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硕士学位论文

基于金属纳米粒子的铜离子检测新方法的  
研究和应用

Study and Application of New Analytical Methods Based on  
Metal Nanoparticles for Copper Ion

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## 摘要

铜 (Cu) 是生物体的必需微量元素。然而, Cu 的过量摄入会引发人体疾病和生物死亡。因此, 检测水和食物中的 Cu 具有重要意义。Cu 的经典检测方法如原子光谱法和质谱法的选择性强、灵敏度高、准确度高, 但需要昂贵且笨重的仪器和配套实验设备, 运行成本高, 不宜在现场应用。相较而言, 分光光度法和电化学法具有简单、轻便、成本低、易操作等优点, 可应用于 Cu 的现场、快速检测。纳米金属粒子凭借其独特的物理和化学性质, 已逐渐成为分光光度法和电化学法测定 Cu 的有效试剂。目前已报道的使用金属纳米粒子检测 Cu 的方法还有一些不足之处, 如金属纳米粒子制备方法复杂、检测灵敏度较低、检测速度慢、难以应用于现场分析等。因此, 使用金属纳米粒子检测 Cu 还有很大的提升空间。本研究旨在发展基于金属纳米粒子的铜离子 ( $\text{Cu}^{2+}$ ) 检测新方法, 最终实现水环境中  $\text{Cu}^{2+}$  的现场、快速测定; 所发展的水样中  $\text{Cu}^{2+}$  检测方法的主要研究内容和结果如下:

(1) 基于  $\text{Cu}(\text{NH}_3)_4^{2+}$  催化  $\text{Na}_2\text{S}_2\text{O}_3$  刻蚀纳米银粒子 (Silver Nanoparticles, AgNPs)、引起 401 nm 处吸光度变化的原理, 结合批次流动分析技术, 建立了“ $\text{Cu}^{2+}$  的批次流动分析-AgNPs 分光光度测定法”。本方法检出限 (Limit of Detection, LOD) 为 0.24  $\mu\text{g/L}$ , 线性范围 0.5-35  $\mu\text{g/L}$ 。连续 7 次测定浓度分别为 10  $\mu\text{g/L}$  和 25  $\mu\text{g/L}$  的  $\text{Cu}^{2+}$  标样, 相对标准偏差 (Relative Standard Deviation, RSD) 分别为 1.21% 和 1.03%, 平行性好。本方法成功应用于自来水、湖水、雨水、矿泉水和粽叶浸泡水中  $\text{Cu}^{2+}$  的检测, 所得结果与石墨炉原子吸收光谱法的结果无显著性差异。本方法具有自动化程度高、灵敏、简单、价廉、快速等优点, 可发展成为现场快速测定环境水体中  $\text{Cu}^{2+}$  的方法。

(2) 基于  $\text{Cu}^{2+}$  引起 L-半胱氨酸修饰的纳米金粒子 (L-Cysteine Modified Gold Nanoparticles, L-Cys-AuNPs) 产生团聚的原理, 将 L-Cys-AuNPs 涂布于滤纸上, 制作测定  $\text{Cu}^{2+}$  的比色试纸, 应用 Image J 软件分析水中  $\text{Cu}^{2+}$  引起的比色试纸颜色变化, 建立了“ $\text{Cu}^{2+}$  的 L-Cys-AuNPs 比色试纸测定法”。方法的 LOD 为 0.09 mg/L, 线性范围 0.1-10 mg/L。对 1 mg/L、5 mg/L  $\text{Cu}^{2+}$  标样各平行测定 5 次, RSD 分别为 6.6% 和 3.5%。本方法制作成本低、试剂消耗少、易于使用, 应用于测定铜矿废水中总铜和溶解态铜的含量, 其结果与《中华人民共和国国家环

境保护标准》HJ485-2009 法的测定结果无显著性差异。本方法在工业废水或污染水体  $\text{Cu}^{2+}$  的现场快速检测中，具有很好的应用前景。

(3) 使用循环伏安法将 AuNPs 电沉积于玻碳电极表面，构建 AuNPs 改性电极，应用于方波阳极溶出伏安法电分析化学体系，建立了“ $\text{Cu}^{2+}$  的 AuNPs 修饰玻碳电极-方波阳极溶出伏安测定法”。方法的 LOD 为  $1.3 \mu\text{g/L}$ ，线性范围  $2\text{-}30 \mu\text{g/L}$ 。分别连续 5 次测定  $10 \mu\text{g/L}$  和  $30 \mu\text{g/L}$   $\text{Cu}^{2+}$  标样，RSD 分别为 6.7% 和 4.2%。本方法成功应用于闽江中游水样中  $\text{Cu}^{2+}$  含量分析，所得结果与石墨炉原子吸收光谱法的测定结果无显著性差异。本方法具有电极修饰简单、测定成本低、分析快速等优点，可发展成为现场测定环境水体中  $\text{Cu}^{2+}$  的方法。

