Determination of Copper in Metal Processing Wastewater by Stripping Voltammetry

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Abstract. In this paper, the trace copper in metal processing wastewater was determined by stripping voltammetry, and the influence of instrument condition on the analysis was discussed. The standard working curve was established and the wastewater samples were determined. The results showed that the optimized conditions of instrument determination were as follows: electrolysis initial voltage was -1.3V, electrolysis time was 1 minute, balance time was 10 S, the rate of stirring was high speed and scanning speed was 0.08 V/S. Under the above experimental conditions, the peak shape was good, the peak current was large and the peak potential was stable at -0.1V. The linear equation of standard working curve was \( y = 0.1683X + 0.0121 \), the standard deviation was \( R^2 = 0.9974 \), the detection limit was 0.2μg / mL, the recoveries of the wastewater samples were 96.6% -100.5%. The method has the advantages of good accuracy, high precision and high sensitivity, and is suitable for the determination of copper in metal processing wastewater.

1. Introduction

1.1. The origin and harm of the copper in the environment

With the progress of science and technology and people's living standards, environmental awareness and self-care awareness, people's understanding of copper gradually deepened, its impact on human health and the environment has been gradually recognized. Copper is a natural element of the normal composition, but the copper concentration is too high will be harmful to humans, animals and plants. Copper mining, smelting and rock weathering can result in increased local copper concentrations in the local environment. Copper pollution in the atmosphere is mainly caused by non-ferrous metal smelting. Copper pollution is caused by smelting, metal processing, machine building, organic synthesis and other industrial copper-containing wastewater discharge. The copper content in the wastewater by smelting and electroplating is the highest, ranging from dozens to hundreds of ppm. The main source of soil copper pollution is copper mine and smelter discharge wastewater, in addition to industrial dust, urban sewage and copper pesticides can cause soil copper pollution. Copper is one of the trace elements necessary for life, and plays an important role in human hematopoiesis, cell growth, activity of certain enzymes and endocrine gland function. Copper is not easy to dissolve, less toxic than copper salts, especially in the soluble salt in copper salt such as acetic acid copper and copper sulfate is toxic. Human copper poisoning is due to excessive intake of copper due to the performance of abdominal pain, rash, diarrhea, vomiting and other symptoms, a large number of long-term ingestion can lead to hepatitis and hemolytic anemia, and Parkinson's disease. The potential
toxicity of copper has attracted great concern, and the regulatory framework for controlling its concentration levels to a greater extent has been enforced in most developed countries. Therefore, in the water quality, environment and food testing, the content of copper has always been an important indicator of environmental pollution and food quality, so sensitive, accurate and rapid detection of copper content is particularly important.

1.2. Existing methods of measurement
Trace copper determination methods are atomic absorption spectrometry, visible spectrophotometry, flow injection chemiluminescence, fluorescence, differential potential dissolution and so on. Atomic absorption spectrometry (AAS) method has the advantages of low detection limit, high accuracy, good selectivity and fast analysis speed. AAS method is mainly applied to the analysis of trace and trace components in samples, and it has become the most widely used analytical method for the quantitative analysis of inorganic elements. Among the analytical methods for copper, the most commonly used is the spectrophotometric method. It has many advantages such as wide application, high sensitivity, good selectivity, high accuracy, wide application range, low analysis cost and easy operation. The spectrophotometry is based on the selective absorption of electromagnetic radiation to establish a qualitative and quantitative analysis method by different molecular structures., this method is simple, easy to promote. Differential potentiometric stripping method of copper, less sampling, high sensitivity, good reproducibility, the reagent used in low cost, fast and simple, easy to popularize [1-3]. For example, Fang Bin [1] by differential potentiometric stripping method on the determination of copper in human hair, accuracy and precision are good, high sensitivity. With a mercury plating method can be used to overcome a lot of secondary pollution problem caused by mercury liquid, at the same time also can reduce the operation process, improve the efficiency of measurement [2]. In this paper, the copper content in metal processing wastewater was determined by stripping voltammetry, so as to realize the rapid determination of the sample in the scene[4].

2. Experimental

2.1. Instruments and reagents
Lk98A microcomputer electrochemical analysis system (Tianjin Lanlike company); Three electrode system (saturated calomel electrode as the reference electrode, silver electrode as the working electrode, platinum electrode as the electrode); The exact analytical balance (accuracy 0.0001g); SYC-15 super thermostatic water-bath boiler, 100mL electrolytic cup, pipette 25mL-1mL; Volumetric flask; Copper sulfate, NaAc, HAc, HgSO4 are analytical reagent and highly pure water for our laboratory.

2.1.1. Reference method [3] preparation. 3.9000 g of copper sulfate volume to 100mL volumetric flask, remove 1mL into 1L volumetric flask, set volume again, get 15.6μg • mL-1 Cu2+ ion standard solution

2.1.2. Configure the HAc-NaAc buffer solution (pH≈5.6). 905mL2mol•L-1NaAc solution was mixed with 95mL 2mol•L-1HAc solution to obtain HAc-NaAc buffer solution (pH≈5.6).

