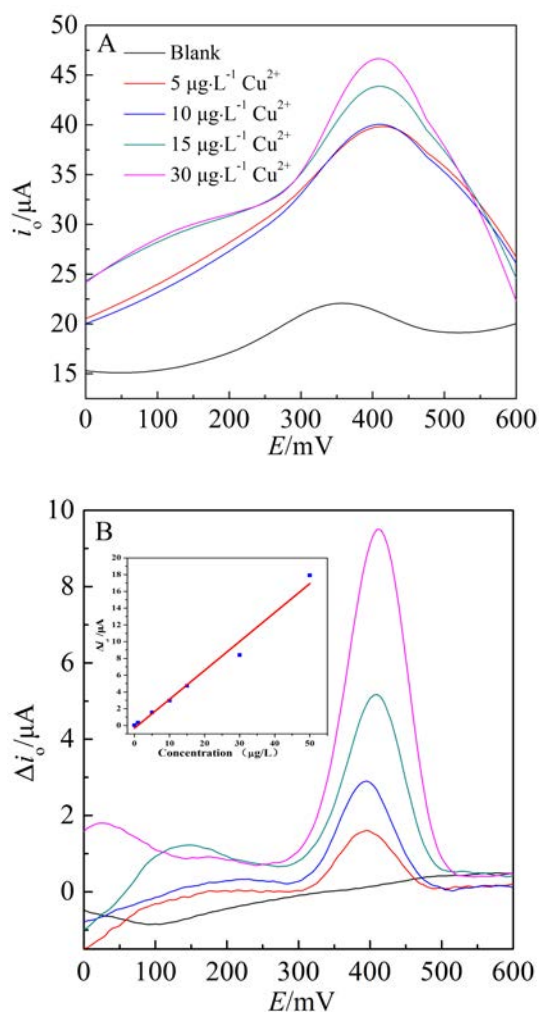


Fig. 3 SWASV curves of the Au NPs-GCE in 0.1 mol·L⁻¹ HNO₃ solution (pH=1) containing different concentrations of Cu²⁺, after the electrochemical deposition at -500 mV for 300 s, which is free (A) or being subtracted (B) by the case of the 30 s deposition.

linear range of the proposed measurement is sufficient for the quantitative analysis towards quality control of the drinking water, not to mention that the electrode preparation is much easier and faster than other techniques shown in Tab. S1.

2.3 Selectivity—Interference from Foreign Metal Ions

Typical trace metal ions in water, including Cr³⁺, Mn²⁺, Fe³⁺, Co²⁺, Ni²⁺, Zn²⁺, Ag⁺, Hg²⁺ and Cd²⁺, were selected to evaluate the selectivity of the proposed Au NPs-GCE-SWASV towards Cu²⁺ in the aquatic environment^[36]. Fig. 4 illustrates the histogram of the ob-

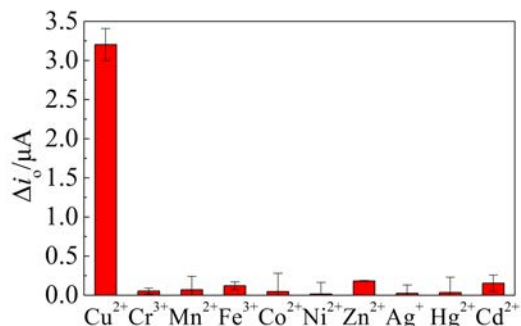


Fig. 4 Interference of foreign metal ions (Mⁿ⁺) on Cu²⁺ detection (Mⁿ⁺, 1 mg·L⁻¹; Cu²⁺, 10 μg·L⁻¹; n=3)

tained Δi₀ at 400 mV for each foreign metal ion at 1 mg·L⁻¹ (a concentration is seldom monitored for the drinking water source), and 10 μg·L⁻¹ Cu²⁺ was used as the reference for comparison. It clearly shows that the existence of foreign metal ions would have positive deviation on the Cu²⁺ detection, nevertheless, the maximum deflection is less than 5% with 100 times higher concentration of the metal ions than that of the Cu²⁺. Therefore, it can be concluded that the Au NPs-GCE-SWASV has a good selectivity towards trace Cu²⁺ detection with little interference from other metal ions.

2.4 Practical Application for Drinking Water Quality Control

First, the reliability of current method was evaluated by measuring the standard river sample containing 17.4 ± 1.3 μg·L⁻¹ Cu²⁺, and the measured concentration was 16.1 ± 0.72 μg·L⁻¹ (n=5), displaying a variation range of 94.3% ~ 103.7% and indicating the trustworthy accuracy of the method. Therefore, using the current method to measure the Cu²⁺ concentrations in the drinking water sources from 11 sampling sites along the midstream of Fujian Minjiang river, the obtained results are listed in Table 1 for comparing with the classical GFAAS method. No surprisingly, the concentrations obtained by the current method fluctuated slightly from those measured by GFAAS method. The slope of the linear regression equation was ~ 0.8 and the linear correlation coefficient was ~ 0.9 by fitting these two sets of data, which implied no significant difference accompanied with a tolerable deviation between these two tech-