**关键词：**铜离子；金属纳米粒子；分光光度法；批次流动分析；比色试纸法；方波阳极溶出伏安法

## Abstract

Copper (Cu) is an essential trace element for living organisms. However, intake of an excess amount of Cu will cause human diseases and death of some organisms. Therefore, detection of Cu in water and food is of great significance. Classical methods for determination of Cu, such as atomic spectrometries and mass spectrometry, are highly selective, sensitive and accurate. However, they are also expensive and cumbersome with high operational cost, thus not suitable for field application. Spectrophotometric and electrochemical methods both have the advantages of simple, light, low cost and easy handling, which makes them appropriate for rapid analysis in field. With unique physical and chemical properties, metal nanoparticles have become a powerful reagent in spectrophotometric and electrochemical detection of Cu. The reported methods using metal nanoparticles to detect Cu still have some shortcomings, such as complex procedure for synthesis of metal nanoparticles, low sensitivity, slow detection speed, or difficult to be applied in field. Therefore, the determination of Cu with metal nanoparticles still has room for improvement. The purpose of this research is to develop new analytical methods based on metal nanoparticles for copper ions ( $\text{Cu}^{2+}$ ), which would be applied in water analysis. The main contents and results of the research are as the follows:

(1) The silver nanoparticles (AgNPs) were catalytically etched by  $\text{Na}_2\text{S}_2\text{O}_3$  in the presence of  $\text{Cu}(\text{NH}_3)_4^{2+}$ , and the absorbance at 401 nm was decreased. Based on this, a flow-batch analysis technique and a spectrophotometric method were integrated for determination of  $\text{Cu}^{2+}$ . The limit of detection (LOD) was as low as 0.24  $\mu\text{g/L}$ , and the linear range was 0.5-35  $\mu\text{g/L}$ . The relative standard deviation (RSD,  $n=7$ ) for samples at  $\text{Cu}^{2+}$  concentrations of 10  $\mu\text{g/L}$  was 1.21% and for 25  $\mu\text{g/L}$  was 1.03%. The proposed method was successfully applied to analyze  $\text{Cu}^{2+}$  in tap water, lake water, rainwater, bottled water and leaf soaking water samples. The results were in good agreement with those obtained with graphite furnace atomic absorption spectrometry (GFAAS). The proposed method had the advantages of high automation, sensitivity, simplicity, cheapness and rapid detection, which could be developed into a method for

rapid determination of  $\text{Cu}^{2+}$  in environmental water.

(2) Based on the aggregation of L-Cysteine modified gold nanoparticles (L-Cys-AuNPs) induced by  $\text{Cu}^{2+}$ , a paper-based colorimetric method for  $\text{Cu}^{2+}$  detection was developed. L-Cys-AuNPs was coated onto a filter paper for testing  $\text{Cu}^{2+}$ , and the color change was analyzed with software Image J. The LOD was 0.09 mg/L, and the linear range was 0.1-10 mg/L. The RSD (n=5) was 6.6% for 1 mg/L  $\text{Cu}^{2+}$  and 3.5% for 5 mg/L  $\text{Cu}^{2+}$ . The proposed method was of low cost, less reagent consumption and easy to use, and had been applied to the determination of total copper and dissolved copper in mineral wastewater. The results agreed with those obtained with *China National Environmental Protection Standards* HJ485-2009. The proposed method had good application prospect on field analysis of  $\text{Cu}^{2+}$  in industrial wastewater or polluted water.

(3) With cyclic voltammetry, gold nanoparticles (AuNPs) were deposited onto a glassy carbon electrode. A square wave anodic stripping voltammetry for the determination of  $\text{Cu}^{2+}$  using the modified electrode was developed. The LOD was 1.3  $\mu\text{g/L}$ , and the linear range was 2-30  $\mu\text{g/L}$ . The RSD (n=5) was 6.7% for 10  $\mu\text{g/L}$   $\text{Cu}^{2+}$  and 4.2% for 30  $\mu\text{g/L}$ . The proposed method was used to the determination of  $\text{Cu}^{2+}$  in the midstream of Minjiang River, and the results had not significant difference with those obtained with GFAAS. The proposed method was simple, inexpensive and fast, and could be developed for field determination of  $\text{Cu}^{2+}$  in environmental water.

**Keywords:** copper ions; metal nanoparticles; spectrophotometry; flow-batch analysis; paper-based colorimetric method; square wave anodic stripping voltammetry

## 常用缩略语表

缩略语	英文全称	中文全称
AAS	Atomic Absorption Spectrometry	原子吸收光谱法
AgNPs	Silver Nanoparticles	银纳米粒子
AgNPIs	Silver Nano-plates	纳米银盘
ASV	Anodic Stripping Voltammetry	阳极溶出伏安法
AuNPs	Gold Nanoparticles	金纳米粒子
CV	Cyclic Voltammetry	循环伏安法
GFAAS	Graphite Furnace Atomic Absorption Spectrometry	石墨炉原子吸收光谱法
ICP-AES	Inductively Coupled Plasma-Atomic Emission Spectrometry	电感耦合等离子体-原子发射光谱法
ICP-MS	Inductively Coupled Plasma-Mass Spectrometry	电感耦合等离子体-质谱法
L-Cys	L-Cysteine	L-半胱氨酸
LDPE	Low Density Polyethylene	低密度聚乙烯
LOD	Limit of Detection	检出限
RSD	Relative Standard Deviation	相对标准偏差
SPR	Surface Plasmon Resonance	表面等离子体共振
SWASV	Square Wave Anodic Stripping Voltammetry	方波阳极溶出伏安法



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