2.1.3. 2 × 10-2mol • L-1 HgSO4 solution preparation.

2.1.4. Standard sample configuration. Respectively, to take a certain amount of standard solution, diluted with high purity water to 0.5,1,1.5,2,4 μg • mL-1.

2.1.5. Simulate the sample to be measured (about 2μg • mL-1Cu2 + ions), digested with reference to the literature, and then diluted to the corresponding concentration.

2.2. Experimental procedures

2.2.1. Connect the instrument and enter the following parameters on the keyboard:
Baseline deduction (off)  IR Compensation (off)
The initial voltage (V) -1.0000  Electrodeposition voltage (V) - 1.0000
Scanning speed (V/s) 0.08       The termination voltage (V) was 0.2000
Electrodeposition time (s) 60    Equilibrium time (s) 10

2.2.2. Add 25 mL of water sample and 1 mL of HAc-NaAc solution (six drops of HgCl) into the electrolytic cup, and place the reference electrode and platinum electrode into the solution (try not to touch the stir bar).

2.2.3. As far as possible without changing the electrode position in the electrolytic cup by adding a certain amount of Cu2+ ion standard solution, press the "start" button, record several stripping voltammetric curve to obtain a stable peak current. Press the Pause key.

2.2.4. Repeat the above steps to draw the standard working curve at different concentrations, the quantitative determination of unknown samples. Determination of the process can adopt quantitative determination by standard addition method. Standard addition method is calculated as follows:

\[
c_x = \frac{c_s V_s}{H(V_x + V_s) - h_x V_x}
\]

Cs, Vs are the concentration and volume of the standard solution, respectively; H is the peak height of the dissolution peak after adding the standard solution, cx, vx, hx are the concentration, volume and peak height of the dissolution peak, respectively; .

3. Results and discussion

3.1. Instrument condition setting

3.1.1. Effect of the concentration potential It can be seen from the figure 1, CU ion peak position in the vicinity of -0.1 volts. As the potential of the enrichment changes from -0.8 to -1.3 volts, the peak current of the CU ions increases, and the front has a tendency to shift to the left, but the peak shape becomes wider and the symmetry of the peak becomes worse. It can be seen that when the concentration of the potential is set at -1.3 volts, a large current peak of Zn can be seen in the vicinity of -1.1 V in the figure.

Figure 1 Effect of the concentration potential

3.1.2. Enrichment time In order to analyze the effect of equilibrium time on the two metal ions, the enrichment potential of the equilibrium time experiment was also chosen to be -1.3 volts. The enrichment time was 1 minute, 1.5 minutes and 2 minutes. It was found that the peak height increased with the enrichment time, and the position of the front shifted to the right, but the symmetry of peak shape became worse in figure 2. Considered, set in 1 minute is more appropriate.
3.1.3. **Balance time** The enrichment time of the experiment was chosen to be -1.3 volts and the enrichment time was 1 minute. The effect of the static equilibrium time was 10S, 20S, 30S respectively. It can be seen that the longer the stationary time, deformation width, peak symmetry worse in figure 3. Hence, balance time of 10S was chosen in the following experiments.

3.1.4. **Stirring speed** The results show that the stirring speed is high and the peak current is big, so it is convenient to analyze and measure. So the high speed stirring is chosen in this experiment.

3.1.5 **Scan speed** Respectively, the scanning speed of 0.06, 0.08, 0.1V / S three cases. It can be seen that as the scanning speed increases, the current peak position is shifted to the left and the peak current value increases, but the increase of 0.08 and 0.1V / S is not obvious, and the scanning speed is 0.08V / S More complete, therefore, this paper that the scanning speed of 0.08V / S is more appropriate.

3.2. **Determination of wastewater samples**

3.2.1. **Standard working curve and linear range** A series of copper standard solutions with different concentrations were prepared. Under the optimized experimental conditions, the linear relationship between the peak current peak current and the concentration at 0.5, 1, 1.5, 2, 4, μg / mL concentration was studied. The standard working curve is obtained: y = 0.1683X + 0.0121, R2 = 0.9974. The linear range was 1 order of magnitude and the detection limit was 0.2 μg / mL.

3.2.2. **Spike recovery** The results showed that the method has high sensitivity and good selectivity, and it can be applied to the determination of the actual samples. The method is simple, accurate and reproducible.
4. Conclusion
HAc-NaAc was used as the buffer solution, and trace copper in the metal processing wastewater was determined by stripping voltammetry[5]. The presence of Zn ions during the assay did not affect the assay. The instrument conditions of the experiment were optimized, and the peak current shape was obtained. The linear regression equation \( y = 0.1683X + 0.0121 \), \( r^2 = 0.9974 \) in figure 4. The detection limit was 0.2 μg / mL. The recoveries of copper in water samples ranged from 96.6% to 100.5% with RSD <3.6%.

![Figure 4 The linear regression equation](image)

Acknowledgments
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