Tab.1 Analytical results of Cu^{2+} in the midstream of Fujian Minjiang River in China

Sample	Station	Cu^{2+} concentration ($\mu\text{g}\cdot\text{L}^{-1}$, $n = 3$)	
		This work	GFAAS
1	Dongqiao	5.15 ± 0.40	5.39 ± 0.04
2	Shuikouminjiang Bridge	5.25 ± 0.18	5.21 ± 0.02
3	Xiguazhou Bridge	4.64 ± 0.23	4.93 ± 0.07
4	Xiguang Bridge	4.82 ± 0.22	5.00 ± 0.10
5	Chengtou Bridge	5.44 ± 0.26	5.24 ± 0.01
6	Lidun Bridge	5.60 ± 0.35	5.44 ± 0.03
7	Xibin Bridge	5.32 ± 0.24	4.99 ± 0.03
8	Yongkou Bridge	4.60 ± 0.46	4.90 ± 0.08
9	Liuja Village	4.01 ± 0.35	4.19 ± 0.02
10	Xiadao Bridge	3.89 ± 0.16	4.12 ± 0.02
11	Minjiang Bridge	3.25 ± 0.42	3.42 ± 0.11

niques. Furthermore, all the Cu^{2+} concentrations monitored were much less than $10 \mu\text{g}\cdot\text{L}^{-1}$, the threshold of water quality at the first level, demonstrating the measured Fujian Minjiang river basin during the sampling period was not contaminated by the copper discharge from the surrounding domestic sewage and industry waste water.

It should be mentioned that the above measured Cu^{2+} reflected the majority copper species in the samples could be acidified to Cu^{2+} in $0.1 \text{ mol}\cdot\text{L}^{-1} \text{HNO}_3$, except the trace complex hardly to be dissociated in acidified environment ($\text{pH} = 1$), such as copper humic complex. The electrochemical measurements of Cu^{2+} in these drinking water free of the acidification pre-process were made. It turned out that ca. 40% of the copper species were in the dissolved state as free Cu^{2+} , and this value might reflect the ratio of the dissolved organic and inorganic copper species in the sample. Therefore, in case of emergency response, the proposed electrochemical technique could be a potential on-site and quick evaluation tool of the dissolved inorganic Cu^{2+} concentration in various drinking water sources.

3 Conclusions

The square wave anodic stripping voltammetry (SWASV) based electrochemical determination of

trace Cu^{2+} in drinking water has been developed, using the gold nanoparticles (Au NPs) modified glassy carbon (GC) electrode. The Au NPs centered at $70 \pm 18 \text{ nm}$ were electrochemically prepared on GC surface via the electrochemical cyclic voltammetry process. For the spiked Mill-Q water, the LOD was $\sim 1.3 \mu\text{g}\cdot\text{L}^{-1}$ with the linear range of $2 \sim 50 \mu\text{g}\cdot\text{L}^{-1}$, while the related RSD ($n = 5$) values were $\sim 7\%$ and $\sim 4\%$ for $10 \mu\text{g}\cdot\text{L}^{-1}$ and $30 \mu\text{g}\cdot\text{L}^{-1} \text{Cu}^{2+}$, respectively. The proposed method displayed reliable outcomes for the determination of dissolved Cu^{2+} in the midstream of Fujian Minjiang River in China. Future work would focus on the large-scale uniformed Au NPs preparation to build a simple, economical and fast on-site detection tool, which could be used in the field determination of Cu^{2+} in environmental water.

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Supporting Information Available

The supporting information is available free of charge via the internet at <http://electrochem.xmu.edu.cn>.

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基于电化学方法测定饮用水源水中的痕量铜离子

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摘要: 本文建立了一种饮用水源水中痕量溶解态铜离子(Cu²⁺)的定性和定量电化学检测方法. 该方法首先通过电化学循环伏安法于玻碳电极表面制备粒径约为 70 nm 的金纳米粒子(Au NPs), 然后采用方波阳极溶出伏安法进行待测水样中 Cu²⁺ 的定性定量分析. 研究表明, 对于标准溶液, 方法的检出限为 1.3 μg·L⁻¹, 线性范围在 2 ~ 50 μg·L⁻¹ 之间, 常见重金属离子对其定性定量分析几无影响. 在此基础上, 将该方法应用于福建省重要的饮用水源水——闽江中游水样中 Cu²⁺ 的含量分析, 所得测试结果与国家标准方法(石墨炉原子吸收光谱法)无显著性差异, 标准偏差在 20% 以内. 本方法具有电极制备简单、测定成本低以及分析快速等优点, 进一步优化电极制备方法以提高方法的重现性和定量准确度, 将可望用于现场测定各种饮用水源水中的痕量溶解态 Cu²⁺.

关键词: 电化学检测; 方波阳极溶出伏安法; 金纳米粒子; 痕量铜离子; 饮用水